
Question 32: What are your best practices for minimizing corrosion in aromatics extraction process from oxygen in the feed? Is the strategy to reduce oxygen ingress or treat the feed? Is the situation different for glycol, Sulfolane, Morpholine, or other solvents?

Ujjal Roy (Indian Oil Corporation)

We have no experience with morpholine as solvent.

We have Udex and Sulfolane extraction units in our refineries. The UOP Udex Unit was first commissioned in 1968 and revamped to 140% capacity in 1992.

Udex unit uses Tetra Ethylene Glycol as solvent. The Udex performance w.r.t. corrosion was not so high initially after revamp, but we started experiencing severe corrosion from 2008 onwards in stripper reboiler, severe thinning of stripper bottom tray panels and unit had to be shut down repeatedly in 4-5 months interval for attending reboiler leaky tubes till M&I shut down was taken up. This coincided with change of feed from semi-regen CRU to new CCRU/Platformer. In shut down, regenerated reboiler was found covered with excessive carbonaceous deposits. During the period of operation, pH of stripper boot water used to be low at 5.0 – 5.5. The likely reason for this significant corrosion problem and repeated failure of stripper reboiler is chloride carry over from upstream reformer. Lean glycol chloride content at that time was significantly high at 130 to 160 ppm. The source of ingress of chloride was feed having 0.7 to 0.8 ppm chloride. Since then, we have upgraded the reboiler metallurgy from CS to Duplex SS and have put alumina chloride guard in feed line. We are able to maintain chloride guard outlet chloride content at 0.06 – 0.45 ppm. Earlier to this incident, from time to time between M&I shutdowns, we have observed stripper reboiler tubes thinning/pitting for which spikes in reboiler temperature during emergencies resulting in glycol degradation and oxygen ingress are the inferred causes.

Sulfolane unit is relatively new, commissioned for regular operation only in 2007 and much tighter unit to prevent oxygen ingress. After 3 years of operation, during M&I shutdown, we have observed uniform pitting in stripper receiver internal surface, solvent regenerator vessel baffle support and tie rods corroded. Also pitting observed in regenerator reboiler tubes.

The approach to minimize corrosion is essentially the same in both Udex and Sulfolane Units. Three basic factors which are known to lead to corrosion in these units, as per our experience, are:

- a) O₂ ingress in the unit with feed and leakages in vacuum circuit.
- b) High solvent temperature due to mal operation/unit upsets.
- c) Chloride ingress with feed or due to leak in some of the coolers/condensers in stripper circuits.

Oxygen should not exceed licensors recommended value of 1 ppm max. in feed. The practices for

minimizing corrosion in these units are:

- a) Proper blanketing in feed and solvent tanks need to be ensured. Nitrogen blanketing system should be properly designed to avoid oxygen ingress through breather valves during sudden drop in ambient temperature. It is better to have DCS indication of tank vapour space pressure for close monitoring. In our Udex Unit, we are unable to route direct feed due to varying feed compositions. It is preferred to directly route the feed to avoid O₂ pick-up in tanks.
- b) Stripper bottom temperature under any circumstances should never exceed 180°C to avoid degradation of solvent. Avoid temperature rise by bypassing the reboiler heating medium in case of lean solvent pump failure or unit upsets. Heating medium inlet temperature to stripper reboiler to be kept as low as possible to avoid high skin temperature which increases the chance of degradation.
- c) Sulfolane recovery column and regenerator columns of both Udex and Sulfolane units operate under vacuum. These two areas are the potential source of O₂ ingress. Before starting the units, the vacuum columns and its associated systems should be thoroughly checked for tightness by holding the vacuum and recording the drop. Now-a-days, sonic leak detectors are used to check for leakages.
- d) The solvent regenerator needs to be online all the time and should be operating at recommended feed rate. We have experienced that, at times, due to regenerator maintenance as a result of vacuum problem or reboiler tube leak, unit was operated without regenerating the slip stream for a considerable time which builds up the degraded solvent in the system aggravating the rate of corrosion and erosion as well. If chloride ingress is suspected, regenerator should be online all the time. Proper operation of the regenerator will ensure adequate removal of impurities. During shutdowns, regenerator demister pad should be thoroughly cleaned and inspected to avoid carry over which in turn would multiply the problem. In revamp, regenerator must be revamped adequately to take up the higher load on account of higher solvent circulation rate.
- e) To minimize O₂ ingress with makeup water, we have changed the makeup water from DM water to BFW obtaining good results in maintaining pH of stripper boot water close to 7.0. Close watch on boot water pH and lean solvent pH (7.0+) is required. At times, when boot water pH drops below 6.0, we increase MEA addition. Our average addition of MEA in Udex is 2 – 3 lit./week (Licensor recommends addition @ 1 lit./week – higher addition indicates excess O₂ ingress). Apart from pH, it is good to check lean solvent acid number (should be < 0.05 mg KOH/gm). Solvent color should be visually checked in every shift by retaining samples and comparing it with previous shifts samples.
- f) If one has lean solvent filter, filter should be cleaned periodically, and nitrogen purging be done before taking it online.
- g) During shutdown, if solvent is transferred to storage, it must be ensured that solvent tanks are properly nitrogen blanketed.
- h) In start-up, system O₂ should be thoroughly stripped off before taking solvent in the system. Purging from every pocket is important to ensure this. There is normally slackness in taking regenerator online after start-up. This should not be delayed as during this period, maximum O₂ is likely to be present in the unit.

i) For chloride guard, we plan to change over to molecular sieve in Udex to capture organic chlorides in addition to inorganic chlorides. Organic chlorides easily break above 100°C to accumulate in lean solvent.

We have no experience with morpholine as solvent.

Michael Windham (UOP)

This is an old question. Eliminating oxygen in the feed and in any vacuum section of the unit works but it can be a challenge. Some operators have reported the use of scavengers (free radical like inhibited phenols) in the feed helps. Finally we have anecdotal reports that the exclusion of chloride from upstream can help. From UOP's standpoint the minimum amount of cost would be the best practice. A unit without leaks receiving feed from directly from upstream production represents the minimum operating cost. Adding a scavenger to the feed may or may not improve actual reliability as you really need to compare units over a long time period and a controlled study has not been made. Operators with chloride removal on the feed also appear to be relatively happy but they have the cost of the chloride removal. In most of the cases of chloride removal the aromatics extraction unit is normally not the prime motivator. Normally chloride remove is installed to protect the debutanizer from ammonium chloride fouling; the improved reliability of the extraction process is normally an unintended benefit.

Glycols and Sulfolane solvent definitely have issues with oxidative degradation. Although UOP has had no direct experience with some of the other solvents, N-Methyl-2-pyrrolidone (NMP) has a similar reputation, deserved or otherwise. If someone is talking about degradation in these processes, you have to be sure they are talking about oxidative attack. Discussing thermal degradation products of the different solvents isn't useful to the operator since we all design to minimize thermal degradation. It's the oxidative degradation you have to worry about.

Since we have seen fouling and corrosion of simple stripper columns processing oxygenated feeds without solvent it is hard to dismiss the role that oxygen plays in the impact of feed handling on these units.

Brad Palmer (ConocoPhillips)

The first objective is to prevent oxygen from reaching the Sulfolane Aromatic Extraction Unit (AEU) by removing it from the feed and stopping ingress through leaks. Purchased feeds should be processed through an oxygen stripper or fractionation tower. Feed and solvent tanks should be kept under nitrogen. Leak checking all negative-pressure equipment should be done any time there is a sudden drop in pH. Other potential sources of oxygen such as oxygenates in lube or seal oils should be checked.

Second, sulfolane decomposition is accelerated with temperature and presence of oxygen. The bulk temperature of the solvent should be kept below 350 F.

Third, corrosion byproducts such as particulates and salts can cause fouling and corrosion in high

temperature areas and particulates can cause erosion. Removal of particulates and salt through frequent regenerator draining and cleaning can help. Solvent systems should have filters to remove particulates; total stream filters with 0.5 micron cartridges are recommended.

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