Corrosion Case Study of SS316L Amine/Amine Plate Heat Exchanger at SPGC Ethane Refining Unit

Reza GHORBANI [1], Seyed Omid RAZAVI ZADEH [2]

[1]*South Pars Gas Complex Co. Asaluyeh, Iran, rezaghgh@yahoo.com*
[2]*Sharif University of Technology, Tehran, Iran, o.razavizadeh@gmail.com*

Abstract
Ethane treatment process unit at South Pars Gas Complex includes sweetening the gas by acid gas absorption with Di-Ethanol Amine (DEA). In this process hot lean amine discharging from regeneration tower, pre-heats the rich amine by a plate heat exchanger (PHE). The operation, in SPGC recorded a noticeable decrease in PHE performance and recommended to isolate for inspection. Primary visual inspections revealed significant scaling in rich amine side. Consequently, chemical composition of scales was analysed which iron oxide detected as predominant compound. Also penetration test (PT) revealed pitting corrosion on gasket seat. Pitting morphology and mechanism investigated using Stereo Microscope (SM), Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). In addition gasket glue was analysed using FTIR spectroscopy to find halide compounds. Results show that the chlorine extracted from PVC compound of gasket glue and caused pitting initiation. Besides, residual stresses from cold work during plate forming activated the Chloride Stress Corrosion Cracking (CLSCC) mechanism which initiated from bottom of pits and then cracks propagated through grain boundary.

Keywords
Plate heat exchanger; Amine; Pitting; CLSCC; Chlorine;

Introduction

Ethane treatment units is designed to eliminate acid gas such as CO_2 delivered from unit 105 (ethane recovery unit). Thus this unit receive and process acidic ethane gas, and exports dried ethane gas to petrochemical plants. Since the H_2S is absorbed in upstream unit, there is no H_2S content in gas. Mixed carbon dioxide is separated in absorption tower by Di-Ethanol Amine (DEA) chemical absorption. Consequently rich amine (fat solvent) produced, which requires purification. Rich amine is stripped from acid gasses in regeneration tower to produce lean amine. Saturated humidity of sieves are reduced by injecting 7% of dried ethane and heated at 300°C onto the sieve beds.

This research focused on the PHE failure to pre-heat rich amine before entering regeneration tower. Plate heat exchangers are chosen over shell-and-tube exchangers with regards to superior priority on heat transfer efficiency, compactness, and lower weight. Efforts to maximize their inherent advantages drive plate heat exchanger design toward the use of thin plate section that require highly corrosion-resistant materials. The carbon dioxide loaded DEA solution ran counter-current to hot lean DEA solution in a PHE. This process improves the tower operation and acidic gas stripping. So that steam generated in boilers separates the acidic gas by a counter current contact [1].

Figure 1 represents a PHE structure and operational flow. These exchangers are made of numerous thin metallic plates that are compacted by stud bolting pressure. Cold and hot fluids flows in opposite direction in decussate spaces between plates. The plate are specially designed to form a laminar flow of fluids which have a high coefficient of heat exchange. Meanwhile narrow flow passages are conductive to fouling. Material selection for plates depends on the temperature, pressure and fluid, but however they are mostly made of steels which can be cold formed [2]. Plate heat exchangers in general require extensive sealing along the edges of the plates. The spaces between each pair of plates can be sealed by laser weld or elastomeric gasket ring. In later type during the PHE assembly the gaskets are fixed in their position by applying polymeric adhesives.

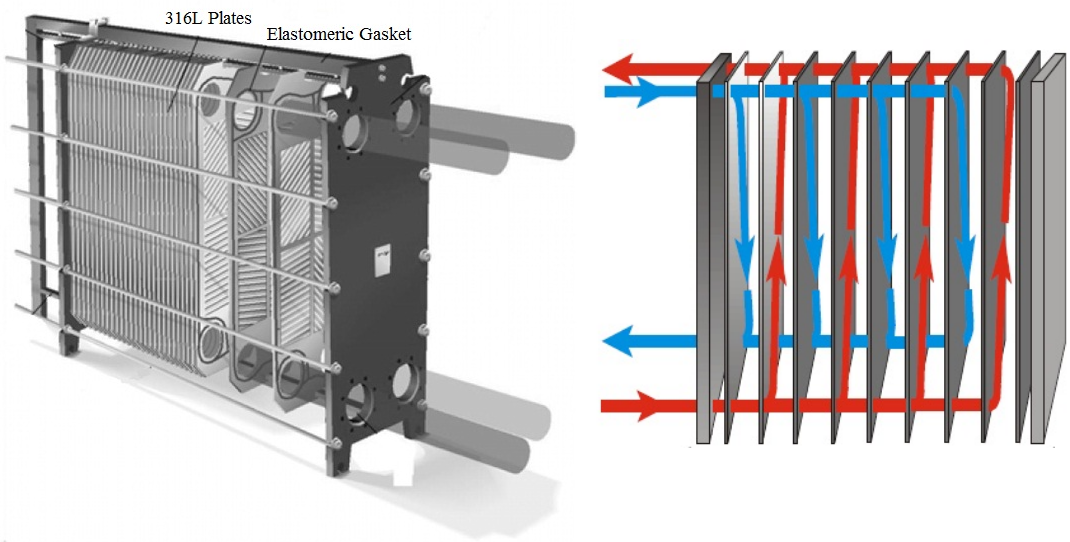

Figure 1. Plate Heat Exchanger structure and process schematic [2].

Case History

The operation division at SPGC fifth refinery noted an abnormal operation and significant reduction in efficiency of PHE (116-E-111). Iron scales coated the opposing plate surfaces in the rich DEA stream. The scale build up was sufficient to block the flow passages in some areas. This PHE operating window information are listed in table 1. Following this notice the

inspection department requested for PHE shutdown and disassembly. Figure 2-a shows this heat exchanger plates in rich amine side after primary jet wash. A section in this plate was magnified and is showed in figure 2-b. This figure shows hard red and black scales.
Crevice corrosion may occur under gaskets or adjacent to seal welds. Localized corrosion may also be initiated and aggravated by the leaching of harmful ionic species into crevices from polymer gasket material.
The plate material was AISI-316L and scales was sent to be analysed by well-known laboratory for further analysis. Presence of thick scales in rich amine side can explain the decreased efficiency due to lowering the exchange coefficient. Also corrosion coupons of lean amine after this PHE retrieved and increased corrosion rate observed. This shows pollution of regenerated lean amine by rich amine in PHE tag number 116-E-111. Thus heat exchanging plates are considered to be leaking, but due to presence of adherent thick scale the visibility was limited. Consequently the scales was removed to access to the underneath surface for further evaluation. A penetration test (PT) performed to detect any crack or hole that can cause leakage, but no corrosion was found under the scales.

Table 1. Rich Amine/Lean Amine PHE operating window data

Item No.	**116-E-111**	
Service	Amine / Amine Exchanger	
Type	Plate and Frame	
Supplier / Manufacturer	TRANTER	
Materials: Frame / Plates	C.S / S.S.A 316L	
Insulation	Yes	
Dimensions	626 mm (W) × 2390 mm (H) × 1076 mm (L)	
Design Heat Load	6600×1.1 kW	
	Cold Side (Plate)	**Hot Side (Frame)**
Fluid	Rich Amine	Lean Amine
Flow Rate (Normal)	141790×1.1 kg/hr	136555×1.1 kg/hr
Design Pressure	14 bar g/F.V.	6.2 bar g/F.V.
Operating Pressure (in/out)	7/6 bar g	1.2 / 0.9 bar g
Design Temperature	130 ºC	150 ºC
Operating Temperature (in/out)	67.2 / 113.2 ºC	126 / 79.7 ºC

Form a corrosion standpoint, heat exchangers like boilers and other equipment that involve heat transfer, are distinguished by a tendency for increased corrosivity due to heat flux effects at metal/fluid interfaces. Boundary layer conditions such as temperature, pressure and corrosive concentration of fluid at the heat transfer surfaces are different from those calculated or measured for the bulk fluids. Boiling may damage protective films or locally high concentrations of harmful solutions. Also scales may deposit on the heat transfer surface, creating concentration cells or producing localized hot spot caused by high temperatures due to insulating effects of scales. Polymer gaskets provide exceptionally tight, deep crevices that are highly conductive to crevice corrosion. Furthermore certain gasket materials may contain/adsorb leachable corrosive ionic species such as chlorides and fluorides that may promote either crevice corrosion or stress corrosion.

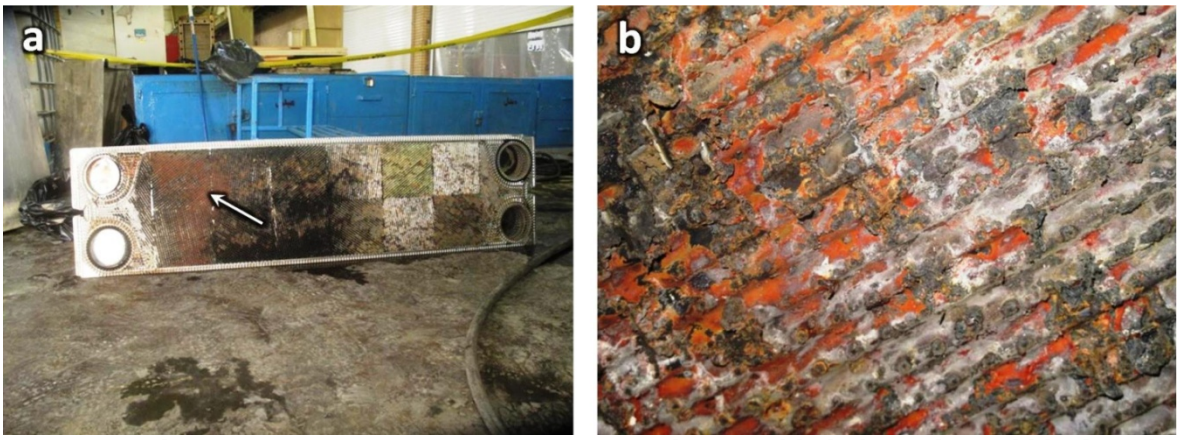

Figure 2. Rich Amine/Lean Amine PHE unit 116, a) disassembled plates, b) Red black scales.

Literature Review

Corrosion failures in plate heat exchangers are discussed with reference to equipment design, service condition and materials of construction in literature.

Hence similar failures of this type of PHE are reported in literature [5,6]. However, in most cases the medium contains dissolved chloride in aqueous solutions, that the pitting on stainless steel plates is predictable [7]. K.M. Deen and colleagues reported corrosion of a set of 316L stainless steel heat exchanger plates of power generation system in Pakistan. In primary and secondary loop water frequent perforation and fouling is reported and results confirmed the susceptibility of 316L SS plates to severe pitting corrosion in CT feed [6].

Stress-corrosion failures are also encountered, particularly at cold formed corrugations incorporated into some designs to contain gasket or to improve heat transfer coefficients [3]. In Jam petrochemical complex (JPC) the ASTM A240 type 316 plates of some process water heat exchangers have been damaged due to the occurrence of cracks at the sitting place of gaskets [8]. S.H.Khodamorad et. al. concluded that results indicate the building-up of the chloride and sulfite ions at the crevices between plates and gaskets at high temperature leads to SCC. However, the stagnant condition within crevice environments produce poor heat transfer and locally high temperature. Harmful solutes such as chlorides can concentrate in the crevices as a result of boiling. In addition a type 304 stainless steel plate failure in lean-rich amine PHE is reported and results shows that erosion-corrosion occurred at the hot end of plates, downstream from the scale deposits, and was attributed to the flashing of carbon dioxide out of solution [4]. Thus the failure root cause and mode are considered improper process design and is dissimilar to the case studied here.

Materials and Methods

In order to investigate the failure mode, a series of root cause analysis performed. Precipitated scales, gasket and gasket glue chemical compositions analysed by chemical methods, according to ASTM D7348-13 and LOI test at 750°C. Plates covered with scales washed in 10% sulfamic acid (H_3NSO_3) at 50°C. Cleaned plates was visually inspected and penetration test (PT) aided in finding micro pits or cracks. Hence PT revealed some localized pits and cracks in gasket seating place as shown in figure 3-b. Further laboratory testing performed to assess morphology of revealed defects. Laboratory testing includes microscopic investigation by stereo microscope (SM) device Dino Lite-AM 4815, scanning electron microscope (SEM) device model Cambridge-360, and atomic force microscope (AFM) device model FEMTO SCAN 2012.

The utilized gasket material was Ethylene Propylene Diene-Monomer (EPDM) in this PHE. This type of material is highly resistive in amine solution at high temperatures up to 170°C.

Also it do not have any side effect on the stainless steel protective coating and is suggested to be used by NACE instructions [4]. Moreover, gasket glue composition was analysed by FTIR spectroscopy (Bomen-MB) according to ASTM E1252-13.
The corrosion mechanisms predicted in forms of: 1. Corrosion Under Deposit (CUD), 2. CLSCC, 3. Pitting and 4. Crevice corrosion as the localized corrosion. Then failure modes are narrowed to the most compatible corrosion mechanisms. In conclusion preventive measures are advised to fight these corrosion mechanism in other operating exchangers of this type.

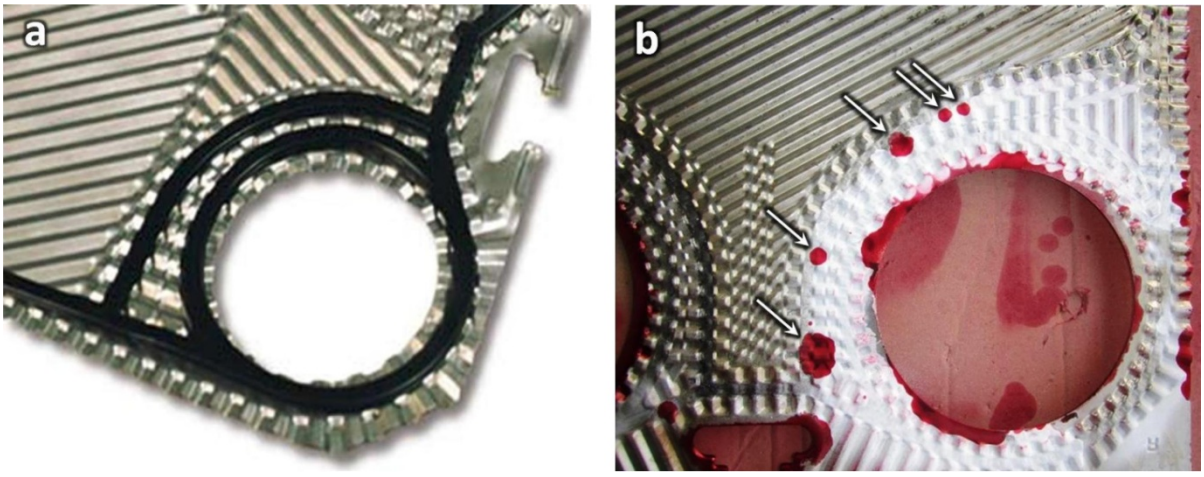

Figure 3. Heat exchanger AISI 316L plate, a) Sealing gasket at edges, b) revealed pits/cracks after penetration test under gasket seat.

Results and Discussion

Chemical analysis and LOI results are presented in table 2. These data shows that iron oxide in the form of Fe_2O_3 has the highest amount is scale (almost 67%). It is noticeable that in this PHE, plates are GX low-theta type which has lower resistance against to fluid flow than high-theta. So, less stagnant fluid or fouling properties is predicted from amine solution. However, suspended corrosion particles from upstream piping can precipitate in planar flow. Moreover, increment of temperature inside exchanger, increases the fouling index. Higher temperature and pressure decreases solubility of some inclusions such as iron carbonate.
As discussed above different scenarios was considered. Under deposit corrosion was not observed on relevant locations of plate; revealed defect was only located on gasket seating location. In defected location no crevice corrosion morphology was observed (figure 4 & 5). So damage mechanisms are narrowed to pitting and CLSCC. Remained mechanisms require presence of chlorine and increment of temperature increases their probability. In addition oxidizing agents must be present to cause rapid failures that are observed in this study. Chlorine content of rich and lean amine was recorded by operation laboratory and was less than 130ppm.

Table 2. Scales chemical composition

Phase	**MgO**	**SO_3**	**Fe_2O_3**	**Al_2O_3**	**CaO**
wt.%	0.33	1.3	67.6	0.098	0.85
Phase	**MnO**	**SiO_2**	**Cr_2O_3**	**La & Lu**	**L.O.I**
wt.%	1.1	0.092	0.072	<1	28.53

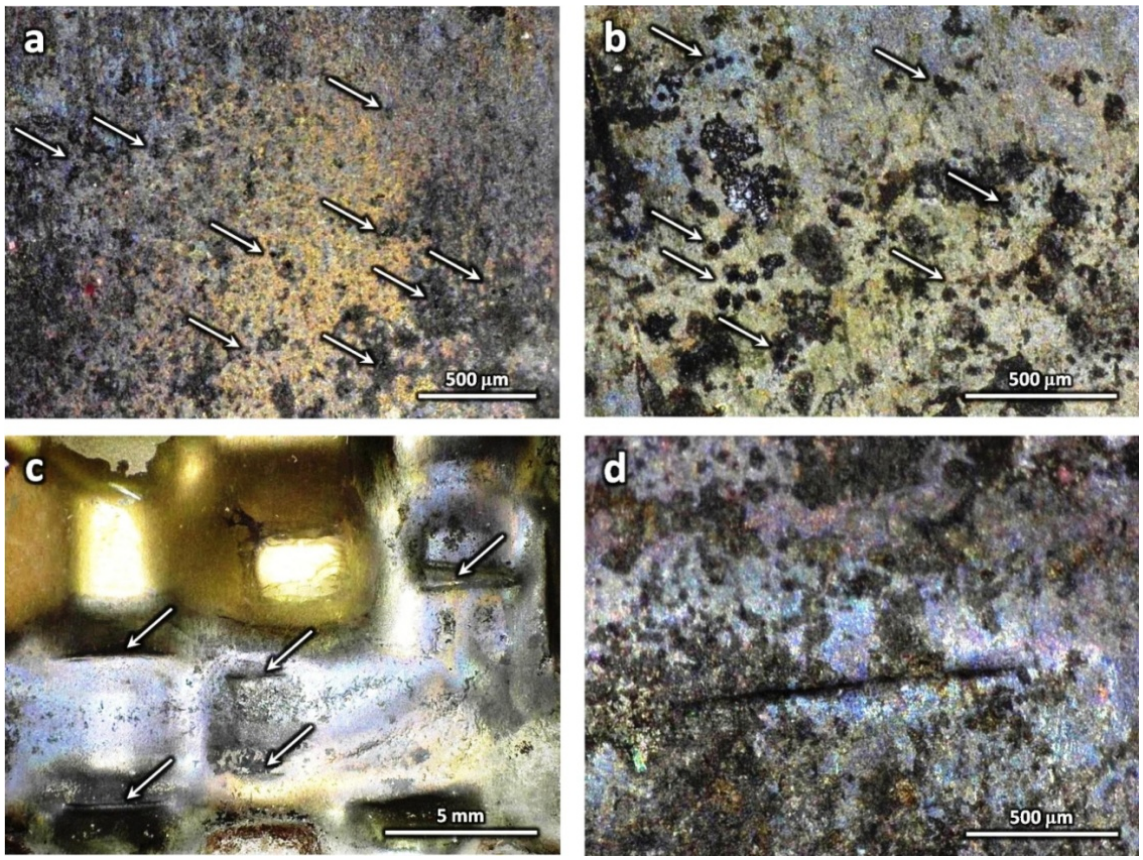

Figure 4. Gasket sitting place microscopic photos of defects by stereo Lite-AM 4815, a,b) pittings, c,d) micro-cracks.

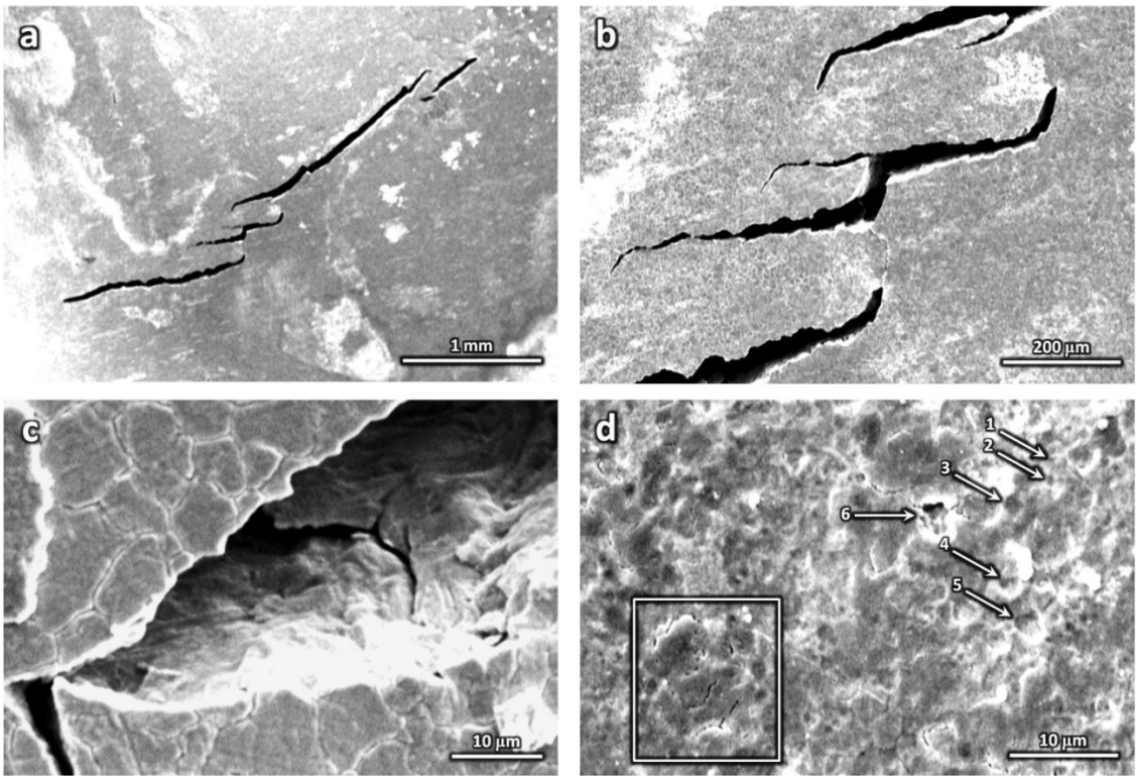

Figure 5. SEM micrographs by Cambridge-360, a,b,c) Micro-cracks, d) Pitting and micro-cracks nucleation and propagation.

This is worthwhile to mentioned that although pitting corrosion on 316 L is predictable for when the temperature exceeded 60°C [9], but this amount of chlorine in amine solution can not cause so extensive pitting nucleation on the stainless steel. Another chlorine source can be gasket glue. Gasket glue composition analysed and found that it contains PVC component. Solution temperature locally increases near Stagnant solution in the gasket vicinity due to lower thermal conductivity, this can cause solution to reach boiling point and extracts chlorine from poly-vinyl polymer. Leached chlorine can cause localized reduction of protective Cr_2O_3 layer and corrosion of bulk material takes place. Moreover acidic gases in rich amine and 1.3 wt.% of SO_3 in scales, proves the existence of oxidizing agents which moves corrosion forward.

On the other hand, these plates are cold formed and high amount of internal stresses are predicted to be remained. Figures 4-c & d, 5-a,b & c shows the resulted micro-cracks from residual stresses. SEM and AFM investigations shows that these micro-cracks are nucleated from bottom of pits and propagates in inter-granular direction (figure 5-c).

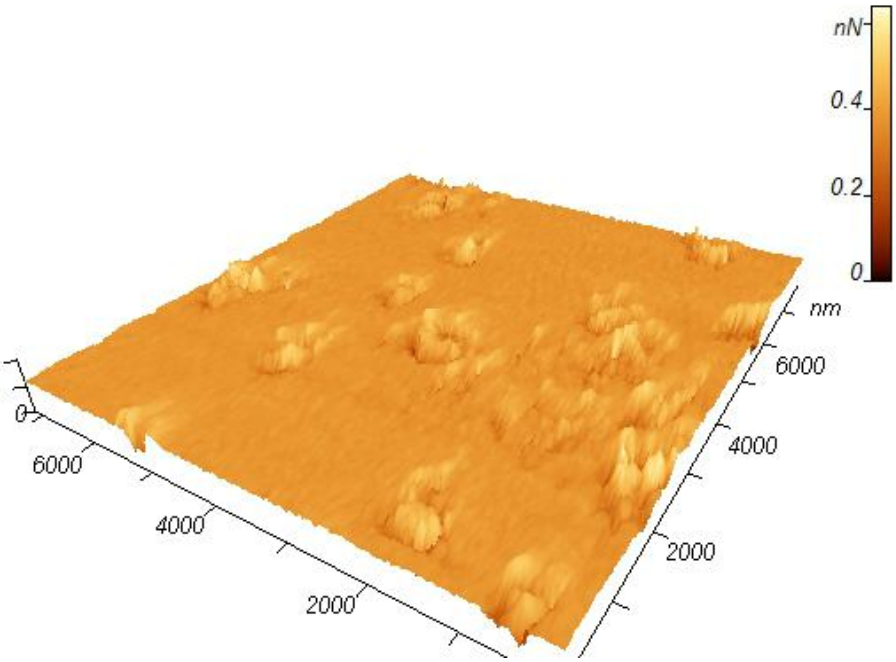

Figure 6. AFM 3D imaging from gasket seating place.

Leached chlorine from gasket glue due to local high temperature causes nucleation of micro-pitting on the surface. Then the pits may be stabilized again by oxidizing solutions, or propagated due to auto catalytic activities and local low pH. In this study, according to figure 5-d and 6, it is observed that almost half of micro-pits are developed in diameter and depth; but they do not reach the plate thickness. On the other hand the failure is caused by side to side cracks. These cracks are nucleated from stress concentration zones in bottom of pits (indicated square in figure 5-d). Besides, grain boundaries of stainless steel 316L material will be sensitized during plate cold forming and residual stresses can orient the crack propagation from pit bottom in step-wise form (figure 5-a).

All in all arrows number 1 to 6 in figure 5-d represents micro-pits growth; and indicated square shows sensitized region on the bottom of a pit which micro-crack clusters are about to join and form an inter-granular crack. This mechanism is similar to what is defined for CLSCC in API 571 or EFC report number 32.

Consequently, AFM investigation revealed that the histogram percentage for pitting's depth higher than 45% of the plate thickness is less than 5%. Meanwhile depth of cracks in 75%

cases reaches 80% (0.4 mm) of the plate thickness. So the crack propagation is considered catastrophic while the pitting requires time to develop. The catastrophic behaviour of the cracks proves the sensitization of the plate during cold work.

Conclusion

Like most plant components, plate heat exchangers are designed to meet expected service conditions at the lowest long-term cost. Due to their compact construction, the flow passages in plate heat exchangers tend to be very narrow, so there is much potential for fouling by suspended corrosion products and scale. Thus considering integrity operating window (IOW) points, the necessity for clean fluid may require employment of filters or highly corrosion-resistant material in upstream piping.

Moreover, in this research the main corrosion mechanism was found to be pitting and CLSCC. The source of chlorine for these mechanisms was gasket glue containing PVC compound. The stress cracking was mostly initiated from bottom of pits as the stress concentration zones. Thus it was noted to apply other compounds of gasket glues such as Bostik1782 that do not contain any form of halides. Compactness of exchanger plates and gasket integrity shall be inspected continually to prevent fluid contact in gasket seating.

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