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Corrosion of Stainless Steels of Cryogenic Hydrocarbon Flare Tips (Burners) *(pp. 124-136)*

H. U. Nwosu[1] and A. U. Iwuoha[2]
[1] Department of Mechanical Engineering, University of Port Harcourt. Nigeria.
[2] Department of Mechanical Engineering, Evan Enwerem University, Nigeria.
Correspondence Email: nmatoha@yahoo.com.

Abstract: Analysis of the corrosion resistance of AISI Type 304 Stainless Steel (SS) used in flare tips (burners) of natural gas (NG) extraction facilities is considered to determine the resistance of this grade of austenitic stainless steel to the aggressive corrosive actions of the environment. It was observed that the grade of SS yielded quite early to corrosion attacks which gave effects to scaling, flaking, pitting, material thinning and flare distortions in the burners contrary to expectations. This necessitated replacements with costs and thus there was need to analyse the causes and find solutions to the problem in such a way that a longer service time could be obtained with minimal shut downs. The solution was found in the grades of SS with balanced higher quantities of nickel, chromium, molybdenum and SS type with partial nitrogen substitution for nickel which helps in stabilization of the austenite structure. There was need to balance the contents of the alloying elements to ensure the desired microstructure is preserved. Further study is required in the area of "weld decay" caused by intergranular corrosion of the weld HAZ.

Key words: corrosion, cryogenic service, environment, scaling, stabilization, stainless steel.

Abbreviations

ASME	**American Society of Mechanical Engineers**
AISI	American Iron and Steel Institute
ASTM	American Society for Testing and Materials
ID	Internal Diameter
HAZ	Heat Affected Zone
NG	Natural Gas
SS	Stainless Steel

1 INTRODUCTION

With the Federal Government of Nigeria fixing a deadline of 2008 for routine Flare-Out of Associated Hydrocarbon Gas in Nigeria Oil/Gas Industry (Umezurike, 2001), the Oil/Gas majors operating in the Nigeria Oil/Gas upstream industry embarked on a programme of commercialization of the associated gas with the installation of associated gas extraction facilities to gather, liquefy and export the gas (Pennwell, 1999). These facilities typically extracted the C_{1-5s} carbon-based gas while the rest is still flared. In addition, the facilities occasionally experienced hiccups in operations and gas is dumped in the flare system. These past eleven (11) years, the flare headers / burners typically made of stainless steels (Yamanaka and Kowaka, 1998), have corroded, which have generated interest to determine the level of resistance these grades of stainless steels could offer to the combustion products and hence provide more effective solutions.

2 THEORETICAL BACKGROUND

Stainless steels technically are called heat and corrosion resistant steels. This is so due to their higher resistance to corrosion and a higher resistance to scaling at high temperatures. The resistance is achieved by the formation of an invisible adherent chromium-rich oxide on the surface as a membrane. The oxide is formed in the presence of oxygen. In general, stainless steels are iron-based alloys containing at least 10.5% chromium. Other elements may be added to improve characteristics such as nickel, molybdenum, copper, titanium, silicon, niobium, selenium. Carbon is from less than 0.03% to more than 1.0% in certain grades. The common groupings for stainless steels are: Martensitic, Ferritic, Austenitic, Duplex (Ferritic-Austenitic), and Precipitation Hardening. Austenitic stainless steels are usually suitable for both cryogenic and high temperature service (Parmar, 2007).

2.1 Effects of Alloying Elements on Steels

Nickel: This has the impart of increasing the strength and toughness of the steel. Generally it combines higher strength level and hardness with enhanced elastic limit, good ductility as well as high resistance to corrosion and creeping at elevated temperatures.

Chromium: Generally the addition of this element improves hardness, strength and elastic properties. The great purpose is that it serves to impart corrosion resistance to steel both at low and high temperatures. Steels combined with chromium and nickel is extensively used in the automobile and oil/gas industries.

Manganese: It improves the strength of the steel be it in the hot rolled or heat treated condition. It is usually added in small amounts. The main uses of manganese steels are in machinery parts serving heavy wear operations as in gears and splines. These steels come in the cast state and are generally ground to finish.

Silicon: They are like nickel steels. Possess high elastic properties compared to ordinary carbon steels. Steels combined with silicon are employed in services requiring resistance to corrosion.

Tungsten: It inhibits the growth of grains, it increases the depth of hardening of quenched steel and stabilizes the property of hardness even when heated to become red hot. Tungsten combined steels are used in the machine tool industry as well as some aspects of the electrical industry.

Vanadium: Vanadium aids in obtaining a fine grain structure in the steel. Addition of small amount of vanadium (about 0.2%) achieves quite a high increase in tensile strength and elastic strength in low and medium grade carbon steels without appreciable reduction in ductility.

Molybdenum: A very small amount of molybdenum is added with chromium and manganese to form molybdenum steels. They possess extra high tensile strength and have anti-creep properties at high temperatures, thus the steel helps to stabilize chrome nickel steels at elevated temperatures.

Steels that must be resistant to creep at high temperatures must contain molybdenum, silicon and chromium. These impart on their resistance to oxidation and scaling at high temperatures. The steels that are satisfactory up to 700 ^{0}C working temperatures are: C = 0.15% maximum, Mn
= 0.5% maximum, Cr = 1.0 – 6%, Mo = 0.50%, Si = 0.5 – 2.0%, Ni = 0%. These are useful particularly for the valves of internal combustion engines. For temperatures of up to 1000 ^{0}C, steels of composition: nickel = 22% and chromium = 26% are used. These fall in the stainless steel group with not so-good mechanical properties at high temperatures. For good resistance to creep at 650 ^{0}C, 20% molybdenum is added (Davies and Oelmann, 2000).

2.2 Pitting Resistance Equivalent Number (PREN)

As a way of mathematical modeling, PREN was devised and has been found useful in providing a good approximation of the pitting resistance of stainless steels. PREN can be calculated as in Treseder(1983) as

PREN = %Cr + 3.3 x %Mo + 16 x %N

Usually once pitting has commenced in a material, it has the tendency to progress at the point though the remaining part of the material may remain intact. This makes it particularly serious. A number of laboratory tests are handy to evaluate the tendency of particular steel to be attacked by pitting corrosion. One of the commonly used is the ASTM G48. A graph can be plotted to show the temperature at which pitting corrosion is likely to occur. See Figure 5.

3 METHODOLOGY

A chemical composition analysis with Belec 2000 Analyser was performed to determine the actual grade of the burner materials and compared with the AISI standards. The governing flare stacks and burners design relations were considered and matched with the facility to determine service requirements level (GPSA, 2004). A theoretical analysis of the requirements of materials suited for resistance to corrosion in such environment was performed and based on that, it was hypothesized that the material chosen was not suitable for the service and new ones were considered relying on the strength of the higher contents of Cr and Ni to provide the desired results. Further, experimental tests based on pitting and "weight loss" analysis was carried out to evaluate the corrosion resistance of the chosen materials in the operating environment. This was based on ASTM G48. The software "statistics" was used to interpret / evaluate the results of the laboratory data. Both visual and metallurgical examinations were made on the corroded burners for any useful facts, for instance intergranular corrosion due to loss of alloying element.

Figure 1: Cryogenic Flare Header / Burner Arrangement

Figure 2: Expanded View of Flare Header / Burner

Manual vents, blowdown outlets and relief valve outlets from cold service vessels and lines are collected in a 50 cm header and routed to the cryogenic flare knockout drum where entrailed liquids are “knocked out” from the gas stream. The normal operating conditions of the vessel are 3.5 Bars guage (3.5 Barg) at 65 ^{o}C. The flare collection header and the vessel are fabricated with AISI type 304 stainless steel for cryogenic service. The design capacity of the vessel and by extension of steady state the volume rate through the flare header is 5.7 x 10^{6} SCMD (200 MMSCFD).

The flare header is 50 cm ID x 48 m tall above mean sea level. The flare header and burner are made from 304 stainless steel. Both flare header and flare burner have normal operation conditions of 2.8-3.5 Barg at -65 ^{0}C. The flare burner is of smokeless combustion design. Any liquid reaching the tip is atomized by the sonic flow jet and burned.

Table 1: Flare Burners Physical Data (Average for the Three Units)

Position above sea level	68 m above mean sea level.
Internal Diameter	45 cm.
Flare Header Material	AISI Type 304 Stainless Steel.
Flare Burner (Tip) Material	AISI Type 304 Stainless Steel.

Table 2: Corroded Flare Burners Service Data. ***Source: Facility Daily Operations logbook***

Unit	1	2	3
Service Time (Months)	37	40	44
Flare Gas	Cryogenic Natural Gas	Cryogenic Natural Gas	Cryogenic Natural Gas
Normal Operating Temperature	-65 ^{0}C	-60 ^{0}C	-55 ^{0}C
Normal Operating Pressure	2.5-3.0 barg	2.8-3.5 barg	3.8-4.5 barg
Gas Exit Velocity at Flare Burner	Sonic jet	Sonic jet	Sonic jet
Environment	Open sea conditions	Open sea conditions	Open sea conditions
Duty Cycle	Continuous	Continuous	Continuous
Duty History	Continuous in service, experienced occasional flare overloading.	4 shut downs of 72 hrs, 20 hrs, 12 hrs and 7 hrs. Otherwise continuous in service, experienced occasional flare overloading.	2 shut downs of 12 hrs and 24 hrs. Otherwise continuous in service, experienced occasional flare overloading.

Figure 3: View showing Bottom Area of Burner

Figure 4: Corrosion Effects in Burner Internal

Table 3: Chemical Composition of Flare Burner Material: AISI Type 304 Stainless Steel.

Element	**Flare Burner Material (% by mass)**	**AISI Type 304 Material (% by mass)**
Carbon	0.08	0.08
Silicon	0.90	1.00
Manganese	1.90	2.00
Sulphur	0.035	0.03
Nickel	8.50	8-10.5
Molybdenum	-	-
Phosphorus	-	0.045
Chromium	19	18-20
Iron	remainder	remainder

3.1 Examination of Corroded Flare Burners

The corroded flare burners were examined visually and metallurgically.

3.1.1 Visual Examination

- Minimal signs of “sweeps” were noticed at both inlet and outlet ends of the burner suggesting erosion corrosion played insignificant role in the corrosion damage.
- Some of the vanes of the burner have broken off at their roots.
- The internals have significantly thinned out (material loss) with scales and flakes.

- Pitting corrosion was prominent in the inlet area of the burner.

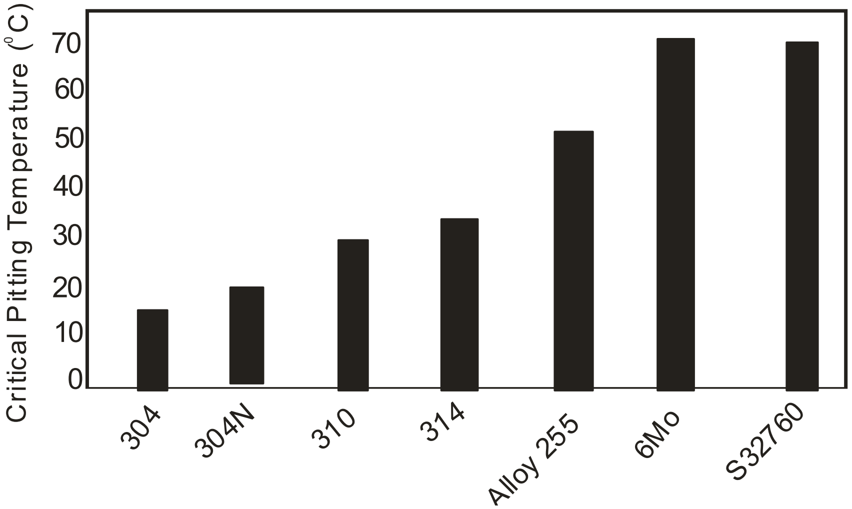

Figure 5: Alloys and likely Pitting Corrossion Temperature

3.1.2 Metallurgical Examination

- A chemical composition analysis result of Table 3 showed that the flare burner material was the same in composition with AISI Type 304 specified**.**
- Metallurgical examination of pitted regions identified cracks at the weldments, an indication of negative response to stress occasioned by the flow and thermal conditions (Cragnolino *etal* 2006). Figure equally suggests that the weldments may not have experienced the desirable post-weld heat treatment (Parmar, 2007).
- The crack direction was observed towards the inner portion of the metal as against running along the surface.

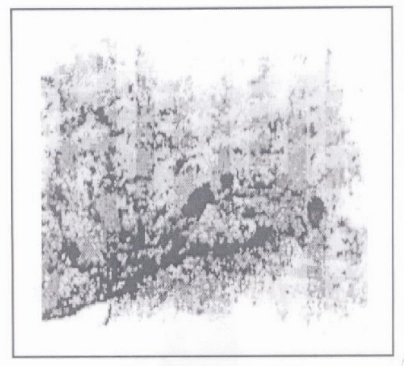

Figure 6: Scaling Flaking and Pitting of Burner

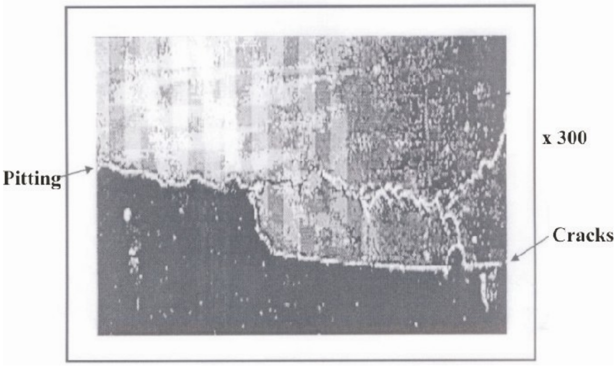

Figure 7: Pitting and Cracks Observed in Burner

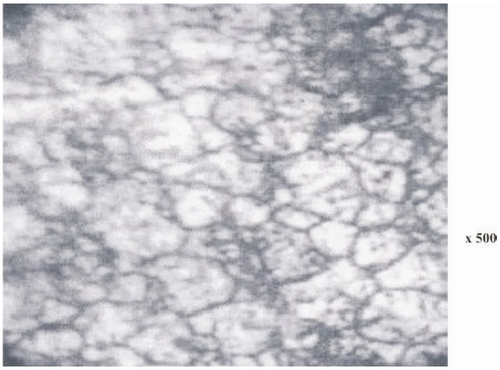

Figure 8: Microstructure of the Weldment

4 RESULTS AND DISCUSSION

The results of this study are presented in table 4.

Table 4: Results of Examination of Flare Burner Units 1 to 3

Flare Burners: Units 1, 2 and 3	Findings	Conclusion
Flare Burners: Units 1, 2 and 3.	Minimal signs of “sweeps” noticed at both inlet and outlet areas burners.	No significant evidence to support erosion corrosion.
Flare Burners: Units 1, 2 and 3.	Pitting corrosion observed in the inlet area of the burner and progressed to the outlet.	Insufficient Ni, Cr contents for longer corrosion resistance in the operating regime.
Flare Burners: Units 1, 2 and 3.	Some vanes of the burner broken off at their roots.	Stress cracking.. PWHT to relief stress.
Flare Burners: Units 1, 2 and 3.	Chemical composition analysis of the burner material showed that the grade of SS is same with type specified.	Inadequate amounts of Ni and Cr produced low corrosion resistance values and stability at the operating conditions.
Flare Burners: Units 1, 2 and 3.	Metallurgical examination of pitted regions identified cracks at the weldments,	An indication of negative response to stress occasioned by the flow and thermal conditions. Equally suggests weldments may not have experienced the desirable post-weld heat treatment.
Flare Burners: Units 1, 2 and 3.	The crack direction was observed towards the inner portion of the metal as against running along the surface.	Intergranular attack.

Based on the results of the analysis, the standard recommendations of this study are found in tables 5, 6 and 7. The following materials were recommended for the flare burners: Material A: AISI Type 304N SS; Material B: AISI Type 310 SS and Material C: AISI Type 314 SS. The recommendations were implemented. Replacement flare burners were produced with the recommended materials and were installed and put to use. The actual elemental compositions of these grades of steels used for the production of the new replacement burners are listed in Table 5 below alongside their AISI standards. Table 7 lists the new burners service data after installation and use.

Table 5: Chemical Composition of Recommended Flare Burner Materials: AISI Types 304N, 310 and 314 SS, Treseder (2000)

Element	Material A: Type304N		Material B: Type 310		Material C: Type 314	
	Flare Burner Material (% by mass)	AISI Type 304N Material (% by mass)	Flare Burner Material (% by mass)	AISI Type 310 Material (% by mass)	Flare Burner Material (% by mass)	AISI Type 314 Material (% by mass)
Carbon	0.09	0.08	0.25	0.25	0.20	0.25
Silicon	1.20	1.00	1.35	1.50	2.50	1.50-3.00
Manganese	1.95	2.00	1.90	2.00	1.90	2.00
Sulphur	0.025	0.03	0.025	0.03	0.025	0.03
Nickel	9.00	8.00-10.50	21	19-22	20	19-22
Molybdenum	-	-	-	-	-	-
Phosphorus	-	0.045	-	0.045	-	0.045
Chromium	22	18-20	24.5	24-26	24.5	23-26
Nitrogen	0.18	0.10-0.16	-	-	-	-
Iron	remainder	remainder	remainder	remainder	remainder	remainder

Table 6: Mechanical Properties of the Stainless Steel Grades, Treseder(2000)

Stainless Steel Grade	Tensile Strength Mpa	Yield Strength (02% Offset) MPa	Elongation in 50.80 mm %	Hardness (Brinell)
AISI Type 304	579	290	55	149
AISI Type 304N	621	331	50	180
AISI Type 310	655	310	45	170
AISI Type 314	690	345	40	180

Table 7: Recommended Flare Burners Service Data. ***Source: Facility Daily Operations logbook.***

Unit	**1**	**2**	**3**
Flare Burner Material	AISI 304N	AISI 310	AISI 314
Service Time (Months)	57 +	60 +	59 +
Flare Gas	Cryogenic Natural Gas	Cryogenic Natural Gas	Cryogenic Natural Gas
Normal Operating Temperature	-65 ^{0}C	-60 ^{0}C	-55 ^{0}C
Normal Operating Pressure	2.5-3.0 barg	2.8-3.5 barg	3.8-4.5 barg
Gas Exit Velocity at Flare Burner	Sonic jet	Sonic jet	Sonic jet
Environment	Open sea conditions	Open sea conditions	Open sea conditions
Duty Cycle	Continuous	Continuous	Continuous
Duty History	Continuous in service, shut down and inspected after 48 months, no pitting, scaling, flaking, material thinning observed. Returned to service and projected for inspection after another 48 months.	Continuous in service, shut down and inspected after 48 months, no pitting, scaling, flaking, material thinning observed. Returned to service and projected for inspection after another 48 months.	Continuous in service, shut down and inspected after 48 months, no pitting, scaling, flaking, material thinning observed. Returned to service and projected for inspection after another 48 months.

5 CONCLUSIONS

The following are the conclusions from the analysis and tests performed:

- The most stable stainless steels in the aggressive corrosive environment are the stainless steels with higher quantities of nickel, chromium, molybdenum and the SS type substituted with nitrogen which help in stabilization of the austenite structure.

- In progressing the quantities of the desired alloying elements, there is need to balance their contents to ensure the desired (austenitic) microstructure is preserved.
- Chloride ions that invariably exist in combustion decrease corrosion resistance of nickel and chromium stainless steels.
- Further study is required in the area of **“**weld decay**”** caused by intergranular corrosion of the weld HAZ.
- It is necessary to investigate / analyse the corrosion attack at the weldments of the flare header and provide mitigating solutions to the same.

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