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Corrosion Properties Of UNS N08935 In Crude Distillation Unit Overhead Service Conditions

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ABSTRACT

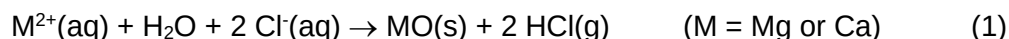
Overhead condensers (OHC) in refinery applications such as atmospheric and vacuum distillation units often experience very corrosive environments due to condensation of hydrochloric acid, HCl. The acid is often neutralized using water washing and addition of a caustic solution such as ammonia (NH₃) or an organic amine such as monoethanolamine (MEA) or dimethylethanolamine (DMEA). While neutralizing the HCl, addition of these bases can lead to chloride salt deposits with following possible pitting corrosion, under deposit corrosion and stress corrosion cracking of the tubes in the OHC. In this work, the recently developed grade UNS N08935 has been tested in a laboratory environment mimicking ammonium chloride under-deposit corrosion and aqueous acidic corrosion in OHC applications. The results from the testing will compare the performance of N08935 to super duplex stainless steel UNS S32750 and nickel base alloy UNS N06625 being exposed to different temperatures, HCl and NH₃ concentrations and flow rates representative of crude unit overhead condenser operating conditions.

Key words: Crude unit, Crude overhead, HCl, Ammonium chloride, Salt formation, Material selection

INTRODUCTION

Crude oil that comes to refineries contains some amounts of water and therein dissolve salts, the salts can mainly be described as sodium, magnesium and calcium chlorides. Most of the water, and thereby the salts, are removed in the desalter prior to the crude being heated and injected into the atmospheric distillation column. Even with a very effective desalting process though, some water and salts will always

remain in the crude. This can quickly become a problem as magnesium and calcium salts that are heated can hydrolyze and form hydrochloric acid (1):



The hydrochloric acid formed in the atmospheric distillation column will mainly exit with the overhead gases at the top of the column. From there it will go to the overhead condenser (OHC) where it will readily condense when the stream is cooled down. The OHC therefore often experience highly corrosive operating conditions. To mitigate the corrosion issues caused by the hydrochloric acid, water wash and injection of a chemical base is commonly employed. The base used can in some cases be just a regular caustic solution such as sodium or potassium hydroxide, but as metal ions are not desirable in the process stream it is more common to use a weaker base such as ammonia or an organic amine such as monoethanolamine (MEA) or dimethylethanolamine (DMEA).

When neutralizing the hydrochloric acid, the base will essentially become a chloride salt dissolved in the water phase. Using ammonia as a base will thus give dissolved ammonium chloride (NH₄Cl), MEA will give MEA hydrochloride, etc. The water solubility of these salts is high but since the amount of water is limited the water phase may still become saturated with salt leading to salt deposits in the OHC. The salt deposits are hygroscopic and will give a very corrosive environment beneath them with a water phase saturated with chlorides. This can then lead to under deposit corrosion and short lifetime of the equipment. Most commonly, problems with under deposit corrosion are seen on the tubes but accumulation of salt in the bottom of the heat exchanger can also lead to corrosion and poor flow in the heat exchanger. Chloride salt deposits are not isolated to the OHC in the atmospheric distillation column but is a frequent problem encountered in many OHC within refineries. To get a better understanding of different materials behavior in OHC service the Honeywell¹ CDU-OH Corrosion JIP was performed². The results from the JIP resulted in the software Predict[®]-CDU-OH³, used for predicting the corrosion rate for different materials in a specific CDU-OHC environment.

Material selection for OHC and tests performed in this work

In case of problems with chloride salt deposits in the OHC, high alloyed stainless steels are usually used for the tubing. Due to pitting, under deposit corrosion and chloride induced stress corrosion cracking (CI-SCC) the austenitic 300-series should be avoided. Duplex 2205 and austenitic 904L, which would be the next natural step when the 300-series stainless steels do not work, usually do not have good enough corrosion resistance either. This leads to the use of super duplex or super austenitic stainless steel or even nickel base alloys in severe cases for the tubes in the OHC.

The newly developed austenitic grade N08935 is high alloyed with nickel, chromium, molybdenum and nitrogen. From its nominal chemical composition, it has a PRE⁴>52, giving it excellent corrosion resistance in chloride bearing environments [1]. In a paper by Delblanc *et al.* it is shown that N08935 has equal pitting corrosion resistance to Alloy 625 [2]. It has also been shown that N08935 has equal or better crevice corrosion resistance in ASTM⁵ G48 Method D & F [3] tests compared to UNS N06625 (Alloy 625) and UNS N01276 (C-276) [4]. In addition, N08935 has very high mechanical strength and excellent ductility which together with very good structure stability gives it favorable fabrication properties. Overall,

¹ Honeywell International Inc., Charlotte, North Carolina, USA.

² Due to the JIP confidentiality, no specific information of test results or photos of the test equipment can be revealed.

³ Predict[®]-CDU-OH is a copyright owned by Honeywell International Inc., Charlotte, North Carolina, USA.

⁴ PRE = Pitting Resistance Equivalent = %Cr+3.3×(%Mo+0.5×%W)+16×%N [5]

⁵ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.