

Keeping Amine in the Treating System ¹

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The majority of gas treatment solvents contain at least one amine. So-called specialty solvents usually have two, and sometimes even three, amines. Of particular interest to the LNG industry are the piperazine-promoted MDEA solvents used for deep CO₂ removal from gas before the gas is dried and liquefied. All amines used as solvents in gas treating are volatile. This is especially the case with piperazine which has a higher volatility than any of the other commonly-used gas treating amine components. Piperazine is also costlier than *N*-methyldiethanolamine (MDEA), the amine with which it is almost always formulated. Being fairly volatile, its volatility is of particular concern.

Solvent can be lost from the treating system in several different ways including:

- Volatilisation,
- Entrainment as a spray, droplets, mist or foam from towers into various product gas streams,
- Physical leaks from glands and seals,
- Spillage and piping misalignments

The amine constituents themselves can also thermally decompose, and they can convert to non-viable species by reacting irreversibly with acid contaminants.

Solvent losses by the first two paths can be largely prevented by water washing the exiting gas streams. (Losses through leaks and spills, of course, are another matter and are usually maintenance and housekeeping issues.) The two amines in piperazine-MDEA mixtures are at quite different concentrations, and they have rather different volatilities, so they should experience quite different rates of vapourisation. Because of this, failure to recover and retain the components in piperazine-activated solvents will almost certainly result in a blend composition that drifts substantially over time. It is noted that thermal decomposition may occur at different rates for different amines, and this too can contribute to drifting blend composition. In this article, the efficacy of water washes and how they are carried out is examined using a specific example.

Where to Wash and with What

Amine treating takes place in a closed circuit using an absorber, a solvent regenerator, possibly a small flash gas treating column, and ancillary equipment such as pumps, heat exchangers, and a flash tank. Received wisdom is to use a stripped solvent that is five to 15 degrees hotter than the sour gas entering the absorber. This goes some way towards preventing condensation of high boiling hydrocarbons into the solvent which may result in foaming with all its accompanying problems. Another less discussed reason for using a solvent hotter than the gas is to ensure there is a small water loss from the system rather than a water gain. Water, of course, must be kept in balance in the solvent circuit and it's often a lot easier to add back water to the system than it is to remove it (without at the same time perhaps removing expensive amine). So

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there are at least a couple of good reasons for keeping the lean solvent hotter than the raw gas entering the absorber.

Potential amine losses just from vapourisation alone into the gas being treated may not be trivial. For example, without taking solvent recovery measures, in a plant producing 200 MMSCFD of treated gas at 46°C using a solvent with 46 wt% MDEA and 4.3 wt% piperazine the annual amine vapourisation loss is many *tonnes* of MDEA and *several tens of tonnes* of piperazine! The cost to replace this evaporated amine is roughly USD 450,000 of which by far the majority is for piperazine. Not only is piperazine a costlier chemical than MDEA, but it is also more volatile and, despite it being at a lower concentration, its losses are also quite a bit higher than MDEA. In piperazine-activated MDEA systems, water washing of product gases is almost always done. In fact, it should be considered mandatory when piperazine is a solvent component. A further concern with specialty solvents is that a drifting blend composition will lead to poorer treating performance over time. Piperazine is highly reactive towards CO₂ and is responsible to taking a raw gas to the < 50 ppmv CO₂ benchmark. Being nonreactive towards CO₂, MDEA is responsible only for bulk CO₂ removal. If piperazine continues to disappear from the solvent, performance will drift into the region where treating specifications cannot be met. Costs are incurred by losses having to be made up. However, the significant economic consequences of lost solvent and off-specification gas can be easily avoided by water washing all product gases.

Figure 1 shows a typical amine treating flow sheet. Water washing the acid gas produced in the regenerator is rather straightforward. It is quite common for there to be a few reflux trays at the top of this column, fed by the reflux produced in the overhead condenser. This makes getting amines down to parts per billion in the acid gas quite straightforward, although using reflux trays is not *always* necessary. The need for reflux trays depends on specifics of the operating conditions, particularly the stripper overhead temperature, and sometimes the condenser alone is sufficient to produce less than 1 ppb amine in the acid gas. The ProTreat® simulator provides solid guidance as to how many reflux trays (if any) are needed to achieve a given level of recovery.

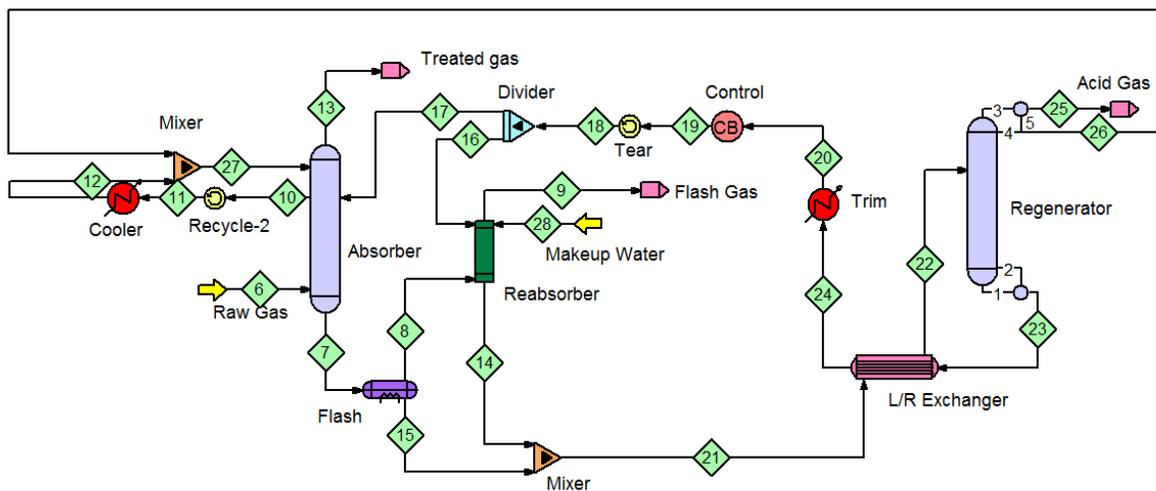


Figure 1 Typical Amine Treating Flowsheet in ProTreat®

Recovering amines from the treated gas can be done with two- or three-tray wash trays at the top of the absorber and using either fresh makeup water or, if inadequate makeup water is

available, by withdrawing part of the condensed water from the regenerator reflux drum and feeding it to the uppermost tray.

Absorber wash trays are commonly bubble cap type because a well-designed bubble cap tray can operate without weeping even at the extremely low liquid loads (flow rate per unit of tray active area) typical of water washes. However, at these very low liquid loads (extremely low L/V ratios), the quality of gas-liquid contacting may be poor. Contacting can be improved by recirculating wash liquid at much higher flow rates, adding fresh wash water, and allowing enough of the wash liquid to enter the absorption section from the bottom wash tray to maintain level control on a small wash-liquid holdup drum in the wash circuit. Lean amine is fed to the absorber immediately below the wash section. This scheme is shown in Figure 1.

It may or may not be worthwhile to wash flash gas from the reabsorber. This column is usually packed and is quite short. It recovers acid gases from flashed hydrocarbon before the flashed gas is discharged, possibly to be used as fuel gas. If simulation shows sufficient economic benefit from recovering amine from this unit, a short packed section fed with makeup water will work well.

Case Study

By way of example, in the absence of absorber wash trays, ProTreat simulation showed the treated gas in the case described above contains 2.2 ppmv MDEA and 9.1 ppmv piperazine. A simple wash using two bubble-cap trays with 6 m³/h of water reduces these values to < 1 ppbv and 20 ppbv for MDEA and piperazine, respectively. However, in this particular case, this much water flow exceeds the makeup needs for the unit as a whole. Therefore, 50% of the condensate from the overhead condenser was withdrawn and circulated it back to the top wash tray in the absorber.

The condensate is 0.3 wt% MDEA and 0.013 wt% piperazine. Two wash trays with this condensate as wash liquid is simulated to produce a treated gas with 130 ppbv MDEA and 8 ppbv piperazine. Vapourisation losses now amount to under USD 100 per year! If the wash trays were to require higher circulation rates for satisfactory hydraulic performance, amine losses would go up because the recirculating wash fluid would then be higher in amine concentration. Nevertheless, losses still would be enormously reduced. Note, however, that adding makeup water to a high flow-rate recirculation will be less ineffective than washing with water alone because the added water will tend to be lost in a sea of recirculation.

In this particular example, the acid gas from the regenerator was already at the parts per trillion level for both amines even without reflux trays in the regenerator. In this case there is nothing to be gained from adding a refluxing section. However, such is not always the case, and sometimes amine losses with the acid gas can be substantial. In the present case, the gas going overhead from the regenerator was only 76°C, quite cold by gas treating standards. Temperatures of 110–120°C are more usual, in which situation the amine concentrations might be high enough to make the inclusion of reflux trays in the regenerator worthwhile.

Whether to water (or condensate) wash varies a great deal from case to case, and only a reliable simulation can help make the right decision. But failing to wash product gases can result in very costly amine losses from the unit. Such losses are easy to prevent.

Entrainment and foaming losses have not been discussed because simulation tools do not usually address these hard-to-quantify issues. Packed columns do not usually exhibit large entrainment rates into the overhead vapour space, but near the top of their operating range trays usually do. A common (albeit arbitrary) definition of tray flood, for example, is 10 weight percent entrainment of liquid into the gas. Towers are almost always fitted with mesh pads or some other form of deentraining device; nevertheless, some solvent will still escape with the treated gas. If

the uppermost part of the column uses wash trays, any entrained liquid will be predominantly water with only a trace of amine; whereas, without water washing the entrained solvent is full-strength solvent. Wash trays help to cut down solvent losses via entrainment.

If the solvent has a foaming tendency, water washing reduces the amine content of the solution in the water wash section which tends both to decrease solution viscosity and increase solution surface tension. These collectively help to reduce the foaming tendency. A water wash will also tend to reduce and collapse the foam as it is carried up into the top of the tower. Again, water washing can help retain solvent in the system.