## Introduction

Overheads, in general, refer to the pipe work, exchangers, and condensers coming off the top of any distillation, fractionation or separation vessel. In other words they are the pipes that come off the top of all those tall relatively thin vessels or columns in a refinery or processing plant. The degree of corrosiveness of overhead systems vary considerably depending of the exact separation or distillation occurring in the column, the feedstock, the operating conditions, the alloys and the inhibitor in use. Corrosion problems and/or inhibitor use are the keys to locations which require monitoring.

### Why Are Overheads A Corrosion Problem?

Any separation or distillation column has the heavier boiling point products exiting at the lower, or bottom part of the vessel while the gases and lighter boiling point products exit at the upper or top part of the vessel. For example in crude units contaminant acid gases, hydrogen sulphide (HS), hydrogen chloride (HCl) produced from chloride contaminants, and sulphur oxides (SO) will carry over in the overheads. These acid gases together with water condensation which is also occurring at this same point produce corrosive acids. In other

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**Fig. 1 Simplified Crude Unit Flow Diagrams Showing Corrosion Control Facilities and Some Typical Overhead Probe Locations**
overhead systems the contaminant gases may produce alkaline conditions such as with ammonium chloride in Fluid Catalytic Crackers (see AN 109). The exact area of maximum corrosion depends on the chemistry, the geometry and the condensation point of the water vapors, since a range of decreasing temperatures exist from the top of the column through the heat exchangers and condensers down to the distillate drum.

Crude Unit Overheads

Crude Unit overheads, are probably the most common single application of CORROSOMETER® probes in a refinery. In addition, corrosion coupons may also be used to provide a complimentary method of assessment. A review by NACE task group T-8-12 published in 1983 showed a breakdown of monitoring practices based on a survey of 129 crude units across 44 companies worldwide as follows.

<table>
<thead>
<tr>
<th>Monitoring Method</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Resistance (CORROSOMETER®, Type)</td>
<td>59%</td>
</tr>
<tr>
<td>L.P.R. (CORRATER®, Type)</td>
<td>1%</td>
</tr>
<tr>
<td>Corrosion Coupons (COSASCO, type)</td>
<td>17%</td>
</tr>
<tr>
<td>None of Above</td>
<td>23%</td>
</tr>
</tbody>
</table>

Crude Unit Overhead Corrosion

Figure 1 shows a typical simplified crude unit flow diagram with some typical probe locations. In this overhead system corrosion is the result of hydrogen sulphide, and hydrogen chloride which is produced by hydrolysis of the salt in the crude. Salt in the crude is either from the production well or as a contaminant of tanker shipment. The salt generally consists of a mixture of sodium chloride, magnesium chloride, and calcium chloride. The sodium chloride is stable and does not hydrolyse significantly in the preheat circuit. However magnesium and calcium salts hydrolyse readily:

\[
\begin{align*}
\text{MgCl}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HCl} + \text{Mg}0 \\
\text{CaCl}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HCl} + \text{Ca}0
\end{align*}
\]

The HCl does not cause corrosion in the preheat section because the water is not present as a liquid phase because of its high vapor pressure at this temperature. The HCl passes up the atmospheric column and into the overheads, where it is absorbed into the condensed water to form highly corrosive hydrochloric acid in the overhead exchangers and condensers. (Additional water vapor may be available from steam injection or stripping which may commonly occur in the bottom of the atmospheric tower). The reaction is further complicated by the presence of H₂S in the overhead gas which is also absorbed into the condensed water. Iron sulphide is precipitated in the overhead system as a result of the reaction of H₂S and the soluble iron chloride from the corrosion reaction of HCl with the steel. This liberates additional HCl. Desalting and caustic additions before the preheat circuit help reduce the HCl in the overheads but not sufficiently to prevent the need for chemical injection in the overheads to combat corrosion.

Several different types of chemical inhibition may be added to the overhead system to neutralize the HCl. Ammonia or neutralizing amine are commonly used to adjust the pH from less than 1 to the range of 6 to 7. Since the neutralization product is frequently a solid, water addition may be used to wash out any solid deposits. Deposits may cause blockage or can be extremely corrosive themselves if they are the salt of a strong acid and a weak base. A filming amine is typically used to provide a protective film on the equipment. The inhibitor film is more persistent in a neutral pH range and hence is usually used in conjunction with a neutralizer to adjust the pH.

Alloy Materials In Overheads.

Alloys resistant to this corrosion may be utilized, but because of the high corrosivity of HCl and the chloride cracking (SCC) it can induce, the use of alloys alone is seldom economic. Hence alloys are usually used in conjunction with inhibition. Quite frequently fresh water or salt water is used in the overhead condensers as the cooling media which may necessitate non-ferrous alloys for the condenser tubes such as admiralty brass, aluminum bronze, monel, or 70 Cu - 30 Ni. These materials must resist corrosion from the water side and the process side. On many occasions parallel exchangers and condensers with isolating valves are used to permit removal from service without system shutdown.

Corrosion Monitoring Methods For Overhead Systems

CORROSOMETER®, probes are the technique most suitable for this service since they operate in gases, or liquids. The only area for use of CORRATER®, probes is on the water side of overhead condensers for general corrosion, or leakage detection where water pressure is less than process pressure.

The CORROSOMETER®, probes provide the continuous corrosion data to enable all the many variables indicated above to be correctly controlled. Coupons may provide additional collaborating data, but because of the typical assessment period of typically one month over which only average corrosion rate is determined, they cannot provide the necessary real time data that is required for proper operation. Chemical analysis of the water from the distillate drum may also be used as an indirect measure of corrosion to collaborate the basic corrosion data from the CORROSOMETER®, probes.