Study of corrosion behavior of carbon and low-alloy steels in CO₂-containing environments

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Abstract. Carbon and low-alloy steels, which constitute the main volume of pipe production, are unstable to the action of aggressive mineralized oil fields environments, which are often in the late stage of development. Recently, attempts have been made to use steels with an economical alloying of chromium up to 0.5% in CO₂-containing media without application of the additional measures against corrosion. The corrosion behaviour of carbon and low-alloy steels with a chromium content of up to 0.5% in CO₂-containing environments was investigated by electrochemical and metallographic studies. The results show that the addition of 0.5 wt% Cr could not effectively improve the corrosion resistance of the low-Cr alloy steel in CO₂-containing environments.

1 Introduction

Corrosion remains a major operational obstruction to successful hydrocarbon production, and its optimum control and management is regarded necessary for the cost-effective design of facilities and their safe operations [1]. Carbon dioxide (CO₂) is a constant component in produced water of almost any oil field. Typical corrosive damage on internal surfaces of pipelines caused by CO₂-corrosion is shown in Fig.1.

Fig. 1. A typical example of corrosion damage on internal surfaces of pipeline transporting CO₂-containing fluids

The industry continues to lean heavily on the extended use of carbon and low-alloy steels, which are readily available in the volumes required and are able to meet many of the mechanical, structural, fabrication, and cost requirements. Their technology is well developed, and they represent an economical materials choice for many applications. However, a key issue for their effective use is their poor general and CO₂ corrosion performance. Given the conditions associated with oil

and gas production and transportation, corrosion must always be seen as a potential risk. The risk becomes real once an aqueous phase is present and is able to contact the steel, providing a ready electrolyte for the corrosion reaction to occur.

In recent years, there has been an attempt to use low-Cr alloy steel (0.5% - 3% Cr) in CO₂ environments without inhibitor injection because adding Cr to low alloy steel could enhance corrosion resistance [2-4]. It has been reported that the addition of Cr contributes to the enrichment of Cr in the corrosion products, which causes the corrosion product layers to be more protective. In addition, an increase in Cr content could lower both the uniform corrosion rate and susceptibility to localized corrosion in CO₂ environments. While some authors have reported the beneficial effects of chromium additions, there is not yet a consensus on the optimum amount of Cr in the steel structure [1].

The objective of the present study was to evaluate the effect of Cr content up to 0.5 wt.% on the corrosion behavior of carbon and low alloy steels under different combinations of pH and temperature.

2 Experimental

2.1 Material

The test specimens with different alloying systems were selected from steels, serially used to produce oil and gas pipes. The steels used in this study are melted in electric arc furnaces with following ladle refining and final aluminium deoxidation and calcium treatment. All materials were analysed for chemical composition using

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atomic emission spectroscopy. Table 1 shows chemical compositions of steels used in the present study.

Table 1. Chemical compositions of steels

Steel	C	Si	Mn	P	S	Cr	Mo
0.20C-Mn (As rolled)	0.18	0.23	0.51	0.009	0.015	0.08	0.01
0.20C-Mn	0.19	0.22	0.54	0.009	0.003	0.08	0.02
0.15C-0.5Cr	0.15	0.23	0.53	0.008	0.002	0.64	0.01
0.10C-0.5Cr- 0.2Mo	0.11	0.38	0.56	0.008	0.005	0.60	0.18

According to Table 1 following steels samples were investigated: (1) C-Mn steel in as rolled condition, (2) C-Mn steel, (3) C-Mn-0.5Cr steel with 0.64 wt. % Cr addition and (4) C-0.5Cr-Mo steel with the relatively lowest carbon content and 0.60 wt. % Cr and 0.18 wt. % Mo additions. Last three steels were heat treated according to commercial production routes in order to obtain microstructures condition.

2.2 Electrochemical corrosion tests

The flat $\approx 0.80 \text{ cm}^2$ specimens were used for static electrochemical corrosion tests. Specimens were sequentially ground with 180, 400, and then 600 grit silicon carbide (SiC) paper with following cleaning, degreasing and drying. The test solution was prepared from deionized water with 5 wt.% NaCl. There were two types of solution regarding pH range that were used at different temperatures: 20, 40 and 60°C. Table 2 represents tests conditions. The pH range information will be used as the test solution description in results and discussion chapter.

Table 2. Corrosion electrochemical test conditions

Solution	Temperatures, °C	pH range
1.5 g/L NaHCO ₃ buffer, 5 wt.% NaCl static, deaerated, CO ₂ saturated	20; 40; 60	5.6-6.0
5 wt.% NaCl static, deaerated CO ₂ saturated	20; 40; 60	3.8-4.2

The solution was initially deaerated by 1 hour nitrogen bubbling. Corrosion tests were performed in a 300 mL cell under atmospheric CO₂ pressure. The cell setup consisted of: (1) three-electrode corrosion cell: Pt counter electrode, Ag/AgCl reference electrode, working electrode); (2) oil thermostat system; (3) CO₂ gas supply set (Fig. 2).

Fig. 2. External view of corrosion electrochemical tests setup

Electrochemical corrosion tests were consisted of open circuit potential (OCP) measurements and potentiodynamic polarization with 0.16 mV/s scan rate in range of OCP $\pm 50 \text{ mV}$ with followed corrosion rates (CR) calculations according to Tafel corrosion current (i_{corr}) extrapolation. Equivalent weights samples values were in range 27.99 – 28.14 depending on actual steels chemistry. Materials density was set to 7.8 g/cm³. Knowing specimen area, density, equivalent weight it was possible to calculate corrosion rates from corrosion current measurements results [5]. Graphic representation of electrochemical measurements procedure is shown in Fig. 3.

Fig. 3. Graphic representation of electrochemical tests measurements

OCP value corresponds to equilibrium corrosion potential and will be referred as potential in further discussion.

2.3 Metallography

Steel microstructure study was carried out with using light optical microscopy. Microstructures that were corresponded to transverse $\frac{1}{4}$ pipeline thickness were revealed by 4% Nital etching. Hardness measurements were performed by Vickers microhardness test with 180 g load.

3 Results and discussion

Prior the electrochemical test results discussion microstructure investigation will be presented. Investigated steels microstructures are shown in Fig. 4.

Fig. 4. Microstructures of investigated steels, $\times 200$, 4% Nital

0.20 C-Mn (as-rolled) and 0.20C-0.5Cr-0.2Mo steels had ferrite-pearlitic microstructures with relative hardness values equal to 175 and 198 HV. The C-Mn (As rolled) steel had not banded slightly coarse microstructure in comparison with 0.20C-0.5Cr-0.2Mo steel that have fine, but not homogeneous structure which is characterized by perlite and ferrite phase distribution. This type of inhomogeneity could be formed during annealing heat treatment and solidification inheritance phenomena occurrence [6,7]. The 0.20C-Mn steel microstructure investigation revealed fine distributed ferrite and pearlite phases. The revealed microstructure hardness is equal to 186 HV. The microstructure of 0.15C-0.5Cr steel is spheroidized annealed microstructure with uniform carbides distribution in ferrite matrix. The hardness was equal to 184 HV. So, as overall investigation it could be concluded that investigated steels are belong to similar strength grade, but with different microstructure conditions as the result of production route technology. The microstructure investigation will be used in electrochemical corrosion tests results interpretation.

As the results of electrochemical tests polarization curves for investigated steels in different environments were obtained and analyzed. For example, 0.20C-Mn steel polarization curves evolution depending on temperature and solution pH is presented in Fig. 5.

Fig. 5. 0.20C-Mn steel polarization curves evolution depending on temperature and solution pH

According to Fig.5 lower pH in non-buffered CO_2 saturated solution shifts OCP from ≈ 650 mV range to ≈ 550 mV with following increasing of cathodic and anodic reactions current densities. This fact is agreed with results of CO_2 electrochemistry study [8]. Also, the possible explanation of observed polarization curves shifts is cathodic reaction evolution due carbonic acid dissociation dependence on pH. The overall electrochemical corrosion tests results are presented in Table 3.

Table 3. Electrochemical corrosion test results

Steel	Temperature, °C	pH 5.6-6.0		pH 3.8-4.2	
		OCP, mV	CR, mm/y	OCP, mV	CR, mm/y
0.20C-Mn (As rolled)	20	-627	0.03	-562	0.33
	40	-641	0.08	-577	1.25
	60	-660	0.13	-588	1.71
0.20C-Mn	20	-632	0.02	-543	0.26
	40	-640	0.04	-564	0.61
	60	-664	0.05	-570	0.79
0.15C-0.5Cr	20	-652	0.06	-571	0.74
	40	-662	0.10	-585	1.43
	60	-677	0.13	-587	2.14
0.10C-0.5Cr-0.2Mo	20	-664	0.02	-541	0.36
	40	-677	0.04	-556	0.77
	60	-682	0.07	-567	1.29

According to electrochemical results (Table 3) the OCP from -682 to -627 were observed in solution with higher pH 5.6-6.0 and from -588 to -541 in non-buffered CO_2 saturated solution with lower pH 3.8-4.2. The corrosion rates measurements results showed following variation: $0.02 \div 0.13$ mm/y at pH 5.6-6.0 and $0.26 \div 2.14$ mm/y at pH 3.8-4.2, where increased rates correspond to increased environment testing temperature. Graphical comparative representation of obtained data (Table 3) is presented in Figures 6 and 7.

Fig. 6. Investigated steels potentials comparison depending on pH and temperature

From corrosion rates point of view steels could be ranged in following order from poor to best corrosion performance in CO₂ environment: 0.15C-0.5Cr, 0.20C-Mn (As rolled), 0.10C-0.5Cr-0.2Mo, 0.20C-Mn. In purpose of additional illustrations for this type of steel comparison Figures 8 and 9 are presented below.

Fig. 7. Investigated steels corrosion rates in CO₂ environment depending on pH and temperature

Fig. 8. Temperature influence on investigated steels corrosion rates in CO₂ environment with pH range 5.6-6.0

Fig. 9. Temperature influence on investigated steels corrosion rates in CO₂ environment with pH range 3.8-4.2

Overall analysis environment parameters influence has shown that by increasing temperature from 20 to 60°C and by decreasing pH from ≈ 6.0 to ≈ 4.0 corrosion rates were dramatically increased. The interpretation for this experimentally obtained fact is complex microstructure/chemistry effect and its interaction with environment.

Corrosion rates measurements results show that there was no benefit in 0.5Cr addition for 0.15C-0.5Cr steel as the result of high carbon content chromium was tied up in carbides and then was no more available to reduce corrosion rate.

The next 0.20C-Mn (As-rolled) is slightly better in comparison with previous example (0.15C-0.5Cr), due to ferrite-perlite microstructure after hot rolling process. The 0.10C-0.5Cr-0.2Mo has shown good performance and it is due to ferrite-perlite microstructure and alloying system but revealed ferrite-perlite microstructure inhomogeneity did not let get CO₂ corrosion benefit from Cr and Mo additional alloying. The 0.20C-Mn steel with relatively low sulphur content (Table 1) in comparison with as-rolled 0.20C-Mn steel and which is had fine well distributed ferrite-perlite microstructure has shown best performance in CO₂ containing environment. It should be noticed that obtained data is more likely corresponds to steel-environment interaction in instantaneous context and it didn't cover a complex topic of CO₂ corrosion products layer formation in time. There was published data [9] that the more uniform the distribution and the smaller the ferrite grain size, the lower the corrosion rate.

4 Conclusions

1. The corrosion and metallography studies of commercially available pipeline steels were provided. It was shown that 0.20C-Mn steel with fine homogenous microstructure had relatively lowest corrosion rates in CO₂ environment.
2. There is no clear evidence benefit significant influence of Cr and Mo addition on corrosion rates. The most possible reason is microstructure condition. For example, the 0.15C-0.5Cr steel in spheroidized microstructure condition have

relatively high corrosion rates in comparison with 0.20C-Mn steels.

3. According to investigated environments conditions, the temperature increasing and pH decreasing leads to steels corrosion rates increasing in CO₂ saturated environment.

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