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Material solution for sour environment of Delayed Coker Unit in a refinery

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ABSTRACT

Coker unit is an oil refinery processing unit that converts residual oil from the Vacuum Distillation Column or the Atmospheric Distillation Column into low molecular weight hydrocarbons. The delayed coker unit has a number of condensers and coolers. The material in such components encounters severe corrosive vapor environment. When it comes to shell side the major problem in condensers and coolers is that the feed to coker which is a residue from Vacuum Distillation Unit (VDU) or Fluid Catalytic Cracking Unit (FCCU) are heavy oils in which sulphur tends to concentrate. At elevated temperatures sulphur compounds crack to form hydrogen sulphide and other active sulphur compounds. Sometimes substantial cyanides may be present in vapors along with hydrogen sulfide and ammonia. Depending on the feed, naphthenic acid may also be present. So grade selected for heat exchanger tubes in components should be able to withstand sour service environments. A case study is presented where UNS N08028 seamless tubes are currently in service for Fractionator overhead trim coolers, First stage discharge coolers, De-butaniser overhead trim cooler and Lean amine coolers at an Indian refinery for last 12 years without any problems.

INTRODUCTION

New green field refineries being set up today are designed to handle more complex crudes which make them easy to handle sweet and sour crudes. The old refineries were designed to handle sweet crudes. In today's changing scenario they have to process crude from various sources including sour crudes, crudes having naphthenic acid, etc. Since the material of construction for equipment and machinery were designed for sweet crude, what we are seeing today is premature failures and degradation of materials under severe conditions. Since there is no flexibility in terms of choosing the source of crude, refineries are looking out for materials which can withstand such severe conditions. Our focus in this paper is on sour crude with high concentrations of hydrogen sulfide. We will be discussing specifically about heat exchanger tubing of debutanizer overhead condensers and stripper trim condenser in one of the refineries where there is wet hydrogen sulfide service on shell side and cooling water on tube side. Admiralty brass has been a major material of construction for heat exchanger tubing's of overhead condensers mainly because of their good thermal conductivity, corrosion resistance to cooling water and resistance to micro-biologically induced corrosion.

For such services where there is the possibility of presence of wet hydrogen sulfide in process fluid of condensers and/or coolers, there is a need to select a corrosion resistance alloys. UNS N08028 is a high nickel, high chromium stainless steel alloy specifically developed to withstand sour services. This material has excellent stress corrosion resistance to H_2S and also has good corrosion resistance to chlorides in cooling waters due to its high chromium, which provides passive layer and helps in pitting corrosion resistance against chlorides. This makes it an ideal choice for corrosion resistance material from both shell side and tube side. This material is also alloyed with copper to give it a good corrosion resistance to acids such as sulfuric/ phosphoric.

DISCUSSION

One refinery in North India was planning to put up a DCU unit and they were expecting sour services in Water cooled heat exchangers in over heads.

A high nickel, high chrome austenitic stainless steel, UNS N08028 was evaluated for such services with moderate to high chlorides in cooling water and in sour service conditions as might be prevailing in the overhead condensers/ coolers and other heat exchangers in refinery. UNS N08028 has high critical pitting temperature (CPT) in chloride-bearing water with salinity comparable to that of sea water. This means that this material can be used in cooling water with moderate to high chloride content and this takes care of resistance to pitting corrosion on cooling media side.

H_2S in itself is not corrosive for stainless steel. Due to its weak acidity, dew point corrosion from H_2S is not of concern. In combination with low pH and/ or high chloride concentration it can enhance hydrogen absorption. This can lead to hydrogen embrittlement of Ferrite/ Sulphide Stress Cracking (SSC). It can also form metal sulphides on the stainless steel surface which is a non-protective surface layer and retard's repassivation of pitting and crevice corrosion.

In any sour aqueous system there will protons (H^+) present which lead to acidity. The lower the pH, the higher the concentration of $H^{+\cdot}$ When metals corrode in sour environments H^+ is readily reduced to hydrogen. This forms as absorbed hydrogen atoms on the metal surface. Two hydrogen atoms can migrate on the surface, combine and leave the metal surface as hydrogen gas. The hydrogen atoms can also be absorbed into the metal, leading to hydrogen embrittlement. Hydrogen sulphide (HS^-) and sulphide (S^-) ions can "poison" the metal surface. This will retard the recombination of adsorbed hydrogen atoms and hydrogen uptake in metal increases dramatically. Ferrite phase is sensitive to hydrogen embrittlement. Hydrogen embrittlement occurs at low temperature, but hydrogen charging of a material increases with temperature due to faster diffusion rate in metal and reaction kinetics. Upon cooling the equipment, cracking due to hydrogen embrittlement can occur leading to possible work-over problems. If the aqueous environment is not acidic and if cathodic protections is not used the risk for hydrogen embrittlement is low.

According to NACE MR0175-ISO 15156-1:2003, UNS N08028 is categorized as solid solution nickel based alloy group 4c and is recommended for any application under the conditions described by table 2 below. In H_2S environment, UNS N08028 in cold worked condition showed excellent resistance to Stress corrosion cracking/ sulphide stress corrosion attack.

Material Type	Temperature Maximum (C)	Partial pressure	Chloride conc.	pH	Sulphur resistant	Remarks

		H2S,pH2S max, kPa (psi)	Max. mg/l			
Cold worked alloys of type 4c, 4d and 4e	232	0.2 (30)	See Remarks	See Remarks	No	Any combination of Chloride concentration and in situ pH occurring in production environments are acceptable
	218	0.7 (100)	See Remarks	See Remarks	No	
	204	1 (150)	See Remarks	See Remarks	No	
	177	1.4 (200)	See Remarks	See Remarks	No	
	132	See Remarks	See Remarks	See Remarks	Yes	Any combination of hydrogen sulphide, chloride concentration and in situ pH production environment are acceptable

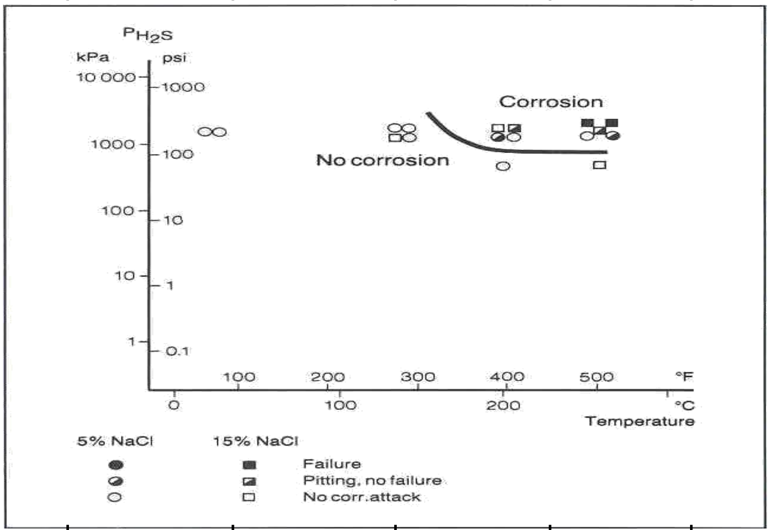

Table 2: Taken from NACE MR0175-ISO 15156-1:2003 table A.14 [1]

Previous research by our R&D Centre to investigate its performance was conducted under laboratory condition as shown below in Figure 3. The partial pressure of CO_2 was set at 1000 psi and pH approx. 2.9. Tests were carried out in 5 % NaCl (30,000 ppm Cl-) and 15% NaCl (90,000 ppm Cl-). It can be seen from Figure 3 that UNS N08028 can be used safely at high H_2S partial pressures and temperatures without any corrosion.

Figure 3: UNS N08028 laboratory sour test result. All specimens stressed to 100% of yield strength

TEST PROCEDURE FOR "U" BEND SPECIMEN

Grade	Pipe dimension	Lot no.	Certificate no.	Pipe test no.
UNS N08028	114.3 mm OD x 6.45 mm w/t	34672-6	A-03-008470	C121
UNS N08028	126 mm OD x 14 mm w/t	34594-2	A-03-008304	C120

Test specimens were made of two sections of pipes which represent tube 114.3 mm OD x 6.45 mm w/t produced with lot number 34672-6 and coupling stock 126 mm OD x 14 mm w/t produced with lot number 34594-2. Five 'U' bend specimens were machined from each product form and prepared in accordance to ISO 7539-3. The 'U' bends were identified by stamping with identification numbers of C120 (A-E) for tube material and C121 (A-E) for coupling stock material to maintain complete traceability.

Sulphide stress corrosion cracking tests were then undertaken in accordance with ISO 7539-1 and ISO 7539-3. The tests, using an independent lab's ¼ litre autoclaves and calibrated proof rings, were performed at a stress level of 90% of the actual 0.2% proof stress of the material. This gave a stress level of 712.8 N/mm^2. Each specimen was placed in an autoclave which was filled with 250 ml of de-aerated test solution in order to fully immerse the test specimen gauge section. The autoclave was sealed, placed in the proof ring and each specimen was stressed to the desired test stress. Following this the autoclave was de-aerated with oxygen-free nitrogen for two hours and then pressure tested to 60 bar with nitrogen. After the pressure test the nitrogen gas was vented from the autoclave and the solution saturated with 3.8 bar H_2S gas at 100 – 200 ml per minute for two hours at room temperature, (the pressure required to achieve 5.5 bar H_2S partial pressure at the test temperature). At this stage the autoclave was over-pressured to 28.4 bar with CO_2, left for 1 hour to allow CO_2 gas to absorb into the test solution and re-pressured at 28.4 bar. It was then heated to 150°C ± 3°C (300˚F ±5˚F) and any excess pressure was bled from the autoclave. The autoclave pressure at the test temperature was 54 bar and the test duration was 720 hours during which period both autoclaves were monitored for temperature and pressure. On completion of the test period, the autoclave was cooled down to room temperature, depressurized and the "U" bend specimens were removed for examination. The "U" bends were cleaned and assessed under a low power binocular microscope at 20X magnification.

TEST PROCEDURE FOR TENSILE SOUR TEST

Test specimens were made of two sections of pipes which represent tube 114.3 mm OD x 6.45 mm w/t produced with lot number 34672-6 and coupling stock 126 mm OD x 14 mm w/t produced with lot number 34594-2. Two sub-sized specimens were machined for each pipe in accordance to ISO 7539-4:1989. The tensiles are identified by stamping with identification number of C123 and C125 for tube material and C122 and 124 for coupling stock material to maintain complete traceability.

The sulphide stress corrosion cracking tests were undertaken in accordance with ISO 7539-1 and ISO 7539-4. The tests were undertaken using an independent lab's ¼ litre autoclaves and calibrated proof rings. The tests were performed at a stress level of 90% of the actual 0.2% proof stress of the material equalling a stress level of 787.5 N/mm^2. Each specimen was placed in an autoclave filled with 250ml of de aerated test solution in order to fully immerse the test specimen gauge section. The autoclave was sealed and placed in the proof ring and each specimen was stressed to the desired test stress. The autoclave was de-aerated with oxygen-free nitrogen for two hours and then pressure tested to 60 bar with nitrogen. Following the pressure test the nitrogen gas was vented from the autoclave. The solution was then saturated with H2S gas at 100 – 200 ml per minute for two hours at room temperature, at 3.8 bar pressure (the pressure required to achieve 5.5 bar H2S at the test temperature). The autoclave was then over-pressured with 28.4 bar of CO2, left for 1 hour to allow the CO2 gas to absorb in the test solution and re-pressurised at 28.4 bar. The autoclave was then heated to 150°C ± 3°C and any excess pressure bled from the autoclave. The total pressure at the test temperature was 54 bar. The test duration was 720 hours. During this period both autoclaves were monitored for temperature and pressure. On completion of the test period both autoclaves were cooled down to room temperature and vented to atmospheric pressure and test specimens were removed, cleaned and examined under binocular microscope at 20X magnification.

RESULT

As we have predicted from literature study, UNS N08028 had performed very well under the test condition. There were no cracks in tensile test specimen and U bend test specimen after 720 hours exposure.

Material Information: UNS N08028

It is a high-alloy multi-purpose austenitic stainless steel for service in highly corrosive conditions. The grade is characterized by very high corrosion resistance in strong acids, very good resistance to stress corrosion cracking (SCC) and inter granular corrosion in various environments, high resistance to pitting and crevice corrosion and good weldability. It is available in various product forms such as Seamless tubes and pipes, plate, sheet, strip, bars, welding wire, electrodes and fittings.

C	Si	Mn	P	S	Cr	Ni	Mo	Cu
≤0.020	≤0.6	≤2.0	≤0.025	≤0.010	27	31	3.5	1.0

Chemical composition (nominal) %[4]

Impact Strength

Due to its austenitic microstructure, UNS N08028 has very good impact strength, both at room temperature and at cryogenic temperatures. At high temperatures: Due to embrittlement caused by precipitation of intermetallic phases, UNS N08028 should not be exposed to temperatures above 600 °C (1110 °F) for prolonged periods.

Corrosion Resistance

Pitting corrosion resistance: UNS N08028 can withstand very high temperatures in aggressive environments without being attacked by pitting. Figure 4 below shows the critical pitting temperature

(CPT) for some alloys in chloride-bearing water with salinity comparable to that of sea water. The figure shows that UNS N08028 has a higher critical pitting temperature (CPT) than Alloy 904L and Alloy 825 even in acidic chloride solutions. The curves are displaced at higher temperatures in solutions with lower salinities.

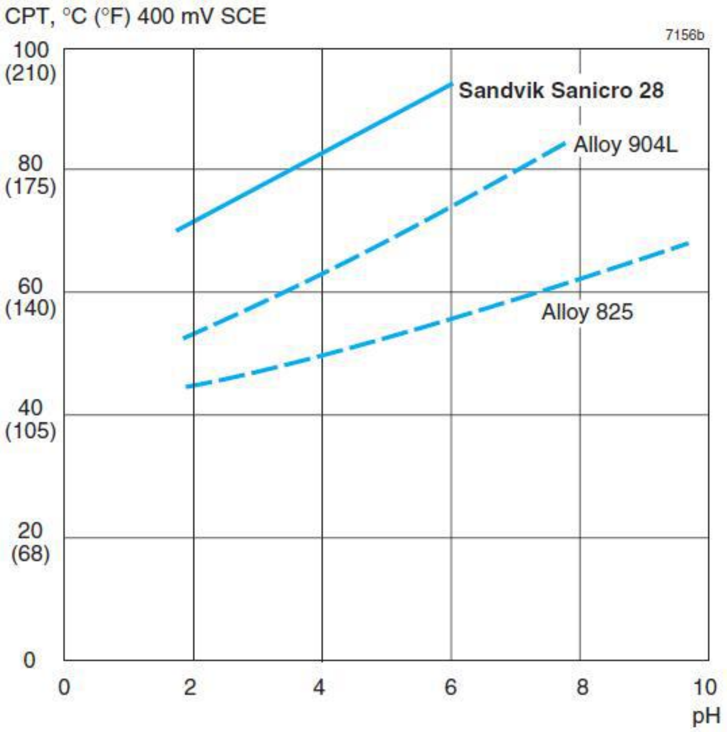

Figure 4: Critical pitting temperature (CPT) at +400 mV SCE for different alloys in synthetic seawater (3% NaCl) at different pH values [4]

Crevice corrosion: Laboratory tests show that UNS N08028 has good resistance to crevice corrosion. In tests according to ASTM G-48 method B (6% iron (III) chloride), the material exhibited better resistance than Alloy 825.

Stress Corrosion Cracking: Ordinary austenitic steels of the AISI 304 and AISI 316 types are susceptible to stress corrosion cracking (SCC) in chloride bearing solutions at temperatures above about 60°C (140°F). This susceptibility declines with increasing nickel content. Chromium contents above 20% can also be beneficial. UNS N08028, which is alloyed with 27% Cr and 31% Ni, exhibits very good resistance to SCC, both in laboratory tests and in practice. UNS N08028 also displays very good resistance to Stress corrosion cracking in environments where hydrogen sulphide is present together with chlorides. This is true for both solution annealed and cold worked material, as well as for welded joints.

Intergranular corrosion: UNS N08028 can be kept in the critical interval of 600-700°C (1100-1300°F) for at least 30 minutes without intergranular corrosion occurring in this highly corrosive medium. In normal welding operations, heat input to the parent metal takes place for a much shorter time than 30 minutes. This means that the risk of intergranular attack after welding of UNS N08028 is minimal, which is also verified by tests on welded specimens.

POSSIBLE APPLICATIONS IN REFINERY

Heat exchanger tubing's exposed to sour/ ammonia and chloride service such as overhead condensers in CDU/ VDU/DCU, Light end recovery units, sour water strippers. Piping and complimentary products tubing's in sour service.

CASE STUDY- OIL REFINERY IN INDIA

UNS N08028 grade of stainless steel has an impressive track record in delayed coke production. A large Indian oil company built a new delayed coker unit as part of an expansion project, in order to crack residual oil into lower molecular weight hydrocarbons. As is typical for such units, it contained sour service environments that contained ample hydrogen sulfide and thus, were very corrosive with a high risk of hydrogen-induced cracking. At some points, substantial amounts of ammonia and cyanide were also present. The main challenge for the plant's designers was, therefore, to specify a material grade for heat exchanger tubes that would withstand such hostile situations and ensure the safe operation of the plant over a long period of time.

Knowing that UNS N08028 is a safe choice for process flows rich in acids, chlorides and hydrogen sulfide they used this grade to form heat exchange tubes in the fractionator overhead condenser, the inter stage cooler, the debutanizer overhead condensers and the Re-contact product cooler. In all, 12 heat exchangers were made from a total of 80,000 m of this material.
After 11 years of operation, the heat exchangers were opened for inspection. The UNS N08028 tubes were inspected visually and via non-destructive eddy current testing. They showed no signs of corrosion.

DCU OVERHEAD HEAT EXCHANGER SUMMARY

EQUIPMENT	SERVICE FLUID		DESIGN PRESSURE		HYDROTEST PR. (KG/CM2)		OPERATING TEMP (CENTIGRADE)		SHELL MOC	TUBE DETAILS	QTY OF TUBES	DATE OF COMM	DATE OF LAST INSP	NO OF TUBES PLUGGED
	SHELL SIDE	TUBE SIDE	SHELL SIDE	TUBE SIDE	SHELL SIDE	TUBE SIDE	SHELL SIDE	TUBE SIDE						
Fractioner Overhead Trim Cooler (Six Numbers)	COKER FRACTIONATOR OVER HEAD	COOLING WATER	5	7	7	9.1	64.4/40	33/45	SA516 GR.60	SB 668UNS8028, Dimen: 20 X 1.6 X 6000	1762 x 6	Aug-06	May-14	Nil
First Stage Discharge Cooler (Two Numbers)	MIXED COMPRESSOR DISCHARGE	COOLING WATER	7	7	9.1	9.1	87.5/40	33.0/45.0	SA516 GR.60	SB 668UNS8028, Dimen: 20 X 1.6 X 6000	736 x 2	Aug-06	May-14	1 tube.
Re Contact Coolers (Two Numbers)	COMPRESSOR DISCHARGE	COOLING WATER	20	13.5	26	20	66.5/40	33/45	SA516 GR.60	SB 668 UNS 8028, 25 X 2 X 6000	858 x 2	Aug-06	May-14	Nil
De Butinizer Overhead Trim Cooler	DEBUTANIZER OVERHEAD	COOLING WATER	12.7	9	16.5	12.7	56.2/40	33.0/45.0	SA516 GR.60	SB 668 UNS 8028 20 X 1.6 X6000	1506	Aug-06	May-14	Nil
Lean Amine Cooler	LEAN AMINE	COOLING WATER	42.3	28.2	55	42.3	45/38	33/38	SA106 Gr.B	SB 668, UNS8028, 20 X 1.6X 600	66	Aug-06	May-14	Nil

Note: Data collected from Refinery

After 11 years of operation, the heat exchangers were opened for inspection. The UNS N08028 tubes were inspected visually and via non-destructive eddy current testing. They showed no signs of corrosion.

CONCLUSION

UNS N08028, which is a high Nickel, high chromium corrosion resistant stainless steel, provides a perfect solution to fight sour services in refinery which are becoming more and more visible. This is perfect solution as against next best alternatives such as copper alloyed, austenitic stainless steels, carbon steel etc. which are not expected to last beyond an acceptable service life of four years. Life cycle cost analysis also shows that the overall cost incurred while investing in high alloyed stainless steels is way less than lower alloyed steels despite their low initial investment cost.

ACKNOWLEDGEMENT

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REFERENCES

1. NACE INTERNATIONAL, Houston Texas. NACE MR 0175/ISO 15156-1:2001 Specification 'Petroleum and natural gas industries – Materials for use in H2S-containing Environments in oil and gas production Part 1: General principles for selection of cracking-resistant materials. 'ISBN 1-5759-1765
2. NACE INTERNATIONAL, Houston Texas. NACE MR 0175/ISO 15156-3:2003 Specification 'Petroleum and natural gas industries – Materials for use in H2S-containing Environments in oil and gas production Part 3 : Cracking-resistant CRA's (corrosion resistant alloys) and other alloys' ISBN 1-5759-1765
3. NACE INTERNATIONAL, Houston Texas, NACE TM 177-96 Standard test method: "Laboratory testing of metals for Resistance to Sulphide stress cracking and Stress corrosion cracking in H2S environment:. ISBN 1-57590-036
4. Sandvik Materials Technology,AB, Sanicro 28 technical datasheet, S-1885, May 2011

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