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Corrosion of Monel Distributor of Caustic Scrubber In MSQ Unit

K K Pandey

Indian Oil Corporation Limited, Digboi Refinery, Tinsukia, India
pandeykk@indianoil.in

Sukla Mistry

Indian Oil Corporation Limited, Digboi Refinery, Tinsukia, India)
mistrys@indianoil.in

S D Chaklader

Indian Oil Corporation Limited, Digboi Refinery, Tinsukia, India)
chakladers@indianoil.in

R Gayen

Indian Oil Corporation Limited, Digboi Refinery, Tinsukia, India)
gayenr@indianoil.in

ABSTRACT

Motor Spirit Quality Upgradation (MSQU) unit of Digboi Refinery was commissioned in the year 2010. The purpose of the unit is to produce combined isomerate stream with an estimated RONC of 87.0 and reduction of sulfur and nitrogen content. Isomerization reactor effluent of MSQ Unit feeds the stabilizer column. LPG, H_2 and HCl are stripped and sent to caustic scrubber column through stabilizer reflux drum. As the off-gas from the stabilizer reflux drum overhead contains HCl, it is caustic treated and water washed before being released. In the caustic solution, the NaOH composition varies from 10% wt to 2% wt as it reacts with HCl to produce NaCl and water. The Caustic Scrubber has been designed in order to ensure full neutralization of the stabilizer off-gas. MONEL alloy 400 (UNS N04400) has been used as material of construction of the distributor of the

caustic scrubber. Several failures in the form of pin holes, cracks, thinning and perforation of connected flanges and distributor were observed since commissioning of the unit. Few of the failures were observed within short period of one year after commissioning. This paper presents the corrosion problem faced in the scrubber along with history and details of different failures in the system. The paper briefly covers the remedial measures taken to mitigate the corrosion problem.

Keywords: MSQU; Isomerization; Stabilizer, Monel, Distributor, Scrubber

INTRODUCTION

MSQU consists of Naphtha Splitter Unit, Naphtha Hydrotreater Unit, Reformer Splitter Unit and ISOM (Isomerization Unit) which is commissioned in Dec-2010 at Digboi Refinery. The purpose of ISOM is to improve the research and motor octane number (RONC) of the light naphtha feed before blending into the gasoline pool. The feed of the ISOM unit is hydro-treated in NHT (Naphtha Hydrotreater Unit) to reduce sulfur and nitrogen content.

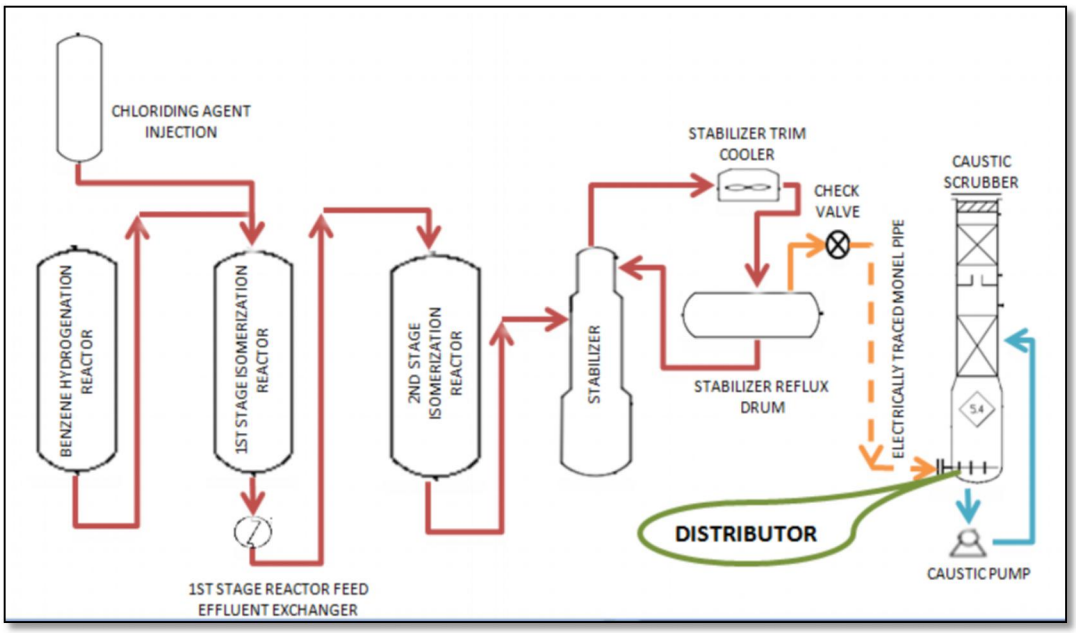

Figure-1 Reactor Section of ISOM showing Caustic Scrubber used to treat Off-gas

Isomerization reactor effluent feeds the stabilizer column. The purpose of stabilizer is to reduce C_4^- rate in the Isomerization reactor effluent. LPG, H_2 and HCl are stripped and sent to caustic scrubber column through stabilizer reflux drum.

As the off-gas from the stabilizer reflux drum overhead contains HCl, it must be caustic treated and water washed before being released. The Caustic Scrubber has been designed in order to ensure full neutralization of the stabilizer off-gas. This off-gas enters in the bottom of the Caustic Scrubber column and goes up through caustic hold-up in a packed bed. A schematic of the section is shown in Figure-1.

The source of HCl in stabilizer off-gas is Tetra-chloro-ethylene, C_2Cl_4 dosing in Isomerization reactors. Tetra-chloro-ethylene, C_2Cl_4 is the recommended chloriding agent which is injected continuously to the Isomerization reactors, as make-up for the small amount of chloride loss from

the chlorinated platinum catalyst (Figure-1). C_2Cl_4 is fully converted to HCl in reactor at normal operating conditions. Hence, chloride lost in the reactor effluent is in HCl form, which is finally converted into NaCl in the caustic scrubber. The gas leaving the caustic wash section, saturated by caustic, is again washed with cold boiler feed water in the top packed section, to remove any entrained caustic. Water is collected in the chimney tray below the water wash packed section, and it is circulated. Water loss to the vent gas leaving the scrubber is made-up periodically by fresh boiler feed water. Then off-gas from water wash section is routed under pressure control to Fuel gas or to Flare.

In the caustic solution, the NaOH composition varies from 10% wt. to 2% wt. as it reacts with HCl to produce NaCl and water. The caustic re-circulated is maintained at 50°C through the caustic recycle heater in order to keep the caustic a few degrees warmer than the feed gas and to avoid potential foaming problems due to any hydrocarbon condensation. A portion of the circulating caustic is sprayed onto the column walls below the caustic wash packed section to avoid any wet hydrogen chloride corrosion in this part of the scrubber. The caustic inventory is drained via the caustic circulating pump discharge line, once the concentration of circulating caustic decreases to about 2% wt. When used caustic is removed, then the tower bottom is filled up with fresh caustic. Frequency of NaOH inventory replacement is 10 days.

MONEL alloy 400 (UNS N04400) has been used as material of construction of distributor of the caustic scrubber. As shown in Figure-1, electrically traced MONEL piping (shown in broken line) has been provided after check valve to the caustic scrubber. At the interface flange joint, the distributor portion extending from the scrubber has a CS (Carbon Steel) nozzle having a SS-304 (Stainless Steel) flange with MONEL raised face.

The first failure was reported in December 2010, within one year of unit operation. A leak was observed in weld joint of flange and the 2″ insertion nozzle. In July 2013, emergency shutdown of MSQU ISOM section was taken due to leakage from flange (MONEL weld overlaid portion) of gas line to Caustic Scrubber. Within 5 years of commissioning, a total 6 numbers of failures had been reported in form of pin-holes, cracks and perforations. During emergency shutdown of 2013, the caustic scrubber was opened and severe perforations were noted across the off-gas distributor arms having Monel-400 metallurgy. The failed portions were repaired during the same shutdown.

OBSERVATIONS

A pinhole leak was found at the toe of the weld joint between WNRF (weld neck raised face) flange and 2” insertion pipe. Following the leakage, the scrubber section was isolated and SS flange with MONEL raised face was found to be severely corroded (Figure 2 & Figure 3). Similar observations were made on another bolting flange (Figure 5). After dismantling the 2” nozzle for maintenance and repair, the internal inspection of the column was carried out.

Figure 2 Severely corroded WNRF Flange

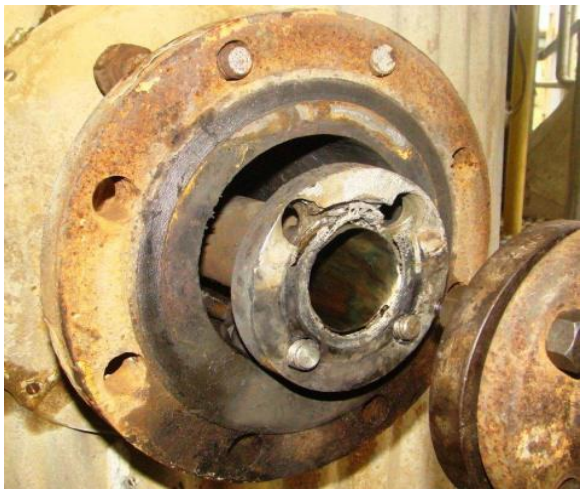

Figure 3 WNRF Flange in As-opened condition

Table 1 : PMI Results Of WNRF Flange

Sr. No	Element	Composition (%)		Observed Composition of Monel (UNS N04400) Weld Overlay (%)				
		Monel	SS 304	1	2	3	4	5
1	Ni	63 Min	08-11	65	64	53.79	68.37	59.81
2	Cu	28-34	-	4.79	4.21	30	6.5	19.82
3	Fe	2.5 Max	65-70	14.71	10.34	9.46	8.23	7.54
4	Mn	2.0 Max	2.0	2.16	3.13	0.97	2.57	2.3
5	Cr	-	16-20	11.6	18	4.64	12.81	9.43

PMI of the flange (SS-304) and MONEL (UNS N04400) weld overlay at raised face was done and the results are as tabulated in Table 1. At the Flange and weld overlay interface, severe corrosion of

the SS flange was observed. The bolting holes were severely corroded and enlarged exposing the Monel piping underneath. However, at the Monel raised face severity of corrosion was less leaving leaf-like structures above the perished SS-304 flange base.

The measured composition of the Monel weld overlay shows values deviating from the actual composition of the metal. Further, a significant proportion of Chromium metal was found in the weld overlaid portion. The Copper content of the Monel-400 alloy was found to have depleted at the interface periphery. Dilution of the Monel weld overlay during welding over the SS-304 flange might have resulted in such compositional variations.

Figure 4 Distributor portion of the Scrubber

Figure 5 Corroded Bolting Flange

Severe perforation at several locations was noticed on the of the distributor arms of the caustic scrubber (Figure 4). The perforations were only on the top portions of the pipe as seen in Figure 6 and Figure 7. The distributor holes on its ribs were found enlarged (approx. 15 mm) from its original size of 6mm due to corrosion. Moderate thickness loss was noted at bottom portion of the distributor. No thickness loss was observed on sides of distributor. UT gauging was carried out on the electrically traced external piping (from NRV to inlet of the Scrubber) of the circuit. No leakage and indication of corrosion in form of thickness loss was observed. Only minor corrosion in the form of pitting was observed in the shell of the caustic scrubber. This shows that the bulk neutralization of HCl is by and large taking place.

Figure 6 Cut Section of Perforated arm of the Monel Distributor

Figure 7 Tee Section of the Distributor

INFERENCES

A detailed study of the process parameters, operating conditions and past failures was carried out to investigate the root cause of the failure and arrive at a permanent solution of the problem. Various possibilities, as mentioned below, were explored and analyzed for identifying the actual cause of failure of the Monel distributor tubes and flanges of the Caustic Scrubber.

A. **Electrical tracing:** The purpose of electrically traced lines is to avoid HCl corrosion by condensed water. This may appear on loss of Off-gas flow. Vapour generated by hot caustic may condense on metal, if metal temperature is lower than vapour temperature. The tracing temperature shall be set as Off-gas temperature plus 5˚C. As per operating manual of the unit the off-gas temperature is kept at 35 ℃ and the caustic temperature is kept at 40 ℃. Caustic supply temperature has been kept at steady value of 45˚C, except for few instances when temperature has gone as high as 58˚C.

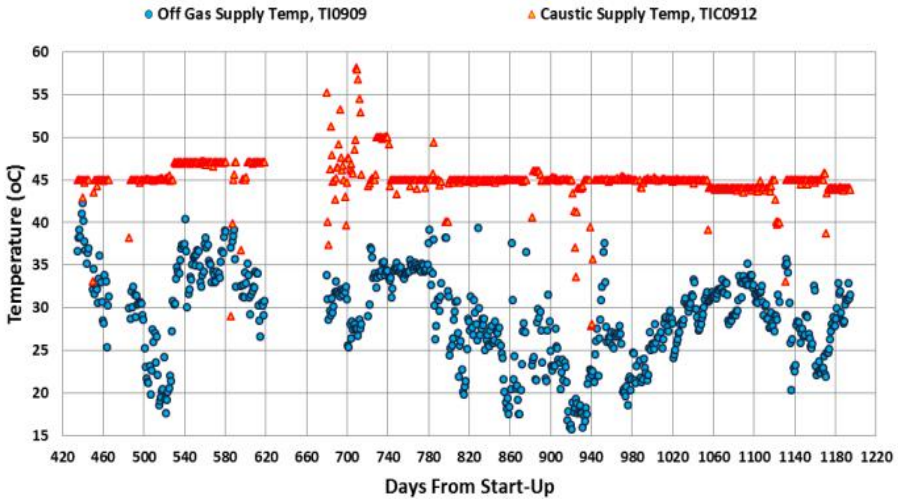

Figure 8 : Caustic Scrubber Temperature Profile [1]

B. **Suitability of Metallurgy:** MONEL alloy 400 (UNS N04400) (Ni 63 % min, Cu 28 - 34 %, Fe 2.5 % max), is commonly used for acids of lower concentrations at higher temperatures. Monel (Ni-Cu) alloy has high strength and excellent resistance to a range of media including seawater, dilute hydrochloric and sulfuric acids, and alkali. PMI of Monel piping and distributor arms was

carried out and result was in acceptable range. However, PMI of WNRF flange showed deviations in the composition.

C. **Leakage of Stabilizer overhead trim cooler (Figure 1):** Stabilizer overhead trim cooler leakage can lead to moist atmosphere of stabilizer off gas and aqueous HCl can become very corrosive. Although leak was observed in past (due to floating head gasket failure), corrosion is ruled out, since shell side operating pressure (11.7 Kg/cm^2) is much higher than the tube side i.e. water side (4.0 Kg/cm^2) pressure. Hence water ingress due to leak is not possible.

D. **Caustic strength:** As per licensor's view "In no case shall circulating caustic strength be allowed to drop below 2.0 wt%. Caustic inventory in scrubber shall be planned for replacement with fresh caustic solution each time the strength reaches 3-4 wt %"[1]. Earlier the frequency of Caustic replenishment was 10 days. Although, bulk strength of the caustic was sufficient to neutralize condensed HCl vapors, but at lower strength localized corrosion due to high strength of HCl cannot be ruled out.

E. **Loss of Off Gas Flow:** During normal unit operation the scrubber pressure is maintained at 5.5 Kg /cm^2 whereas the off-gas pressure is 6 Kg /cm^2. The difference in the pressure does not allow caustic water mix to flow back in the off-gas circuit. However, during commissioning stage stabilization period, unit upsets and shutdowns the caustic back flow up to the NRV installed in off gas line cannot be ruled out. Off-gas in presence of condensed water will introduce highly corrosive environment.

As inferred from the above possible explanations, the most likely reason of failure of the flanges and Monel distributor was due to condensation of highly acidic HCl (low pH). As seen in Figure-9 & Figure-10 Monel 400 shows aggravated corrosion rates as the temperature and acid Concentration increases.

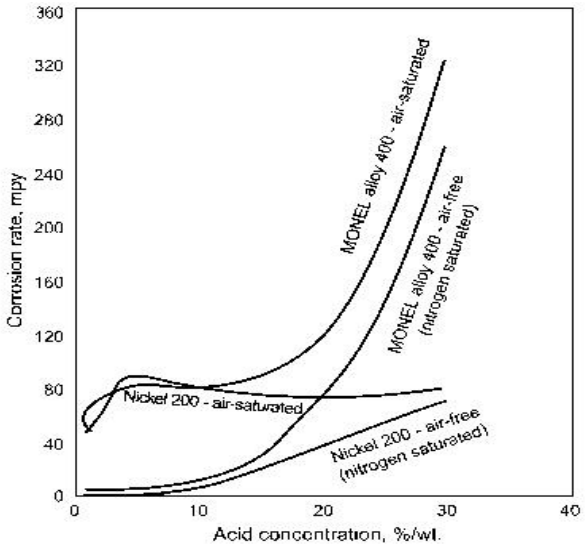

Figure 9 Corrosion of Nickel-200 and Monel-400 at 30° C[2]

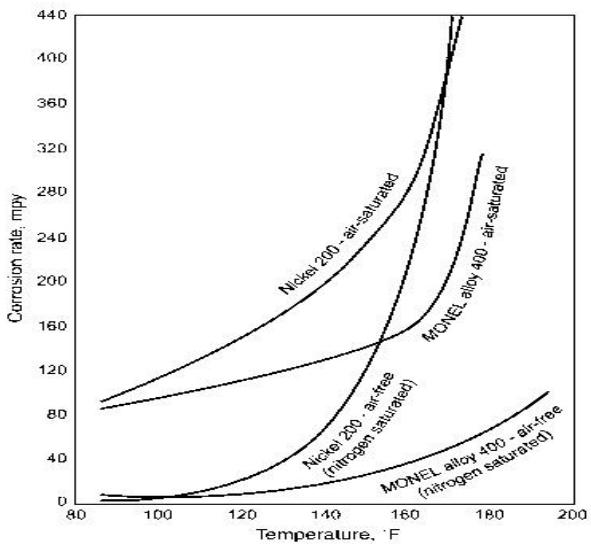

Figure 10 Effect of Temperature on the corrosion of Nickel-200 and Monel-400 in 5% HCl [2]

The raised face of the insertion nozzle flange was prepared by weld overlay of Monel-400 alloy over base metal SS-304. Positive material identification shows dilution of the weld overlay by chromium (refer Table-1). The diluted alloy will not have the desired corrosion resistance. Moreover, the weld overlay will leave a high energy area along with chances of inclusions and defects. These areas will act as preferable sites for corrosion in presence of highly acidic environment. Due to absence of electrical tracing at the flanges (inlet nozzle of the scrubber), HCl condensation had started at the flange joint and continued to the distributor. No significant corrosion was found in the electrically traced portion of the piping. The newly formed acid is usually concentrated and highly corrosive. The low pH had resulted in wasting away of the Monel weld overlay and subsequently the SS-304 flange. Further, due to the dissimilar weld between Monel weld neck raised face and SS-304 flange, dilution of the weld overlay occurs. This had resulted in poor corrosion resistance and led to premature failure of the flange.

Uniform thinning and perforations (Figure 6 & 7) were found across the arms and tee-joints of the Monel distributor. The highly corrosive HCl which started condensing at the flange, continued eating away the Monel distributor section. This had preferably been found at the welding joints towards the top potion (12 o'clock). The distributor exit holes had enlarged, which were also positioned at the top. The site of corrosion inside the distributor can be attributed to the flow dynamics of the off-gas. Due to this, condensation had also occurred at the top positions. The low strength of the caustic and its frequent fluctuations in the temperature resulted in inadequate neutralization of the Off-gas near the exit holes. The holes of the distributor provided exit for the off-gas, which are a preferable high energy location for corrosion.

CONCLUSIONS

The failure of the Inlet Nozzle flange end of the Scrubber and the distributor section has occurred due to formation and condensation of hydrochloric acid (HCl). The acid condensation is the result of variations in temperature difference of the off-gas and the caustic used for neutralization. The design was inadequate to handle the corrosion problems. Due to dilution of the Monel weld neck raised face which was weld overlaid on the SS-304 flange, the corrosion resistance of the flange deteriorated and led to its failure under the effect of acidic corrosion. The thinning and perforation of the Monel distributor arms was under the highly corrosive nature of the acid forming due to Off-gas condensation inside the distributor.

The original Monel overlaid SS 304 flange has been removed and replaced with Monel Flange to avoid any degradation of the metal. The severely corroded and perforated distributor arms were replaced completely. Replenishment of the caustic has been reviewed and is being done to maintain a minimum of 3% to 4% rather than earlier practice of 2% minimum strength. Close monitoring and maintenance of electrical tracing set point at 5 C above the Off-gas temperature and variation of temperature difference between caustic and Off-gas is being done. After the replacement and corrective measures in March 2015 turnaround of the unit and continuous operational control, no failures have been reported till date.

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