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Investigation of Naphthenic Acid and Chloride Corrosion in the Crude Oil Preheat Exchanger of Shiraz Refinery According to API 581 Standard

Alireza Mohebbi [1*], Jamal Bagheri [2]

[1] Senior Refining Operations Operator, Shiraz Refinery, Shiraz

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1. ABSTRACT

In the crude oil preheat network of the Shiraz refinery, the tube bundle of a heat exchanger that uses gasoil to raise crude oil temperature has been replaced several times due to corrosion. Naphthenic acid and chloride are widely recognized as dominant corrosive species in crude oil refining processes. Using HTRI simulation, the skin temperature of the tubes in heat exchanger tube passes were calculated. Then, an assessment was conducted to determine whether the HTRI-calculated temperatures overlap with the naphthenic acid corrosion susceptibility range defined in API 581. According to API 581 standard, 316L stainless steel containing at least 2.5% molybdenum is recommended for heat exchanger tubes to improve corrosion resistance. Molybdenum stabilizes the protective layer and increases the resistance to pitting corrosion.

Keywords: Corrosion, Naphthenic Acid, Chloride, API 581 Standard, Molybdenum.

2. INTRODUCTION

Oxide layer that forms on the metal surface has been recognized as effective film in reducing the rate of corrosion of the alloys. So, if this protective passive film breaks down due to the presence of aggressive anionic species (chloride ions) with a high diffusivity, dissolution of underlying metal speeds up. Presence of molybdenum on the active sites of surface leads to low susceptibility to pitting. In environments with nonaggressive species, local breakdown of passive film is rapidly rehabilitated. But, migration of aggressive anions like chloride ions to the metal interface with assistance from high electric field in the film, hinders repassivation.

Corrosion resistivity of stainless steels is not acceptable in a certain corrosive environment due to a breakdown of the passive film. As a result, stainless steel corrodes in the form of pitting. In pitting (localized corrosion) the rate of corrosion is greater in some parts than the others. In pitting corrosion, high ratio of large passivated area (cathode) to small active area (anode) causes rapid galvanic corrosion (electrochemical oxidation-reduction process) and detrimental local dissolution of the metal.

Naphthenic acids may destabilize impurities on protective films and decrease a material’s corrosion resistance. Naphthenic acids act as corrosive agents of liquid phase in refinery equipment. The presence of naphthenic acids in the feedstock leads to the reaction of the acid with iron in the metal and formation of oil-soluble iron naphthenates [1, 2].

According to Figure 1, the tube bundle of the crude oil heat exchanger at the Shiraz refinery has been replaced due to the first tube pass corrosion.

* alireza2010mh@gmail.com

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Figure 1. Replacement of the heat exchanger tube bundle at the Shiraz refinery

The tube skin temperature is one of the most important factors affecting naphthenic acid corrosion and subsequent chloride corrosion. One of the important capabilities of the HTRI software is the calculation of the tube skin temperature. Using HTRI simulation, the skin temperature of the tubes in heat exchanger tube passes were calculated. Then, an assessment was conducted to determine whether the HTRI-calculated temperatures fall within the naphthenic acid corrosion risk temperature range specified in API 581 guidelines. By analyzing the simulation results, an appropriate material for the heat exchanger tubes has been presented according to the API 581 standard.

3. RESULTS AND DISCUSSION

3.1. Naphthenic Acid

Naphthenic acids may destabilize impurities in the passive layer and decrease a material's corrosion resistance. Naphthenic acid corrosion occurs in the range of 204 °C to 399 °C (above 204 °C) where liquid phase is present. Iron-chrome (5 to 12 % Cr) alloys and carbon steel used in refining services are susceptible to naphthenic acid corrosion. To provide the excellent resistance to naphthenic acids, a minimum molybdenum content of 2.5 % is necessary in the molybdenum containing austenitic stainless steels [3].

As can be seen in Figure 2, the skin temperature of tubes is above 204°C only in the first tube pass, which is consistent with the experimental corrosion result that shows corrosion only in the first tube pass.

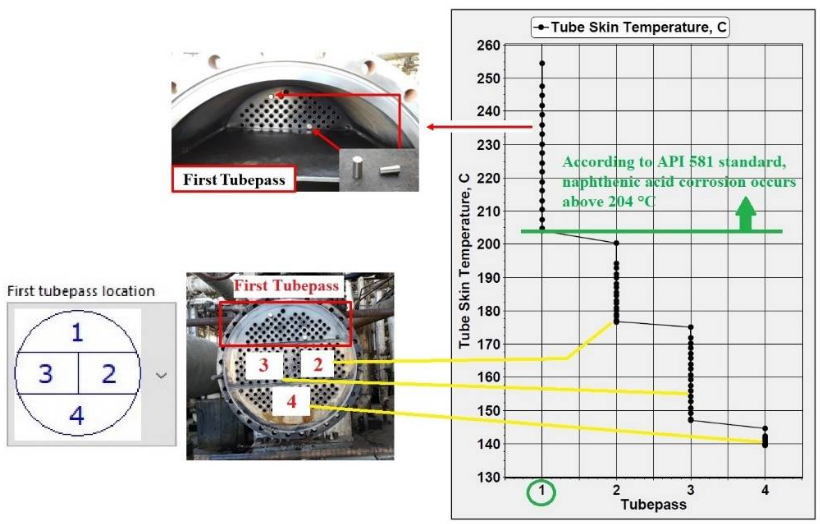

Figure 2. Calculation of skin temperature of the tubes in heat exchanger tube passes by HTRI software

3.2. Pitting Resistance Equivalent Number (PREN)

The presence of chromium, molybdenum, and nitrogen in the stainless steel enhances the resistance to localized corrosion. PREN is presented by the following equation:

PREN = %Chromium + 3.3 %Molybdenum + 16 %Nitrogen

PREN is a number to predict the resistance of material against pitting. A higher PREN reflects better resistance to pitting corrosion. Molybdenum has a significant effect on pitting resistance property of an alloy. Effect of molybdenum addition on PREN is three times greater than chromium addition in increasing resistance to pitting [4, 5].

As illustrated in Figure 3, proposed material of molybdenum-containing 316L stainless steel has a higher PREN that represents a better ability to resist pitting.

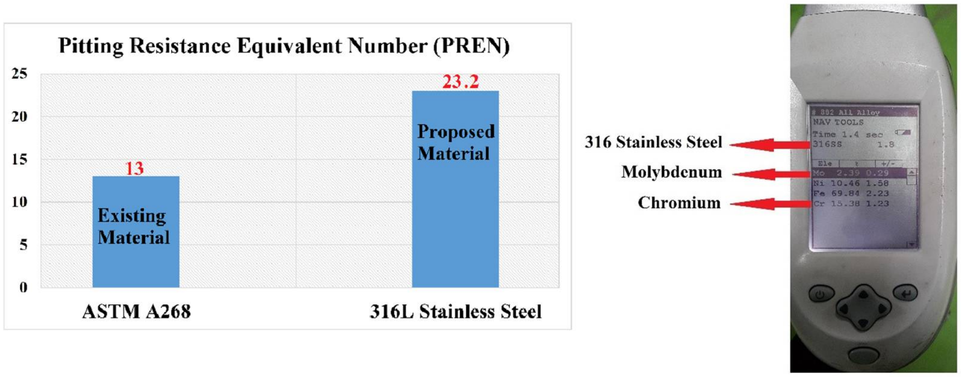

Figure 3. Comparison of PREN for first tube pass of the heat exchanger

4. CONCLUSION

The primary objective of the present work is to identify the root cause of corrosion failure. The calculated skin temperatures in the first tube pass were found to overlap with the naphthenic acid corrosion susceptibility range defined in API 581. Consequently, naphthenic acid corrosion is considered the most probable corrosion mechanism in this region. This interpretation is corroborated by plant inspection results, which revealed corrosion damage exclusively in the first pass of the heat exchanger tubes. Therefore, material selection for the heat exchanger tubes should be conducted in accordance with the recommendations of API 581.

The presence of molybdenum in stainless steels enhances the stability of passive films in naphthenic acid environments while simultaneously increasing resistance to chloride-induced pitting corrosion. As a result, 316L stainless steel, owing to its molybdenum content, adequate chromium level, and excellent weldability, can be considered an appropriate material for heat exchangers operating in streams containing both naphthenic acids and chloride ions.

Nevertheless, corrosion mitigation is not limited to alloy modification. The addition of inorganic salts such as sodium molybdate introduces molybdate anions into the process medium. These anions function as corrosion inhibitors by adsorbing onto the metal surface, strengthening the passive layer, forming insoluble compounds with metal ions, suppressing pit propagation, and promoting repassivation. Consequently, chloride ingress is restricted and the pitting corrosion rate is significantly reduced.

5. REFERENCES

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