

Wide range buffering capacity of HLP solution for long-term HIC testing under mildly sour conditions

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ABSTRACT

Hydrogen Induced Cracking (HIC) is a major issue of carbon steels for pipelines exposed to wet sour environments. For Fitness-for-Purpose (FFP) HIC evaluations which require a longer test duration than the conventional 96 h, Solution C was registered in NACE TM0284. However, because Solution C requires frequent pH adjustment using HCl and NaOH during HIC testing depending of the sour conditions, there is a strong need for a FFP testing solution with higher pH stability. The High-strength Line Pipe (HLP) Committee of The Iron and Steel Institute of Japan (ISIJ)⁽¹⁾ proposed a 5.0 wt% NaCl + 0.93N (CH₃COOH + CH₃COONa) solution (HLP solution). In this study, the pH stability of the HLP

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solution during HIC tests was investigated under a wide range of sour environments, and the effect of the solution volume for achieving higher pH stability without pH adjustment was also investigated. The results confirmed that the HLP solution is applicable to a wide range of pH and H₂S partial pressure conditions and requires less or no pH adjustment during the HIC test. Based on these advantages, the HLP solution is expected to enhance the use of high grade linepipe steels for mildly sour environment.

Key words: Sour environment, Hydrogen Induced Cracking, pH stability, HLP, Linepipe steel

INTRODUCTION

In linepipes for transportation of natural gas, suppression of hydrogen induced cracking (HIC) caused by H₂S contained in the transportation medium is an important issue. HIC is a phenomenon in which hydrogen atoms generated by a corrosion reaction penetrate steel and are accumulated in the central segregation part and inclusions in the steel, internal pressure is increased by gasification, and finally cracks occur.

As a result of optimization of the steel composition and Thermo-Mechanical Controlled Processing (TMCP) in the plate production process, linepipes up to API5L-X65 grade have been widely used in sour environments. More recently, the sour resistance property under mildly sour conditions has also been discussed with the aim of increasing the use of high strength steels such as X70 or higher grades. As specified in NACE MR0175/ISO 15156, environmental severity is determined depending on the H₂S partial pressure and pH and SMYS (specified minimum yield strength) values of up to 550 MPa (80 ksi) are valid only for the restrictions of SSC region 1, which means a lower H₂S partial pressure and higher pH.¹ The same concept has also been applied to HIC resistance and discussed in recent years.

HIC resistance characteristics are evaluated by the method specified in NACE TM 0284.² Test Solution A (5.0wt% NaCl + 0.50wt% CH₃COOH) under the condition of 1 bar H₂S partial pressure with a test duration of 96 h is most used to evaluate HIC susceptibility. In recent years, Fitness-for-Purpose (FFP) assessment to select the optimum material according to the severity of the linepipe use environment has been discussed, and as a result, the required HIC test conditions have become more diverse.³⁻⁹ The European Pipeline Research Group (EPRG) studied an HIC evaluation method for mild sour environments, and the FFP HIC test method was standardized in the 2016 revision of NACE TM0284. Test Solution C (5.0wt% NaCl + 0.40wt% CH₃COONa) was proposed as a buffered solution, and the H₂S partial pressure and pH are set to a target condition by using H₂S/CO₂ mixed gas and adding HCl or NaOH to the solution. Since TM0284 requires a longer test duration for the lower H₂S partial pressure condition, pH adjustment needs to be conducted during the test even with Solution C. However, the pH adjustment must be done manually in many testing laboratories because not all laboratories can afford an automatic pH adjustment system. Therefore, there is a strong need for a test solution with higher pH stability which eliminates the need for pH adjustment in a long-term HIC test.

The High-strength Line Pipe (HLP) Research Committee of the Iron and Steel Institute of Japan (ISIJ) has long been investigating the FFP HIC evaluation method and proposed a high-acetic acid test solution (5.0% NaCl + 0.93N (CH₃COOH + CH₃COONa)) called the HLP solution which offers excellent pH stability.¹⁰⁻¹⁶ This solution is also reflected in NACE TM0284-2016 and has been introduced as an alternative solution with a strong buffering capacity. In a 30-day test with the HLP solution, it was reported that pH adjustment was not necessary under the test conditions of pH 4.5 and a 0.01 bar H₂S partial pressure.¹⁶ This extremely strong buffering capacity is due to the high concentrations of the CH₃COOH and CH₃COONa reagents. However, since pH stability is greatly affected by the pH and H₂S partial pressure, it is important to verify the performance of the HLP solution under various conditions for practical use. In this study, the pH stability of the HLP solution during HIC tests was investigated under a wide range of sour environments with various pH and H₂S partial pressures. The effect of the solution volume for achieving higher pH stability without pH adjustment was also investigated.

EXPERIMENTAL PROCEDURE

HIC test conditions

HIC tests were carried out in accordance with the NACE TM0284-2016 using Grade X65 to X80 steels to clarify the pH stability of the HLP solution (5.0 wt% NaCl + 0.93N (CH_3COOH + CH_3COONa)). 5.0 wt% NaCl + 0.93 N- CH_3COOH and 5.0 wt% NaCl + 0.93 N- CH_3COONa were prepared separately so that the pH of the HLP solution could be adjusted to any desired value by changing the mixing ratio of acetic acid and sodium acetate. Table 1 shows the mixing ratio for determining the target pH in the HIC test. pH was measured while mixing the solutions to obtain the target pH. The initial pH was adjusted to the target $\text{pH} \pm 0.2$ units by mixing each solution before saturation with $\text{H}_2\text{S}/\text{CO}_2$ gas mixture. Figure 1 shows a schematic drawing of the test apparatus for this experiment, and Table 2 shows the test conditions. The H_2S partial pressure was 0.01 or 0.1 bar, and the test durations were 30 and 14 days, respectively, according to NACE TM0284-2016. The initial pH of the HLP solution was adjusted in the range of 3.5 to 5.5 to investigate the buffering properties of the solution over a wide pH range. The pH drift during a HIC test depends on the “ratio of the volume of test solution to the total surface area of the test specimen” (hereinafter refer to “solution volume”). The solution volume was based on 5 mL/cm², which is the lower limit of NACE TM0284-2016, and 10 mL/cm² was also examined in some cases.

Table 1
Mixing ratio for determined target pH in HIC test
Rough mixing ratio of two solutions (g for 1kg HLP solution)

Target pH	5%NaCl + 0.93N CH_3COOH	5%NaCl + 0.93N CH_3COONa
3.5	900	100
4.0	760	240
4.5	530	470
5.0	310	690
5.5	120	880

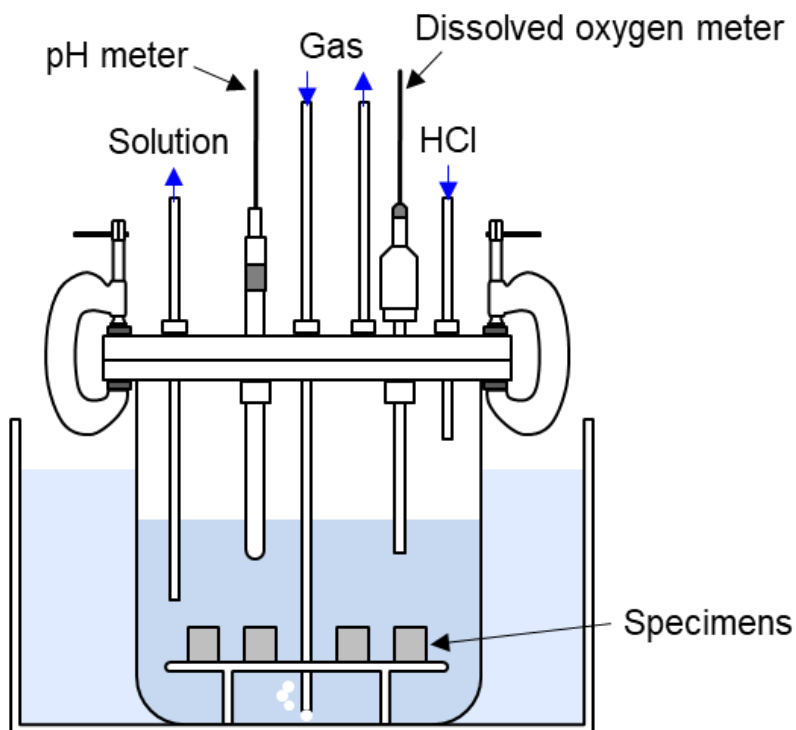


Figure 1: Schematic drawing of HIC test apparatus for pH adjustment.

Table 2
HIC test conditions in this study ; (a)0.01 bar- H₂S, (b)0.1 bar- H₂S

(a)				(b)			
pH	pH ₂ S (bar)	Duration (hr)	Solution volume (mL/cm ²)	pH	pH ₂ S (bar)	Duration (hr)	Solution volume (mL/cm ²)
3.5	0.01	720	5 ~ 6	3.5	0.1	336	5 ~ 6
			10 ~ 11				10 ~ 11
4.0			5 ~ 6	4.0			5 ~ 6
			10 ~ 11	4.5			5 ~ 6
5.0			10 ~ 11	5.0			5 ~ 6
			5 ~ 6	5.5			5 ~ 6
			5 ~ 6				
5.5			10 ~ 11				

pH adjustment was performed manually based on the measured pH values. In general, solution pH increases as test specimen is corroded and the protons in the solution are consumed by the corrosion reaction. When the solution pH approached the upper limit of pH, pH adjustment was conducted by adding a small amount of HCl. In mildly sour HIC tests, the standard provides that the solution pH shall be maintained within a 0.2 unit from the desired pH value.

The test temperature of the solution was kept at 25±3 °C (77±5 °F) by using a constant-temperature water bath. The test solution was intentionally not stirred to avoid acceleration of corrosion by a solution flow. However, the test solutions were slowly stirred by the continuous bubbling of the H₂S and CO₂ gases. The amount of corrosion was calculated from the difference between the initial weight of the specimen and the weight after the test, and the corrosion rate was calculated.

RESULTS

Comparison of pH drift between HLP solution and Solution C

First, one of the previously reported test results will be reviewed.¹⁶ Table 3 shows the test conditions, and Figure 2 shows the pH drift of Solution C and the HLP solution with exposure time. The arrows in Figure 2 represent the additions of the HCl solution for pH adjustment. Although pH was maintained at around 4.5 specified for acetic buffer solutions, pH adjustments were required 14 times to keep pH near 4.5 during the 30-day HIC test. Even after adding HCl, the solution pH quickly increased and almost reached the upper limit (pH 4.7) within about 2 days. Thus, the solution pH had to be adjusted frequently for a successful test. Since it was possible that pH might exceed the upper limit during weekends, when no one was available to check pH and add HCl, pH was lowered to near the lower limit before weekends. In contrast, the pH of the HLP solution did not reach the upper limit of 4.7 and eventually the pH shift from the initial value was 0.16 in 30 days, demonstrating that the HLP solution has a strong pH buffering capacity compared with Solution C. As a side note, this test also confirmed that the corrosion rate and HIC damage in the HLP solution and Solution C were similar.

Table 3
HIC test conditions for comparing pH stability of Solution C and HLP solution

pH	pH ₂ S (bar)	Duration (hr)	Solution volume (mL/cm ²)
4.5	0.01	720	5 ~ 6