CORROSION AND MATERIALS SELECTION FOR AMINE SERVICE

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ABSTRACT

Amines are used in refineries and gas plants around the world to remove both H2S and CO2 from feed gas. The corrosion in amine plants is not caused by the amine itself, but is caused by the hydrogen sulphide, CO2, and by amine degradation products. Amines are compounds formed by replacing hydrogen atoms of ammonia, NH3 by organic radicals. Problems with amine units can be corrosion or by cracking (sulphide stress cracking, hydrogen induced cracking associated with hydrogen blistering, stress-orientated hydrogen induced cracking, and alkaline stress corrosion cracking).

Areas to have a close look at is where impingement erosion could occur, where there is elevated temperatures, where flashing off of CO2 could occur, and where heat stable salts could cause scaling.

Carbon steel and stainless steel are suitable for most applications, with the choice of material being determined by the susceptibility to the damage modes in each location. Careful consideration should also be given to the repair of plant (controlling weldment hardness).

1. INTRODUCTION

Amines are used in refineries and gas plants around the world to remove both H2S and CO2 from feed gas. The gas may be either feed gas in terms of a Gas plant, or it could be off-gases and olefinic and saturated liquefied Petroleum Gas (LPG) streams generated during the operation of Catalytic Crackers. Sulphur recovery units in Refinery operations also use amines.

CO2 can cause problems in gas processing plants and refineries alike. It may cause problems in hydrate formation, and affect specification of products such as ethylene in gas cracking units. The corrosion in amine plants is not caused by the amine itself, but is caused by the hydrogen sulphide, CO2, and by amine degradation products (Metals Handbook, Vol 13). The interest in amine units has been particularly strong by NACE and the like since the Unocal disaster in 1984.

Amines are compounds formed by replacing hydrogen atoms of ammonia, NH3 by organic radicals. The chemistry of acid gas removal by amine solutions is relatively complex, but the simplified reactions (exothermic) are:

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\begin{align*}
H_2S + R_2NH & \leftrightarrow R_2NH_2^+ + HS^- \\
CO_2 + R_2NH & \leftrightarrow R_2NH_2^+ + R_2NCOO^-
\end{align*}
\]

Types of Amines used include primary amines (NH2R) such as Methanolamine (MEA) and diglycolamine (DGA), and secondary (NHR2) and tertiary amines (NR3) such as diethanolamine (DEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA).

In the case of the Methanolamine (MEA), the methanol molecule loses an H bond and attaches to the amine molecule (which also loses an H bond. The formula is CH2OHNH2. Secondary amines such as diethanolamine (DEA) and diisopropanolamine (DIPA) are similar except that there are two alcohol molecules for the one amine molecule (i.e. NHR2), where the R represents the alcohol radical. A tertiary amine has 3 alcohol radicals to the N atom (i.e. NR3).

MEA has been reported to be responsible for stress corrosion cracking (SCC) failure of vessels in the late 1980’s. Conversion to MDEA eventually leads to low corrosion rates and elimination of SCC.

2. PROBLEMS IN AMINE UNITS

Problems with amine units can be split in to two categories:

Corrosion

Corrosion of amine units is usually not caused by the amine itself, but more the dissolved acid gases, primarily hydrogen sulphide and carbon dioxide. Heat stable salts resulting from the amine degradation can also cause corrosion problems.

API RP945, Avoiding Environmental Cracking in Amine Units, indicate that, in low pressure systems, corrosion of amine units used primarily to remove carbon dioxide has been historically more severe than that of units used to remove either hydrogen sulphide, or carbon dioxide and hydrogen sulphide. This is supported by Schmeal et al. In high pressure systems
where there may be high hydrogen sulphide partial pressure, corrosion of carbon steel can be severe.

_Safruddin et al_ indicated that, by tests using Linear Polarisation resistance (LPR) probes, corrosion rates were lower at higher concentration rates (possibly related to lower circulation rates). Lower circulation rates can mean less propensity towards erosion corrosion. There are velocity limits for the different materials. Carbon steel has a maximum velocity of 1.5 m/s, while stainless steels generally have a minimum and maximum velocity limit.

Pure amines are not generally corrosive due to the high alkalinity, but in the presence of acid gases, the corrosivity is largely determined by the stability of protective scales.

Corrosion monitoring can be done either by corrosion coupons/probes, or by monitoring iron content in solution.

_Cracking_

There are four basic cracking mechanisms for carbon steel:

**Sulphide Stress Cracking**

Corrosion of the carbon steel by hydrogen sulphide liberates atomic hydrogen which diffuses through the steel and accumulates at areas of high hardness or high stress and embrittles the steel. The cracking tends to be mainly transgranular in low strength steel and mixed mode or intergranular in high strength steels and localised hard spots.

As the high hardnesses are generally found in the weld metal or HAZ, the importance of correct weld technique is important in avoiding this type of cracking.

**Hydrogen Induced Cracking Associated with Hydrogen Blistering**

Hydrogen blistering results from the atomic hydrogen entering the steel and diffusing to voids, laminations and other discontinuities where it collects as atomic hydrogen. Susceptibility to hydrogen blistering in increased where there are high inclusion levels in the steel. HIC is the internal cracks that join the blisters.

**Stress-Orientated Hydrogen Induced Cracking**

This is a type of HIC that usually occurs in the base metal, adjacent to the HAZ, or any other areas of stress concentration.

**Alkaline Stress Corrosion Cracking**

This occurs as a result of corrosion in alkaline environments containing H$_2$S and CO$_2$, and tensile stresses. It is branched and intergranular in nature.

This type of cracking is largely temperature dependant, and is more severe at higher temperatures. It generally occurs in lean amine treating solutions containing H$_2$S and CO$_2$, and within a pH of 8 to 11. It involves stress induced protective film rupture and local anodic dissolution of iron at breaks in the normally protective corrosion product film.

The Nickel Development Institute indicates that the basic grades of stainless steel are susceptible to caustic SCC in highly caustic environments at temperatures above 120°C. This paper primarily addresses amine related corrosion in the oil and gas industry. As in the case of the pulp and paper industry, consideration should always be given to the use of duplex stainless steel if required. Likewise, 304 and 316 stainless steels are susceptible to intergranular cracking when sensitised by welding. Sensitisation can be avoided by specifying the low carbon grades or even duplex stainless steel.

### 3. PROCESS ISSUES

The process consists of several parts:

**Acid Gas Removal**

Gas (sour or sweet) is fed in to an absorber below the bottom tray. The gas rises against a lean solvent (amine), with treated gas exiting the top of the absorber column. The gas may go through a knock out process in which the gas passes through a knockout drum which disengages the entrained solvent. While the pressure may be high, the temperature of the incoming gas is generally low (typically 16°C), while the exit temperature out of the Absorber column is upwards of 40°C.

CO$_2$ will form carbonic acid which is particularly aggressive towards steel. In normal circumstances, the shell would protect itself by a stable iron oxide-carbonate layer. This could be destabilised by any inhibitor treatment, or turbulence within the column. The liquid level in the bottom of the Absorber is typically 70%. Therefore, it would seem likely that the vapour space at the bottom of the Absorber would be an area that careful examination would be required. Usual NDT methods (C-scan) in this area could be carried out to determine the condition of the shell. Column internals would invariably be stainless steel, and corrosion would be less likely.

Depending on whether the gas inlet distributor is submerged or above the liquid level would determine what possible failure mechanisms could exist. If the distributor is submerged, failure of bolts due to vibration could be possible. Depending on the product properties (i.e. any entrained liquids/solids), impingement erosion could occur. Incorrect sizing of distributors can lead to rising bubbles causing erosion.

**Material Choices**

The shell is usually carbon steel with either 304 or 316 internals. Stainless steel 316, is generally considered to give better resistance to corrosion in environments of chlorides, Naphthenic acid. The pitting resistance of 316 SS is typically 22.5, as opposed to 304 SS that is
Amine Circulation

The lean solvent that enters the Absorber column is upwards of 40°C, and potentially upwards of 50°C when it exits the Absorber column as rich amine. The simple amine sweetening plant schematic shown in the paper by Lunsford and Bullen is typical of many plants in which the rich amine is invariably flashed off in a knockout vessel before going through a Lean/Rich Exchanger (or series of Exchangers) in which the rich solvent is heated up from a temperature upwards of 50°C to approximately 90°C. The lean solvent exits the bottom of the Stripper or Solvent Regenerating Column at a temperature of greater than 100°C, before being cooled in the Exchangers down to 50°C, and entering at a temperature of greater than 100°C, before being cooled in the Exchangers down to 50°C, and entering the Absorber Column above the top tray.

The rich amine exits the bottom of the column. Bosen warns about the propensity towards corrosion of bypass lines around valves. This is due to the bypass line isolation valve being invariably closed, causing a dead leg to be formed. Bypass lines above the control valve may experience generation of gases that stop the amine wetting the surface. Subsequent condensation in this area could result in weak carbonic acid solution that could cause significant corrosion. Likewise, bypass lines below the control valve can lead to sedimentation and under deposit corrosion.

In most circuits, there will be flash tanks. It is important that the inlet nozzle is correctly designed to minimise erosion, and also that consideration be given to the possibility of under deposit corrosion in the flash tank since the velocities will be much lower in the vessel than in the piping, so sedimentation could occur.

Both lean and rich solvent could potentially be passed through the tube side of the exchanger. However, it is usually the rich solution that is put through the tube side as it is potentially more fouling than the lean amine. Bosen recommends that inlet for the rich amine is at a lower elevation than the rich amine outlet.

Material Selection

Material selection is influenced by a number of factors including areas of turbulence, temperature.

Depending on the configuration of lean/rich exchangers, the lean solvent would either flow through the shell side or the tube side, depending on temperature.

The lean solvent is hottest as it leaves the Solvent Regeneration column. It would generally flow through the tube side of the exchanger because above 85°C acid gases are released from solution and it is more economical for the tubes to be made out of stainless steel than the shell. In contrast to the above, the fat solvent which is at a cooler temperature is more viscous. To minimise the required heat transfer area and size of the exchanger, the rich solvent flows through the shell side.

In certain circumstances, it may be necessary to consider the cladding of areas of high such as nozzles (where turbulence exists). Cladding of the shell is an option in some cases.

Amine Regeneration

In the Amine regeneration circuit, the rich amine (liquid) from the Lean/Rich Exchangers enters the Regeneration column towards the top of the column at approximately 80°C. The rich solvent flows down the column where the acid gases are stripped by the rising steam. The lean solvent exits the bottom of the Regeneration Column at approximately 110°C.

Some flashing of the feed can occur in the Regenerator column. Mechanical forces associated with this can lead to failure of distributors. Splash plate distributors can cause erosion by themselves. If the plate fails due to vibration, then erosion of the column could occur opposite the inlet, and also lead to moisture entrainment in the vapour stream leaving the column.

Corrosion is typically worse at locations that the acid gases are flashed off. This could be at the regenerator reboiler and lower portions of the Regenerator column.
If there is concern about \( \text{CO}_2 \) corrosion in the overheads, then amine injection can be considered to maintain alkalinity.

Care should be taken to ensure that solvent chloride levels are kept below 1000ppm to avoid chloride stress corrosion cracking. The reboilers should be immune to amine stress corrosion cracking, though care should be taken where there is high residual stress (non PWHT welds, locations of bad fit-up and threaded connections

**Material Selection**

Regenerator columns can be lined with type 405 stainless steels. This is a ferritic stainless steel with lower yield strength than 410, 420 or 440 martensitic stainless steel. 405 Stainless Steel generally has lower corrosion resistance than type 304, 316 or 430 stainless steels (Vedder). Some literature reports corrosion to have occurred with 410 stainless steel in hot rich steels (Vedder). Some literature reports corrosion resistance than type 304, 316 or 430 stainless steel. 405 Stainless Steel generally has lower yield strength than 410, 420 or 440 martensitic stainless steels. This is a ferritic stainless steel with

304 stainless steels are often used for column internals, for valving and downstream of control valves to control corrosion accelerated by high flow turbulence.

Corrosion of reboilers is typically pitting of tubes. Groove type corrosion can also be seen due to vapour blanketing of part of the tube bundle leading to overheating of the tube and subsequent turbulence and velocity accelerated corrosion. The vapour blanketing can also lead to a reduction in the amount of tube surface available for heat transfer and therefore higher heat flux through the rest of the tubes.

Tubes may be carbon steel, but may need to be 304 or 316 stainless steel if process issues such as vapour blanketing cannot be resolved. Monel has been used where only CO2 is handled.

Other material issues might be the choice of high silicon cast iron impellers over normal cast iron impellers in low pressure amine service where corrosion is an issue, and the use of 316 stainless steel impellers in high pressure amine service.

**Heat Stable Amine Salts (HSAS)**

Amine unit contamination with HSAS, by either acid or inorganic salt incursion, or solvent degradation is reported to be a common problem. Burns et al\(^\text{11}\) indicate that HSAS in MEA (primary amine) is addressed via “reclaimers”. This is not considered feasible for DEA and MDEA or formulated solvents. Oxygen can degrade amines to form carboxylic acids, while H2S can react with degradation products to form strong acid anions such as sulphate and thiosulphates.

The process involves the absorption of acid gases (an exothermic reaction) in an acid/base equilibrium reaction. This occurs in the Absorber column. The rich liquid is then heated in the Regenerating column, which reverses the reaction. If the absorbed acid is very strong (with pKa much lower than that of the amine), then the amine is deactivated in terms of gas treating. Price and Burns\(^\text{13}\) indicated that the build up of HSAS is a result of formate incursion. These acids are not thermally regenerable. However, they can also include acetate, glycolate, propionate, oxalate, chloride, sulphate, thiosulphate and thiocyanate. Burns et al\(^\text{11}\) indicates that in the natural gas industry, acetic and hydrochloric acids used in well treatment activities can result in HSAS. Likewise, entrainment of formation water can add chlorides and sulphates.

While corrosion by salts is an issue, there is also the effect that the salts have on the scaling/heat transfer properties. The scaling may result in under-deposit corrosion and may also lead to foaming of the columns due to suspended solids.

There are many methods of dealing with HSAS. These include:

- Use of a neutraliser to raise pH and convert the amine salts to inorganic salts. However, while inorganic salts are not corrosive in themselves, they can increase fouling and lead to crevice corrosion
- Vacuum distillation – does generate “waste” and therefore only suited to certain applications
- Ion Exchange
- electrodialysis

It is not the intention of this paper to address recovery methods. Having said that, HSAS can cause severe corrosion, as evidenced by HSAS with the MDEA solvent in which the entire thickness of a reboilers shell could corrode away in a 2 month period.

## 4. REPAIR CONSIDERATIONS

A standard interpretation by the US Department of labor\(^\text{14}\) concluded that “the manner of field modification and repair of amine absorbers and associated equipment is critical to safe operation. Of particular concern are welding procedures and methods”.

NACE Standard RP0472-2000, *Methods and Controls to Prevent In-Service Environmental Cracking of carbon Steel Weldments in Corrosive Petroleum Refining Environments*\(^\text{15}\), addresses some of the issues associated with carbon steel materials (a common material for this application). The practices in the standard are intended to help avoid in-service cracking, rather than cracking associated with fabrication (i.e delayed hydrogen cracking).

The Standard mentions hydrogen stress cracking (HSC), sulphide stress cracking (SCC), and alkaline Stress Corrosion Cracking (ASCC) in such environments as alkanolamine solutions containing \( \text{CO}_2 \) and/or \( \text{H}_2\text{S} \). While controlling weldment hardness does not prevent ASCC (high tensile stresses may still be present), it is desirable to control weld deposit hardness to 200HB maximum. This is usually not a
problem for SMAW and GTAW. This is best achieved by preheating and high heat input.

The maximum allowable hardness for procedure qualification should be 248 HV. This is best controlled by preheating of the base metal, minimum hold time of 1 hour to ensure complete heat treatment (particularly if a lower than normal temperature is used). It should be noted that when PWHT is being performed to reduce HAZ hardness, the lower temperatures are not as effective. Initially it was recommended that PWHT be carried out on all welds where operating temperature is >60°C, but experience through the years has resulted in the “temperature limit” dropping to the extent that some companies recommend PWHT of all welds in amine service.

NACE RP0472-2000\(^\text{\cite{15}}\) also recommends that small fillet welds be avoided, and that one sided welding be used, as the highest hardness in weldments is generally in the HAZ of the last pass. One sided welding ensures that the prone areas are not exposed to the internal fluids. The temper bead technique can also be used (weld bead within 3mm of base metal).

API Recommended Practice 582, *Welding Guidelines for the Chemical, Oil, and Gas Industries*,\(^\text{\cite{16}}\) is a general document which supplements ASME section IX (and similar codes). It provides information on welding consumables, shielding gases, preheat and interpass temperatures, PWHT.

5. CONCLUSION

While carbon steel and stainless steels are widely used in amine service, great care should be taken in correct design of plant, choice of materials in different parts of the amine circuit, inspection and evaluation of susceptible areas, and any remedial work that needs to be carried out.

References

1. Price J. and Burns D., Clean amine solvents economically and online, Hydrocarbon Processing, August 1995
2. Kapadia A.C., Koorse M.M. and Ghosh D., carbon Dioxide in Natural Gas – Problems and Utilisation, Gas Processors Association
3. Safruddin, Sutopo & Rahmat, Twenty Years Experience in Controlling Corrosion in Amine Unit, Badak LNG Plant, Corrosion 2000
4. API RP945, Avoiding Environmental Cracking in Amine Units
6. Stainless Steels and Specialty Alloys for Pulp and Paper, NiDL, Nickel Development Institute, Series No 11 025
8. Bosen S.F, Cause of Amine Plant Corrosion – Design Considerations, Dow Chemicals
12. Lui H.J & Dean J.W., Neutralisation Technology to Reduce Corrosion from Heat Stable Amine Salts, Dow Technical Article, Gas Treating Products & Services
14. Miles J.B., Dept of labour memo 04/11/86 – Potentially Hazardous Amine Absorber Pressure Vessels Used in Refinery Processing, 14/7/2005
15. NACE Standard RP0472-2000, *Methods and Controls to Prevent In-Service Environmental Cracking of carbon Steel Weldments in Corrosive Petroleum Refining Environments*
16. Recommended Practice 582, *Welding Guidelines for the Chemical, Oil, and Gas Industries*