CHARACTERIZATION OF CORRODED TUBING UNDER CO_2 ENVIRONMENT

Juan Carlos González [1], Giuseppe Cumino[1] , Renato Spelgatti [1]
Teresa Pérez [2]

[1] *DALMINE SPA (Dalmine BG Italy)*
[2] *Center for Industrial Research -CINI FUDETEC(Campana Argentina)*

SUMMARY: Carbon dioxide corrosion is one of the most important problems, in the Oil and Gas Industry, for production tubing and line pipes. The main types of corrosion are:

- Generalized corrosion (Loss of weight).
- Mesa-type corrosion (Localized corrosion under form of mesetas).
- Localized corrosion.

The main factors affecting the corrosion resistance are metallurgical (microstructure, heat treatment and presence of some elements like Chromium) and operational (flow rate temperature and partial pressure of CO_2 in the corrosive environment). Two field experiences are presented, representing two different situations of the used materials.
The first is relevant to C-Mn and C-Mn-B steels, the second to 1% Cr steels with different microstructures. Better results were obtained with 1% Cr steel (J55), normalized and with perlite-ferrite microstructure. For higher grades of tubings (like N80 or C95), the quenched and tempered (Q + T) materials are the only possibility ; thus, it's necessary to explore the role of different alloy additions like Cr, Cu, Ni to enhance the resistance CO_2 corrosion.

KEY WORDS: CO_2 corrosion. tubing, Carbon Manganese steel, Chromium steel, ferrite-perlite microstructure, sweet corrosion, tempered martensite, quenching and tempering.

INTRODUCTION

Carbon dioxide corrosion of production tubing and line pipes is one of the most important problems in the oil and gas industry: it is the cause of premature failures. This phenomena is well documented in the technical literature. The main types of corrosion mechanism are: generalized corrosion (loss of weight), mesa type corrosion (localized corrosion under form of mesetas), and localized corrosion. Recently, a new interest on carbon steels operating in corrosive environments containing CO_2 has been observed. It was demonstrated that the microstructure, heat treatment and the presence of some elements, like Cr, affect in some extent the steel corrosion resistance. Additionally to the above mentioned materials characteristics, there are some operative factors that affect the performance of the materials: these are flow rate, temperature and partial pressure of CO_2. Here, two field experiences are presented : the first with a C- Mn steels in quenched and tempered condition, the second with 1 % Cr. steels. In all cases, samples were taken after a work over and some of them showed very severe corrosion.

The effects of chemical composition and microstructure of carbon steels on corrosion resistance were also evaluated in laboratory, using a Loop and autoclave.

FIELD EXPERIENCES

The performance of C-Mn and Cr steels was evaluated.

C-Mn steels

Eight samples of C-Mn Q & T N80 steel were examined after service in a Russian field, with a water cut of 10 %, 8 % CO_2, total pressure 140 atm and a bottom hole temperature of 65 ºC . Chemical compositions are shown in table I. All the specimens presented different types of corrosion.

Table I : C-Mn and C-Mn-B Steels . Chemical Compositions

Sample	C(%)	Mn (%)	S (%)	P (%)	Si (%)	Ti (%)	B (%)
Nº1	0.33	1.38	0.018	0.015	0.19	0.003	0.003
Nº2	0.25	1.37	0.007	0.018	0.26	0.008	0.030
Nº 3	0.36	1.38	0.007	0.015	0.20	0.003	0.002
Nº 4	0.27	0.93	0.004	0.020	0.21	0.026	0.013
Nº 5	0.34	1.44	0.015	0.025	0.24	0.003	0.004
Nº 6	0.35	1.42	0.015	0.020	0.20	0.003	0.003
Nº 7	0.25	1.32	0.006	0.015	0.25	0.007	0.027
Nº8	0.26	0.93	0.005	0.017	0.21	0.024	0.018
Nº 9	0.36	1.41	0.012	0.014	0.21	0.003	0.002

- Sample analysis and results

  - Chemical analysis

    As shown in table I there are two steel groups the samples n° 1, 3, 5, 6 and 9 corresponding to C-Mn steel, and the samples n° 2, 4, 7, and 8 corresponding to C-Mn-Boron steel. The Ca contents resulted very low to achieve a full non metallic inclusion modification. Nevertheless the steels are very clean from the chemical point of view, having a very low Sn (≤ 0.005) and Cu (≤ 0.08%) content.

  - Macrographic analysis

    The internal surfaces of all the pipes (Figs. 1, 2, 3, 6, 7, 8, and 9) take the form of deep pitting. All the tubings were attacked in sharp, well defined pits, typical of sweet corrosion, originating the full penetration of the tubing wall, from the internal to the external surface. This is a typical appearance of CO_2 corrosion or “sweet corrosion” of carbon steel. Sample n° 4 (Fig. 4) showed a “line mark” corrosion with deep pitting. It is possible that the use of sucker rods or wireline tools had produced “wear” and also aggressive environment caused “abrasion-corrosion”. As regards sucker rods, the problem is over come by centralizing rods with plastic (nylon) centralizers. As shown in Figs. 5 and 7 (samples n° 5 and 7), the corrosion attack takes the form of “steps” with more quantity of loss metal, plus pits. Sample 7 (Fig. 7) shows an external tubing corrosion. It is possible that the contamination in the annulus zone was due to microbiological corrosion. If this is the situation it is very important to use an effective biocide according to the types of bacteria present in the oil field.

- Micrographic analysis
  All the samples, analyzed in an optical microscope at magnification X500, showed tempered martensite as microstructure (Fig. 10).

<u>1% Chromium steels</u>

Carbon steel with the addition of 1 % Cr were evaluated in wells with high level of CO_2 and water. These tests were done starting from 1992 in South America in 125 wells of 8 fields. The carbon- manganese tubings were substituted with 1 % Cr steel tubings and the operational results were very good, showing a strong reduction of the corrosion rate.

Table II: Chemical composition and microstructures.

Material	C (%)	Mn (%)	Si (%)	Cr (%)	V (%)	Microstructure	Yield Strength (ksi)
1% Cr Q+T	0,37	0,96 ,	0,22	1,04	-	Tempered Martensite	80
1% Cr F+P	0,37	0,96 ,	0,22	1,04	-	15 %Ferrite 85 %Perlite	70
C-Mn F+P 0,27 % C	0,27	1,28	0,33	-	-	50 %Ferrite 50 %Perlite	55
C-Mn-V F+P 0.32%C	0,32	1,46	0,29	-	0,12	30 %Ferrite 70 % Perlite	80
4140 1%Cr B	0,43	0,85	0,28	0,93	-	Tempered Bainite	80

LABORATORY TESTS

Steels with and without Cr addition were evaluated (Table II) . The effect of microstructure was also considered. Laboratory tests were performed in a special loop under different flow rates of the corrosive media, having a controlled chemical composition at a fixed temperature and pressure. The flow rates were 1,3 ÷ 3,5 and 6 m/sec. The tests were done with and without inhibitors. The test conditions are summarized in the table III and the results are shown in the tables IV and V. From these tables it is clear that without inhibitors at high flow rates (6 m/sec), all the materials are affected by localized corrosion. At lower flow rates (3,5 m/sec) the steel in the Q + T condition shows localized corrosion both with and without inhibition.

Table III : Test conditions

Test Conditions	Loop	Autoclave
Flow rate (m/sec.)	1,3- 3,5 y 6	3,5
Temperature (ºC)	100	100
Total Pressure (bar)	20,7 (300 psi)	20,7 (300 psi)
CO_2 Partial Pressure (bar)	3,1 (45 psi)	3,1 (45 psi)
Inhibitor	Two runs : with and without inhibitor	No
Test Duration (days)	14	14
Test Solution Composition (mg/lt.)		
Cl^-	15000	15000
Ca^{2+}	1000	1000
Mg^{2+}	2000	2000
HCO_3^-	200	200
SO_4^{2-}	100	100
Na^+	92500	92500

CONCLUSIONS

The two experiments presented, represent two different situations of the materials used for the corrosive environments containing CO_2 in the oil and gas industry. The first example, relevant to C-Mn and C-Mn-B steels, shows in a lot of cases the typical pits of the “sweet corrosion”, with full penetration of the tubing wall. Other cases show a corrosive attack with the form of steps and with presence of pits. The behaviour of the steel is very bad and it seems correlated with the microstructure (tempered martensite). The ferrite-perlite microstructure presents a better performance in CO_2 environment as demonstrated in literature and in other experiences in different oil fields. A further improvement is obtained, for the perlite-ferrite microstructure, adding 1% Cr in the chemical composition. The second example in fact, regarding steels with 1% Cr and different microstructure, shows a better behaviour of the steel J55 normalized with perlite-ferrite microstructure, compared with the same steel in the Q+T condition (laboratory test) and with the carbon steel (oilfield experience).

Particularly this last experience is very significant because of the high number of wells involved and of the long service period. It is clear that when tubing with higher Yield Strength are required because of the well design, for instance N80 or C 95, the Q+T materials are the only possibility. Thus, it is necessary to explore the role of different alloy additions like Cr, Ni, Cu to enhance the resistance to CO_2 corrosion.

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Table IV : Loop Tests without inhibitor

Material	Flow velocity	1,35 m/seg	Flow velocity	3,05 m/seg	Flow velocity	6 m/seg
	Average corrosion rate (mm/year)	Localized corrosion rate (mm/year) Attack type	Average corrosion rate (mm/year)	Localized corrosion rate (mm/year) Attack type	Average corrosion rate (mm/year)	Localized corrosion rate (mm/year) Attack type
1% Cr Q+T*	2,8	11 P+G	4	5 P+G	3,9	15 P+G
1% Cr F+P	1,8	3 (G)	1,2	- U	1,7	4 G
C-Mn 0,27 % C F+P	0,7	- U	-	- U	1,30	4 P
C-Mn-V F+P	0,7	- U	0,7	- U	0,8	2 (P)
4140 B	1,5	- U	1,2	- U	1	- U

* The test solution was saturated with Ca.

P = pitting; (P)/(G) very incipient pitting or crevice; G = crevice; U= uniform corrosion

Table V : Loop Tests with inhibitor

Material	Flow velocity	1,35 m/seg	Flow velocity	3,05 m/seg	Flow velocity	6 m/seg
	Average corrosion rate (mm/year)	Localized corrosion rate (mm/year) Attack type	Average corrosion rate (mm/year)	Localized corrosion rate (mm/year) Attack type	Average corrosion rate (mm/year)	Localized corrosion rate (mm/year) Attack type
1% Cr Q+T*	5,5	34 P+G	2	34 P+G	3,7	31 P+G
1% Cr F+P	0,40	- U	2,1	6 G	2,7	11 P+G
C-Mn 0,27 % C F+P	0,2	- U	0,76	- U	0,8	- U

P = pitting; (P)/(G) very incipient pitting or crevice; G = crevice; U= uniform corrosion

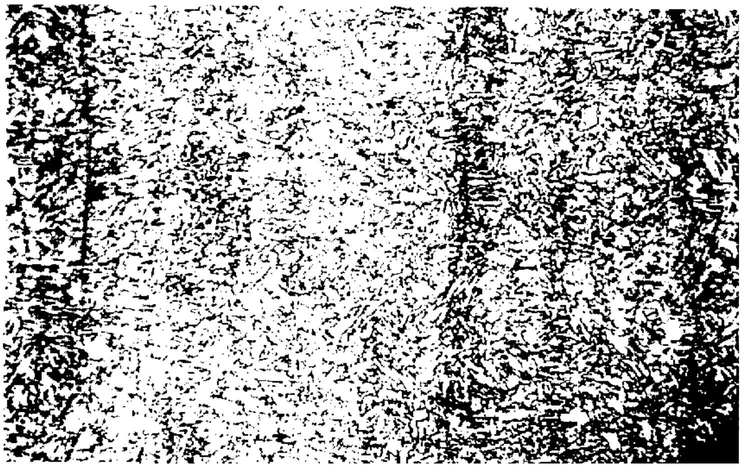

Figure 10 - tempered martensite 500X

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

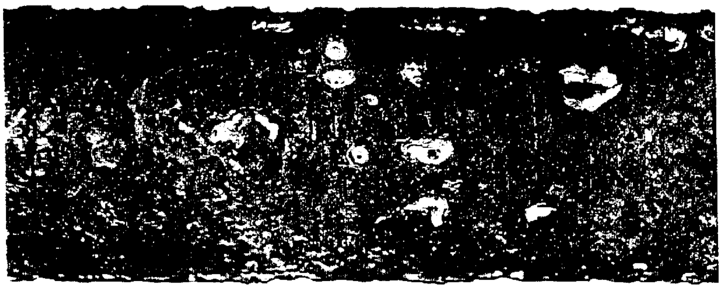

Figure 7

Figure 8

Figure 9