Failure Analysis of Extraction Steam Condensate Piping and Aldehyde Purge Lines in MEG (Mono Ethylene Glycol) Unit-A Case Study

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ABSTRACT

In MEG (Mono Ethylene Glycol) unit, the products of the glycol reactor are mainly water (~89 Wt. %), traces of aldehydes and glycols (mainly MEG). This stream is treated in the evaporator columns at several stages. The overhead vapor of these evaporators is mainly steam with traces of process contaminants (aldehydes; such as acetaldehydes and formaldehydes), and it is used in re-boilers of columns for heating column bottom streams. In one installation, several failures have been observed in the condensate system of this process steam.

Each re-boiler that is connected with the evaporators is equipped with one purge connection for removal of occasional aldehydes. Failures have also been seen in this section of piping. The subject

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paper provides a brief description of the process section of the failure prone area in the evaporator section in the MEG unit, role of contaminants in the operation and its effect on integrity of equipment / piping and future actions taken to avoid such failures. The paper also discusses recent changes of philosophy in material selection of such services in this plant.

Keywords: MEG: Mono Ethylene Glycol, Aldehydes, And Evaporator.

INTRODUCTION

In the MEG unit, the products of the glycol reactor are mainly water (~ 89 Wt. %), traces of aldehydes and glycols (mainly MEG). This stream is treated in a train of seven effects in the evaporator section, which consists of seven effect evaporators operating successively at lower pressures, Figure 1. The heat required for the evaporator columns are provided by their corresponding re-boilers, and re-flux for these columns is done by addition of treated water.

The overhead vapor of these evaporators, which is mainly steam with traces of process contaminants (aldehydes such as acetaldehydes and formaldehydes), are used as a media for supply of heat as in re-boilers of column / into the column. In the evaporator column of each system, the overhead vapor that is extraction steam is used for heating the re-boilers of subsequent evaporators. After condensation of the extraction steam, condensate is routed to the condensate drum of each re-boiler. Each condensate drum outlet is routed to the next effect condensate drum, and the final condensate drum collects all condensates and sends it to collection in the recycle water tank after cooling.

Several failures of process steam condensate piping and aldehyde piping have been observed in the MEG unit in the last four years. The failures have been reported mainly at 90 deg bends in the carbon steel segment of piping, as well as at a few locations on straight portions of piping. The leaking segments were replaced with similar material specification of piping, i.e., with carbon steel, but, the leaks have reappeared in few locations. An attempt has been made to understand the problem and its root cause along with necessary remedial measures that are given in detail in the paper.

Figure 1: Flow diagram of process steam condensate of typical mono ethylene glycol unit
PAST HISTORY

History of leakages in process steam condensate piping

a) Fifth stage evaporator overhead stream (process steam) leaked into the section where it is converted into condensate in June 2014 (Material specification: Carbon steel). This was rectified by replacement of the leaking segment of piping with similar material.
b) Fifth stage evaporator overhead stream (process steam) leaked again into the same section of piping in February 2016. This was temporarily replaced with similar material.
c) Sixth stage evaporator overhead stream (process steam) leaked into the lower temperature section in March 2016 (Material specification: Carbon steel)
d) Sixth stage evaporator overhead stream (process steam) leaked again at a different location in a similar section in January 2017 (Material specification: Carbon steel)

History of leakages in aldehyde purge piping

a) Leakage in the aldehyde purge line from the Fourth effect re-boiler in June 2014. (Material Specification: Carbon Steel)
b) Leakage in the aldehyde purge line from the Third effect re-boiler in December 2015. (Material Specification: Carbon Steel)
c) Leakage from the aldehyde purges line near the DEG/TEG columns ejector system in June 2016. (Material Specification: Carbon Steel)

OBSERVATIONS OF FAILED PIPING

a) Process Steam Condensate Circuit:
The leaking segment of piping was inspected after splitting into two halves. On inspection, excessive grooving was observed inside the pipe surface (Fig 2(a)). Same observation was noticed when the leaked pipe of another evaporator steam condensate circuit was inspected by splitting into two halves (Fig 2(b)).

Fig 2(a). Metal loss in the form of small bubbles on the internal surface of pipe

Fig 2(b). Metal loss in the form of grooving on the internal surface of pipe
b) **Aldehyde Purge Circuit:**
The leaking section of the aldehyde piping was inspected after splitting into halves. Erosion marks were observed on the internal surface of all the three leaked pipe pieces. These were just after the socket weld joint downstream sections (Fig 3(a) and 3(b)). Grooving marks were also observed on around 1 meter straight pipe piece downstream of socket weld joints.

![Fig 3(a) External surface of piping](image1)
![Fig 3(b) Internal surface of piping](image2)

**MATERIAL SELECTION PHILOSOPHY IN EVAPORATOR SECTION**

Acetaldehyde and formaldehyde are the common impurities which are formed in the ethylene oxide reactor which get carried over along with ethylene oxide in the glycol reactor and may remain unconverted in the evaporator section. Acetaldehyde normally is removed through the condensate in the first four stages of the evaporator condensate drum. Hence, the condensate stream piping containing acetaldehyde is specified as SS304 material. However, from the fifth stage onwards the material selection for process condensate piping is mainly carbon steel considering no acetaldehydes are present in the process steam.

**CONTROL OF FORMATION OF ALDEHYDES**

Aldehydes are reactants involved in the formation of by-product impurities, which significantly affect the glycol product quality. To minimize this effect, all the acetaldehyde and formaldehyde made in the ethylene oxide plant as well as the acetaldehyde that is formed by MEG decomposition, must be efficiently purged to prevent their buildup in the glycol reactor feed.
The glycol reactor effluent is fed directly to the evaporator stripping trays. The stripping trays enhance acetaldehyde removal in that effect. Acetaldehyde, which is more volatile than water, distills overhead in the evaporator. Most of this acetaldehyde is condensed in the initial two stages of re-boilers, and is removed via a vapor purge from the condensate flash into the condensate tank.

**DISCUSSION ON FAILURE**

In the EO reaction system, the aldehydes (primarily acetaldehyde and formaldehyde) are formed in a small quantity. These aldehydes are separated from the ethylene oxide and the ethylene glycol in the purification sections. Aldehydes are easily oxidized to carboxylic acids containing the same number of carbon atoms, as in parent aldehyde. The reason for this easy oxidation is the presence of a hydrogen atom on the carbonyl carbon, which can be converted into -OH group without involving the cleavage of any other bond. Thus, even weak oxidizing agents like bromine water, Ag+, Cu²⁺ etc. are effective in converting the aldehydes into respective group carboxylic acid. This conversion of aldehydes into acids leads to preferential corrosion of carbon steel equipment / piping.

\[
\text{R–C} = \text{O} + [\text{O}] \rightarrow \text{R–C} = \text{O}^-
\]

Aldehyde Group Oxidizing Agent Carboxylic Group

All the failures have taken place in the extraction steam condensate system at different locations but mainly in the evaporator section fifth and sixth stage. Extraction steam, which has been used for heating of evaporator and other re-boilers, contains slight amount of aldehydes that get carried over from the reactor in the glycol stream. These aldehydes convert to acid in the evaporator system even under mild oxidizing conditions. This conversion causes localized dropping of pH in the evaporation section and subsequent corrosion of carbon steel equipment and piping. Light acids are removed in the drying column overhead. Also at higher throughput due to excessive velocity and two phase flow (mainly in condensate system), failure has been observed in 90 deg bends.

**Chemical analysis of extraction steam condensate**

After analyzing the aldehyde content in the streams of the evaporator steam condensate and aldehyde purge condensate, significant amount of acetaldehyde and formaldehyde were found present in both the streams. Also, acidity content as acetic acid and formic acid was found present in both the streams. However, inorganic acids were not found in the samples. This indicates the presence of acidity in the streams due to acetic acid and formic acid in the streams. Details of the analysis are given in table 1.
Table 1: Aldehyde content and acidity in Evaporator condensate and Aldehyde purge condensate streams.

<table>
<thead>
<tr>
<th></th>
<th>Acetaldehyde (in ppm)</th>
<th>Formaldehyde (in ppm)</th>
<th>ACIDITY as Acetic acid (in ppm)</th>
<th>ACIDITY as formic acid (in ppm)</th>
<th>Inorganic Acid (in ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Evaporator Steam Condensate</strong></td>
<td>Max: 41.5</td>
<td>28.3</td>
<td>3.9</td>
<td>3</td>
<td>Nil</td>
</tr>
<tr>
<td></td>
<td>Min: 27.3</td>
<td>18.6</td>
<td>1.6</td>
<td>1.3</td>
<td>Nil</td>
</tr>
<tr>
<td><strong>Aldehyde purge condensate</strong></td>
<td>Max: 300.7</td>
<td>205</td>
<td>3.2</td>
<td>2.5</td>
<td>Nil</td>
</tr>
<tr>
<td></td>
<td>Min: 122.7</td>
<td>83.7</td>
<td>1.6</td>
<td>1.29</td>
<td>Nil</td>
</tr>
</tbody>
</table>

On analyzing sample streams of evaporator overhead steam condensate and aldehyde stripper overhead condensate for pH, low pH in the range of 4.9-5.6 was observed in the samples of Aldehyde stripper overhead condensate. Also, low pH in the range of 5.2-6.4 was observed in the samples of evaporator overhead steam condensate. Low pH results confirm the formation of acid constituents in the process steam condensate piping. pH trends of the evaporator overhead steam condensate stream and aldehyde stripper overhead condensate stream are shown in Figure 4.

Figure 4: pH trend of evaporator overhead steam condensate stream and aldehyde stripper overhead condensate stream
Process Licensor Opinion

In view of the failures observed in the extraction steam condensate and aldehyde purge piping, feedback from the licensor was sought in this regard. Based on the recent practices and development of material selection for process steam condensate lines in MEG units worldwide, the licensor recommended upgrade of material from existing CS to SS304. The licensor recommendation was based on failure observed mainly in the bends of the process steam condensate piping due to higher velocity at higher throughput and mild acidic conditions that prevail in the circuit. For aldehyde piping localized corrosion can be avoided by upgrading it to SS304 from existing CS material.

CONCLUSION

Formation of aldehydes in the mono ethylene glycol unit as an impurity in the reaction section for ethylene oxide formation is inherent. The extent of aldehydes can be controlled based on operational severity and using high selectivity catalyst. However, elimination of formaldehyde in the evaporators section is not done completely. The presence of aldehydes primarily formaldehyde in the evaporator section process steam lead to formation of formic acid. This causes dropping of pH of streams handling condensate and thus causing corrosion. Since any neutralizing agent cannot be added in the process stream as this may lead to several issues with the final product quality, upgrade of the material of construction to sustain the operation is the optimum solution to deal with the corrosion phenomena discussed in the paper.

Based on this, upgrade of material is planned for condensate lines having aldehydes contaminants and the purge piping used for occasional removal of aldehydes.

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REFERENCES