Electrochemical Behaviour of High Stress Steel (AISI 4340) in CO_2 Environments with the Presence of H_2 Gas

Yuli Panca Asmara[1a*], Januar Parlaungan Siregar[1b], Tezara Cionita[2c], Juliawati Alias[1d]

[1]Department of Mechanical Engineering, Universiti Malaysia Pahang 26600, Pekan, Pahang, Malaysia

[2]Department of Mechanical Engineering, Faculty of Science, Technology, Engineering and Mathematics, INTI International University, 71800 Nilai, Negeri Sembilan, Malaysia

[a]YPanca@ump.edu.my, [b]januar@ump.edu.my, [c]tezara_cionita@yahoo.com, [d]juliawati@ump.edu.my

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Abstract. This research studied effects of CO_2 and H_2 gases on electrochemical behaviour of high stress steel (HSS) by using scan polarization graph to measure corrosion rate, corrosion potential and pitting potential. The tensile test samples with and without notches were tested under constant stress of 20% and immersed in 3% NaCl solutions. During experiments, CO_2 gas was injected into the samples. To generate H_2 gas, the samples were employed cathodically over potential at - 1700 mV (Ag/AgCl) for three days. The results indicated that both CO_2 and H_2 gases have increased the corrosion rate. Potentiodynamic graph showed that there were changes in pitting potential where the effect of CO_2 gas would decrease the pitting potential. However, the presence of the notch did not show any significant difference in corrosion rate.

Introduction

The selection of steels for oil and gas environments containing CO_2 and H_2 gases require appropriate testing to ensure resistance to cracking in the field conditions [1, 2]. The employ of CO_2 and H_2 gases in the environments of oil and gas production are one of the important stages in considerations to design the pipelines. Other factors such as total tensile stress, residual stresses, process temperature and exposure time should also be accounted. Hydrogen stress cracking can occur under applied stressed or strained conditions. It propagates perpendicularly to the tensile stress direction [3].

Hydrogen gas can be produced by the dissolution of atomic hydrogen in the steel as a result of reduction of water molecules by cathodic overprotection. This condition is another potential source of reduced H^+ ions [4]. Those gases are widely exist in the oil fields and could increase corrosiveness of the environments. Its existence serves as indication as source of early failures of the pipeline. Degree of corrosiveness of H_2 gas is influenced by environmental conditions such as temperature, CO_2 partial pressure, corrosion film properties and mechanical properties of the materials [5].

Experimental Setup

The specimens tested were HSS steel (AISI 4340) with chemical composition as shown in Table 1. The geometry of the specimens were as follows: gauge length: 25 mm, and diameter: 6 mm. Before immersing, the specimens surfaces were polished successively with 240, 400 and 600 grit SiC paper, rinsed with methanol and degreased using acetone. The test matrix which was used in the experiment is presented in Table 2. Samples were applied pre-strained under tension stress of 20% as presented in Fig.1.

Table 1. Compositions of high stress steel (AISI 4340).

Steel	C(%)	Si(%)	Mn(%)	P(%)	S(%)	Cr(%)	Mo(%)	Ni(%)
080A15	0.148	0.175	0.799	0.01	0.032	0.069	0.014	0.065

Table 2. Experimental matrix used in the test

Steel Type	SAE 1015
Aqueous solution	3 wt% NaCl
Purged gas	CO_2, H_2
Total pressure	Atmospheric
Cathodic potential	-1700 mV(Ag/AgCl)
Temperature	22°C
pH	4
Measurement techniques	Linear polarization resistance (LPR),

Electrochemical set-up to corrosion test. Glass cell was fitted with graphite electrodes as auxiliary electrode and a Ag/AgCl as a reference electrode. All experiments were conducted in 1-litre glass cell equipped with Ag/AgCl reference electrode and stainless steel as the auxiliary electrode. CO_2 gas was purged for 1 hour into 3% sodium chloride solution at 1 bar pressure for 1 hour. The linear polarization resistance (LPR) technique was applied to measure the corrosion rate. The procedure is similar to ASTM Experimental test G 5-94 [9]. To generate hydrogen productions, the samples were impressed under constant potential of -1700 mV Ag/AgCl.

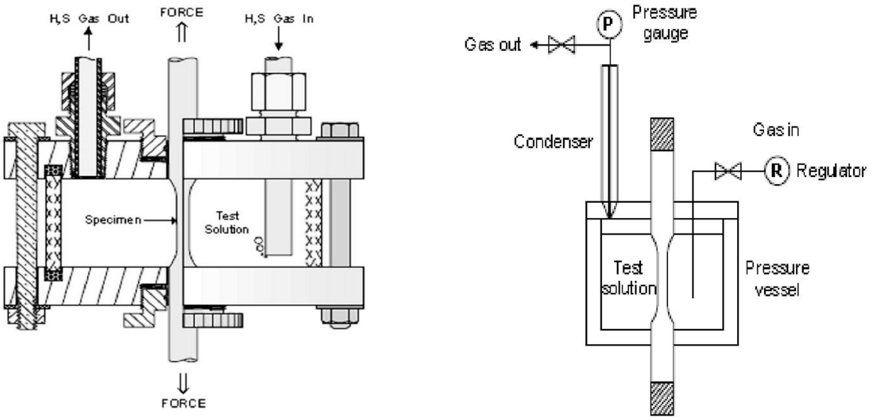
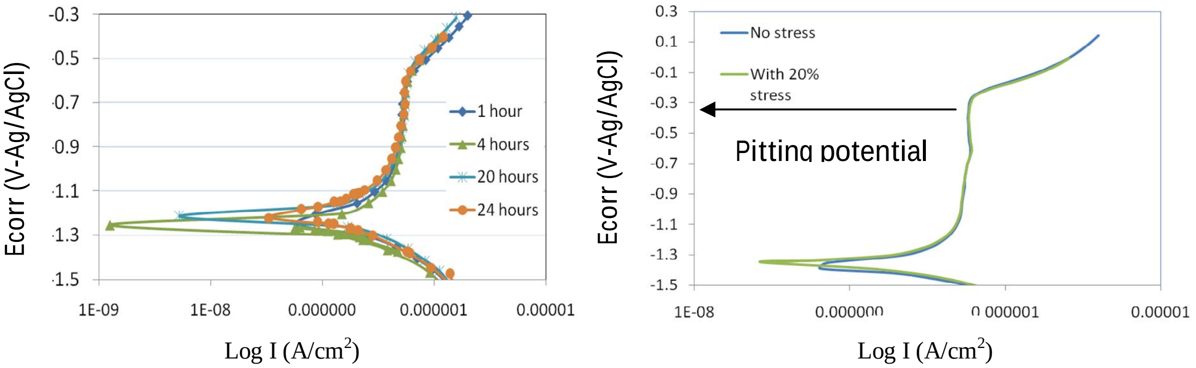


Fig.1: Schematic arrangement of test equipment [7].

Results and Discussions

Effects of initial stress on polarisation diagram. The polarization sweeps were conducted to study effect of CO_2 gas on corrosion rate. The results are presented in Fig. 2.a and Fig. 2.b. Fig. 2.a shows effects of immersion time on corrosion rate. It presents that the increase of corrosion rate as an effect of exposure time. The corrosion rate continuously increases up to four hours and start to remain constant after that. From the Fig. 2.b, it shows that there are no differences of polarization graph between materials with initial stress and without initial stress in CO_2 and 3% NaCl for three days exposure time. Although current density slightly increases in the stressed materials, but the tafel slope did not indicate significant differences.

Table 3 shows experimental data effects of CO_2 gas and H_2 gas on corrosion rate and corrosion potential (E_{corr}). It displayed that the significant factor in contribution corrosion rate is the presence of CO_2 gas which contributes 16 %. The increase of corrosion rate is not appearance on the effect of initial stress. Initial stress caused 7 % of decreasing corrosion rate. It indicated that the samples have experienced strain hardening. The hardening is able to strengthen metal by plastic deformation which can inhibit corrosion rate. This strengthening occurs because of dislocation movements and dislocation generation within the crystal structure of the material [6]. When CO_2 and H_2 gas were injected, the corrosion rate will increase dramatically. It shows 58% of increasing corrosion rate.



(a) (b)

Fig.2: (a) Polarisation diagram of samples at varying time under total pressure of 1 bar, saturated CO_2, 3 % NaCl. (b) Comparison polarisation graph of samples with and without initial stress at same conditions at three days experiment.

Table 3. Effect of CO_2, H_2 gas and initial stress on corrosion rate.

E_{corr} (V-Ag/AgCl)	Corr. rate (mm/y)	Conditions
-1.25	1.4×10^{-3}	CO_2 + stress
-1.35	1.2×10^{-3}	Blank + stress
-1.4	1.3×10^{-3}	Blank + no stress
-1.4	1.9×10^{-3}	CO_2+ stress+ H_2

Effects of H_2 gas on potential corrosion and corrosion rate. Fig. 3 is presented the effect of H_2 gas on HSS corrosion potential. H_2 gas was generated from cathodically protection (CP) of samples at -1.7 V. Comparing data before and after injecting current, it indicates that corrosion potential will decrease as an effect of H_2 gas production.

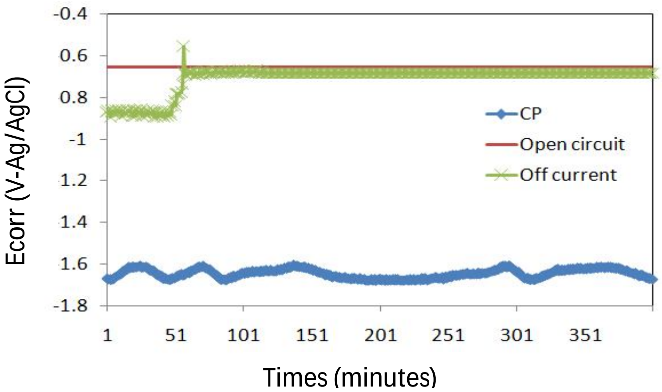


Fig. 3: Potentiostatic graph of effect of H_2 gas on HSS corrosion potential (E_{corr}).

Effects of H_2 gas on corrosion rate of notched materials. As can be seen from Table 4, there is increasing corrosion rate as an effect of H_2 gas on notched samples. From the Table 4, increasing corrosion rate will reach to 50%. Potential corrosion goes to negative. The corrosion rate increases to $1.3x10^{-3}$ mm/y. As mentioned by reference [8], the growth of crack tip on the surface occurs continuously until it has reached a critical crack length. This crack is used to accumulate stress concentration which may accelerate corrosion process.

Table 4. Effect of CO_2 gas, H_2 gas and initial stress on corrosion rate on notched materials.

E_{corr} (V-Ag/AgCl)	Corr. rate (mm/y)	Conditions
-0.9	0.7×10^{-3}	CO_2+ stress+ notch
-1.3	$1.3x10^{-3}$	CO_2+ stress+ notch + H_2

Conclusions

- In the presence of H_2 gas in 1 bar of saturated CO_2, the average corrosion rate increased approximately of 50% compared to free H_2.
- The introduction of initial stress has caused the corrosion rate to decrease.
- The anodic polarization behaviour did not change significantly with the additional of H_2 gas and CO_2 gas.
- Effects of H_2 gas on notched materials will also contribute to the 45% of increment of corrosion rate.
- The dominant factors that govern the reaction process are CO_2 and H_2 gas.
- Behaviour of anodic reactions is not consisted significant effects.

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