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Corrosion Behavior of UNS N08935 In Refinery Sour Water Services

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ABSTRACT

The nature of hydroprocessing reactor effluent air coolers (REAC's) to form hydrogen sulfide (H_2S) and ammonia (NH_3) from sulfur and nitrogen species present in the feed makes them prone to ammonium bisulfide (NH_4HS) corrosion. Various industry driven research have helped understand the relationship between the hydrogen sulfide or the ammonia partial pressure with NH_4HS concentration and their impact on the corrosion rate of several alloys in these services. Nowadays, the significance of flow rates, temperatures, H_2S and NH_3 present in the system have been well established and the corrosion performance of duplex stainless steels, or nickel grades, such as Alloy 825 and Alloy 625, in these environments have been widely accepted throughout the refining industry.

This study demonstrates the corrosion performance of UNS N08935 in refinery sour water services. Tests have been performed in H_2S -dominated environments with different NH_4HS concentrations. A total of six different H_2S -dominated environment environments are tested with three different H_2S partial pressures. The NH_4HS concentrations ranges between 5-30 wt%, two different temperatures are used and both stagnant and flowing conditions are evaluated. The results from these tests is showed comparing different alloys ranging from super duplex stainless steels to nickel base alloys exposed to the same conditions.

Key words: REAC, Reactor Effluent Air Cooler, Ammonium Bisulfide, Sour Water, H_2S , Hydroprocessing

INTRODUCTION

In hydroprocessing units, the effluent from the reactors entering the reactor effluent air coolers (REAC's) contains ammonia (NH_3) and hydrogen sulfide (H_2S) which will form ammonium bisulfide (NH_4HS). Additionally, H_2S is often in excess compared to NH_3 , so "free" H_2S can be expected in the effluent. In case chlorides are present in the feed to the hydrotreater/cracker, hydrogen chloride can form which together with ammonia will form ammonium chloride (NH_4Cl). To avoid getting solid salt deposits that lead to under deposit corrosion, erosion or blockage of the system, water wash is often implemented as a mitigation strategy.

Throughout the years, ammonium bisulfide corrosion (NH_4HS) in refinery sour water services has been the topic of investigation led by a joint industry program (JIP) that has seek to understand the origin and mitigation strategies as well as best practices to avoid this prevalent corrosion issue in the refining industry. Some of the key findings from the JIP addressed the factors influencing the corrosion of several alloys. For carbon steel, the corrosivity and risk for erosion-corrosion from the water phase is highly dependent on concentration, flow rate and turbulence in the system and 2% NH_4HS is considered to be the upper limit to avoid corrosion, but up to 8% NH_4HS has been acceptable with proper water wash and limitations on flowrates. In case of formation of solids salt particles and deposits, erosion-corrosion rates will increase for carbon steel and the risk for under deposit corrosion will also increase. For stainless steel and nickel-based alloys, much higher NH_4HS concentrations and flowrates are acceptable. Furthermore, H_2S partial pressure proved to be of significant effect on the corrosion of carbon steels and high alloyed materials. Overall, this study generated a relative ranking of the corrosion resistance of different alloys to REAC environments, where super duplex stainless steel 2507 (UNS S32570) was ranked among the best material for this application making it a superior alternative to nickel base alloys such as alloy 825 and alloy 625. A simplified summary and visual representation of this study is shown in figure 1 below and a similar ranking based on this research has since been adapted by API 932-B.¹

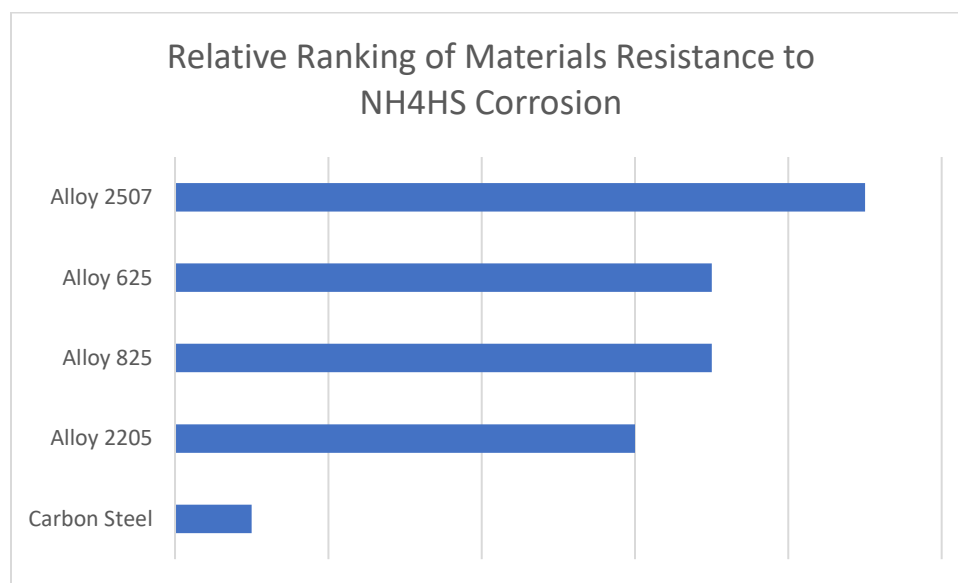


Figure 1. Simplified summary of alloys performance in NH_4HS ranking obtained from JIP.

Material selections for REAC's are nowadays almost solely based on the recommendations in API RP 932-B. Traditionally, the base material used for REAC's has been carbon steel. As discussed above, this solution works well if NH_4HS concentration, flowrates and water wash are all well controlled. Due to the risk of different hydrogen cracking mechanisms and blistering, a very strict inspection scheme needs to be adopted though. Duplex stainless steel of type 2205 has shown very good corrosion resistance in REAC's service. This together with a favorable price compared to nickel-based alloys and high alloyed

austenitic stainless steel has made this material solution very popular. However, due to fabrication issues resulting in high ferrite content in weld HAZ's, especially in header boxes, very severe failures and fires have been seen over the years which has led to several end users banning duplex 2205 for REAC applications. Nowadays, the increased demand for ultra-low sulfur fuel along with the high risk of corrosion, particularly cracking, associated with the current metallurgy used in REACs have shifted the refining industry to focus into proactively upgrading carbon steel and duplex stainless steels units with higher corrosion resistant metallurgy. Today, Alloy 825 or Alloy 625 are the next best available options depending on project economics and corrosion needs.

Utilizing the same testing laboratories, protocol and conditions used by the JIP referenced above, this study aims to compare the corrosion performance of Sanicro® 35¹ (UNS N08935) to that of Alloys 28, 825, 625 and super duplex stainless steel 2507 in ammonium bisulfide corrosion in refinery sour water services. UNS N08935 is a newly developed super austenitic alloy with a pitting resistance equivalent number (PREN) of 52 based on its 27% chromium, 6.5% molybdenum and 0.3 % nitrogen content. The alloy has a critical pitting temperature (CPT) of 110 °C (230 °F) in the modified (3 M MgCl₂) ASTM² G150 and a critical crevice temperature (CCT) in the 1 M NaCl ASTM G150 of 100 °C (212 °F).² Additionally, with its 35% Ni content, the alloy has shown excellent resistance to stress corrosion cracking. Furthermore, it has proven to have similar crevice corrosion resistance to nickel alloys 625 and C-276 in ASTM G48 Method D & F tests making it an attractive option for material selection for aggressive service conditions.³

EXPERIMENTAL PROCEDURE

Key testing conditions previously conducted in the sour water corrosion JIP¹ referenced before were selected to evaluate the corrosion performance of UNS N08935 compared to proven metallurgy commonly used in REACs. Sandvik Materials Technology supplied raw material in bar form for each alloy with chemical composition as seen in Table 1. Corrosion coupons specimens machined according to lab specifications were identified as shown in Table 2 below. All samples were exposed for 48 hours in flow-through conditions or static zone that simulate ammonium bisulfide (NH₄HS) corrosion under refinery sour water service conditions as shown in Table 3.

Table 1: Chemical composition of raw material supplied for corrosion specimen machining.

UNS	Heat	C	Si	Mn	Cr	Ni	Mo	Cu	N	Other
N08935	553864	0.017	0.20	0.64	27.0	35.1	6.3	0.16	0.31	-
N06625	048803	0.018	0.06	0.09	21.3	63.3	8.3	0.04	-	Nb=3.35
N08028	556364	0.013	0.39	1.72	26.7	30.8	3.4	0.86	0.06	-
S32750	554985	0.010	0.34	0.44	25.3	6.5	3.9	0.12	0.29	-

Table 2. Corrosion coupon and material identification.

Coupon Code	Material	No. of Flow-through Specimens	No. of Static Zone Specimens	Flow-through specimens ID	Static Zone Specimen ID
14670	Alloy 28	14	14	F-1 ... F-14	S-1 ... S-14
14671	Alloy 35	14	14	F-1 ... F-14	S-1 ... S-14

¹ registered trademark

² ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA

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