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Reduce amine plant solvent losses

Parts 1 & 2

A systematic technical approach will identify and
quantify losses into five categories

E.J. Stewart and R.A. Lanning
GAS/SPEC Technology Group

INEOS LLC

As part of a Federal Trade Commission mandated remedy to the merger of The Dow Chemical Company and the Union Carbide Corporation, INEOS plc was able to purchase both Dow's Ethanolamines and GAS/SPEC MDEA-based specialty amine businesses. This purchase became effective on February 12, 2001.

INEOS LLC was set up as the newly acquired company, which includes the GAS/SPEC Technology Group. All the key Ethanolamines and GAS/SPEC personnel were retained by INEOS LLC. All GAS/SPEC products, technology and know-how became the exclusive property of INEOS on a global basis.

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PART 1

Reduce amine plant solvent losses

A systematic technical approach will identify and quantify losses into five categories

E. J. Stewart and R. A. Lanning, Dow Chemical Co., Freeport, Texas

A systematic approach to amine plant solvent-loss reduction begins with an accurate measurement of current plant loss rates. To do this, look at long-term inventory and alkanolamine solvent purchases and calculate amine losses on a daily or hourly basis versus plant production, i.e., lb amine loss/MMscf of gas treated. If long-term data are not available, makeup rates and vessel levels can be trended daily to determine loss rates. Once a good estimate of total loss rate is found, categorize individual losses.

Next, gather plant data for characterizing losses in each major category:

- A complete laboratory analysis of the treating solvent including heat stable salt and degradation product levels.
- Plant design drawings
- Operating conditions and procedures, i.e., filter change-out procedures, absorber overhead temperatures, absorber pressures, treated gas/liquid flow rates and solvent concentrations.

An approximation should be made for losses due to vaporization, solubility, entrainment and degradation. The difference between estimated losses and actual current plant loss rates is attributed to mechanical losses. Individual mechanical losses are identified by a thorough plant inspection and review of operating procedures. The five categories of losses should then be ranked from highest to lowest loss area. This ranking establishes order of importance for equipment and operational changes.

The most common ranking of loss categories from highest to lowest in a gas treating plant is mechanical, entrainment, vaporization and degradation. However, when a liquid treater is part of the process, the ranking becomes mechanical, liquid entrainment and solubility as high-loss areas. Smaller losses are due to gas entrainment, vaporization and degradation.

A problem and solution . . .

Solvent losses in alkanolamine gas and liquid treating plants are about 95 MMlb/yr in the U.S. While some loss is expected in all operations, extreme losses can negatively impact economics of operating any amine unit. Understanding and controlling amine losses is an important aspect of successful plant operation.[1]

To reduce amine solvent losses in alkanolamine gas treating plants, a systematic approach is vital. Amine loss rates have become a more important economic factor in operating gas or liquid treating plants due to increased disposal concerns and chemical costs.

Amine plant losses stem from vaporization, solubility, mechanical, degradation and entrainment. To cut losses, target the largest loss areas and focus troubleshooting on design and operational changes to reduce losses.

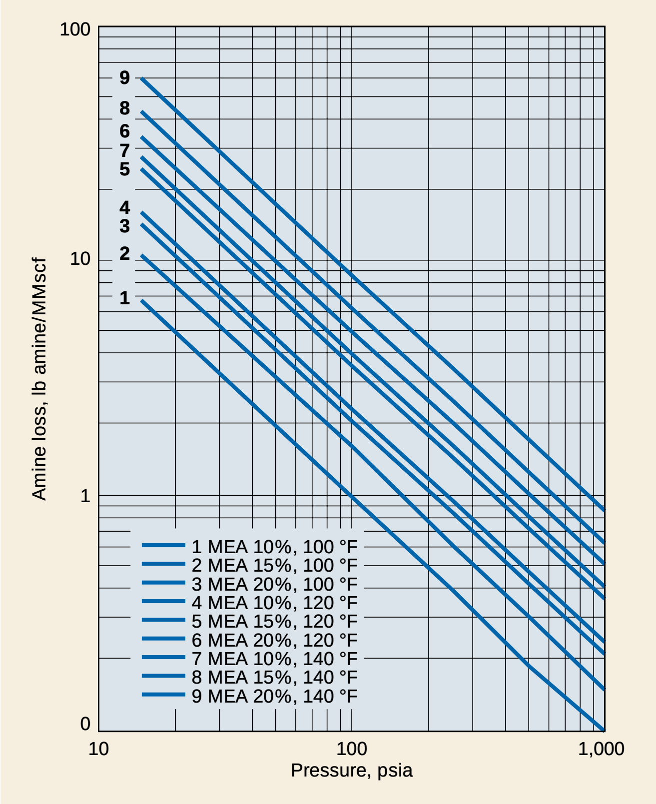

Fig. 1. MEA vaporization losses.

An important loss-reduction consideration is that current system losses are providing a purge for the amine system. As losses are reduced, this built-in purge is removed and contaminant levels increase. By maintaining periodic solvent analyses, buildup of contaminants in an amine system can be monitored and controlled while reducing losses.

VAPORIZATION

These losses are associated with all alkanolamine treatment of gas streams. They are a direct result of alkanolamine vapor pressure in the treating solution on the contacted gas stream. The amount of vapor-phase alkanolamine is governed by overhead operating conditions of the absorber, stripper and flash tank vent. These are the three main areas of vapor

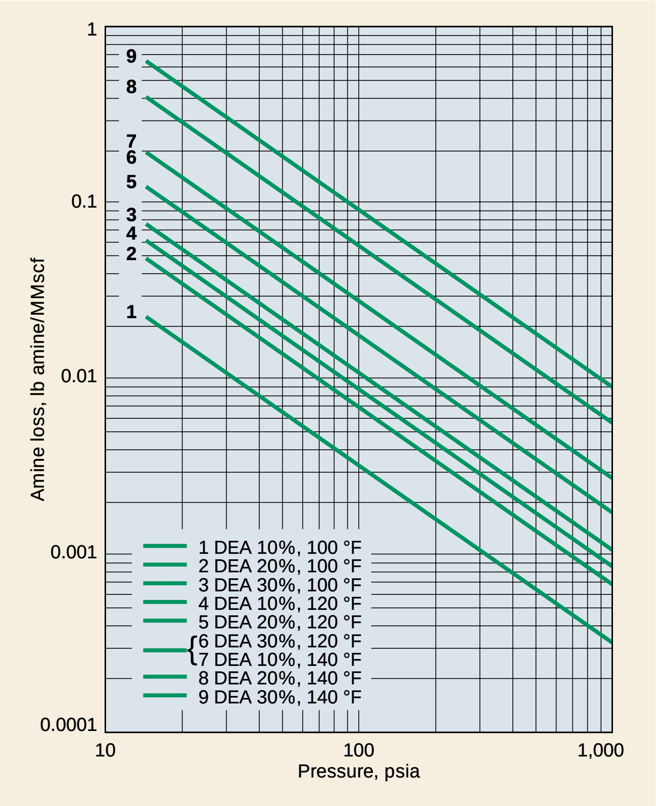

Fig. 2. DEA vaporization losses.

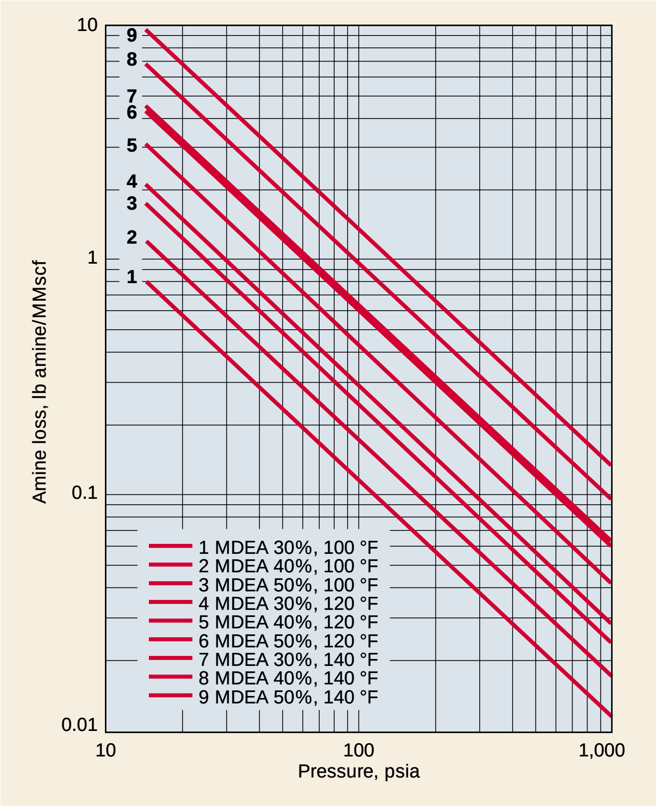

Fig. 3. MDEA vaporization losses.

losses in alkanolamine treating systems.

Parameters that govern the amount of vaporized amine are temperature, pressure and amine concentration. These parameters establish an equilibrium between the amine vapor pressure in solution and the partial pressure of amine in the gas stream. As temperature increases and/or pressure decreases, the amount of gas-phase amine increases due to higher vapor pressure exerted by the alkanolamine on the gas. Because treated gas is continuously being replaced by new gas moving up the tower, additional amine must move into the gas phase via vaporization to maintain equilibrium.

Amine vaporization losses can be calculated for each solvent based on vapor-pressure data of the specific amine and the gas stream temperature and pressure. Figs. 1 to 3 demonstrate amine vaporization losses predicted for monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). These were developed from pure-component vapor-pressure data assuming ideal solution behavior (Raoult's Law). Since the graphs are equilibrium based, actual losses will be lower than predicted.

Table 1. Estimated vaporization losses at 700 psia and 120°F

15% MEA	0.54 lb/MMscf
30% DEA	0.004 lb/MMscf
30% MDEA	0.035 lb/MMscf
50% MDEA	0.061 lb/MMscf

Table 2. Amine loss estimation

MEA	< 0.1 lb amine/MMscf acid gas
MDEA	< 0.01 lb amine/MMscf acid gas
DEA	< 0.001 lb amine/MMscf acid gas

Reflux drum operation at 120°F and 25 psia

Estimated losses per MMscf of gas treated by an absorber operating at 700 psia and 120°F are in Table 1. Losses are shown for each solvent at typical operating concentrations. This shows that MEA is much more volatile than DEA and MDEA. Using the graphs and specific plant conditions, an estimate of amine losses can be obtained for the absorber and flash tank vent. Gas flow from the flash tank vent may be estimated if a direct measurement cannot be made.

Because the reflux water returned to the system typically contains 1% to 5% amine, acid gas exiting the stripper is water washed. In addition, flow of acid gas is usually a small ratio of the absorber gas rate. Therefore, vaporization losses from the stripper are usually small. An estimation of amine losses can be made from Table 2 for stripper amine vaporization losses.

To reduce vaporization losses in any amine system, conditions of the carrying gas/solvent equilibrium must be manipulated to return amine to the liquid phase. Major parameters to work with are temperature, pressure and amine concentration. Treated gas coolers are commonly used to return water to the amine system and to reduce load on gas dehydration units. The cooler returns only a portion of the vaporized amine to the main circulation system. However, by using a water-wash system, amine concentration is lowered and much more of the vaporized amine can be recovered. The water wash has a low concentration of amine and a low amine vapor pressure. Amine partial pressure in the gas establishes a new equilibrium by forcing amine into the water phase.

The two most typical water-wash designs are a set of trays above the lean amine feed point in the absorber plus a separate tray, or a packed water-wash vessel downstream

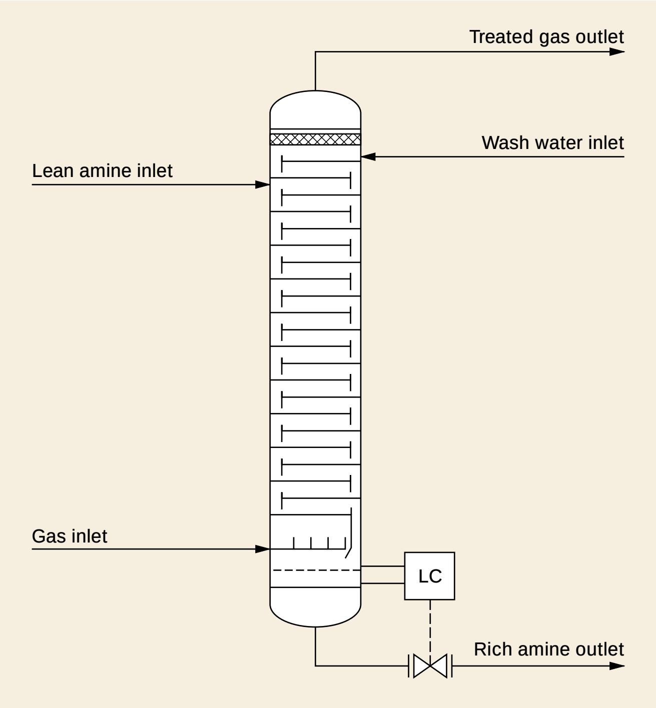

Fig. 4. Incorporated wash tray design.

of the contactor. Figs. 4 and 5 show these systems. Since the amine system water balance often limits makeup water, stripper reflux can be used as an internal source of low-amine wash water. However, in H_2S systems, use caution because sour reflux water may affect the treated gas specification.[2]

A gas treating survey completed in 1990 of West Texas alkanolamine plants showed an average amine loss rate of 3 lb amine/MMscfd treated gas for MEA, DEA and MDEA products. Almost all of these plants operate at elevated pressures, making vaporization loss a small fraction of the total loss rate. This indicates that even though some vaporization losses will always occur, the bulk of amine losses occur in other loss categories. One area of high loss similar to vaporization is amine solubility in liquid hydrocarbons.

SOLUBILITY

These losses are associated with any alkanolamine treating of liquid hydrocarbons. Similar to vaporization losses, an equilibrium between amine in the hydrocarbon phase and the alkanolamine in aqueous solution is established.

Amine in the liquid hydrocarbon phase is governed by temperature, pressure and amine concentration at the exiting interface of the two liquids. These parameters establish the amine equilibrium between the two phases. In general, as temperature increases or pressure decreases, more amine is carried by the hydrocarbon. As the hydrocarbon at the interface is replaced with new hydrocarbon moving up the tower, more amine moves into the hydrocarbon and is removed from the system. In liquid/liquid amine treaters, temperature and pressure typically operate within narrow limits to maintain the hydrocarbon as a liquid. The most important parameter to control is amine concentration.

Amine solubility in hydrocarbon can be estimated from physical properties to determine amine loss rates. Figs. 6 and 7 show solubility of amine in propane and butane.

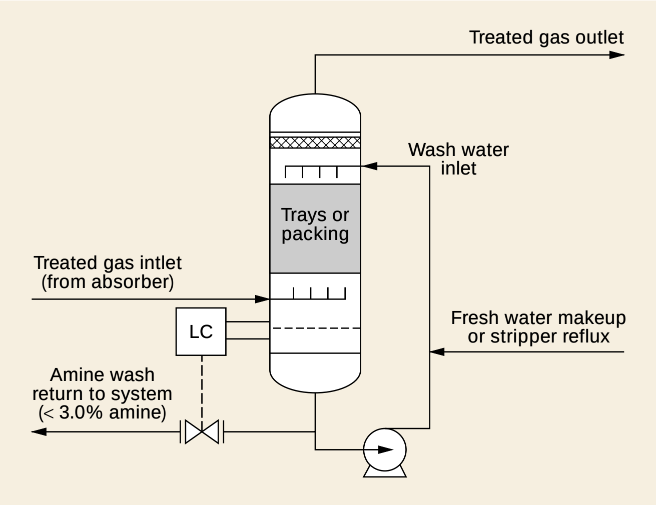

Fig. 5. Separate gas water-wash system.

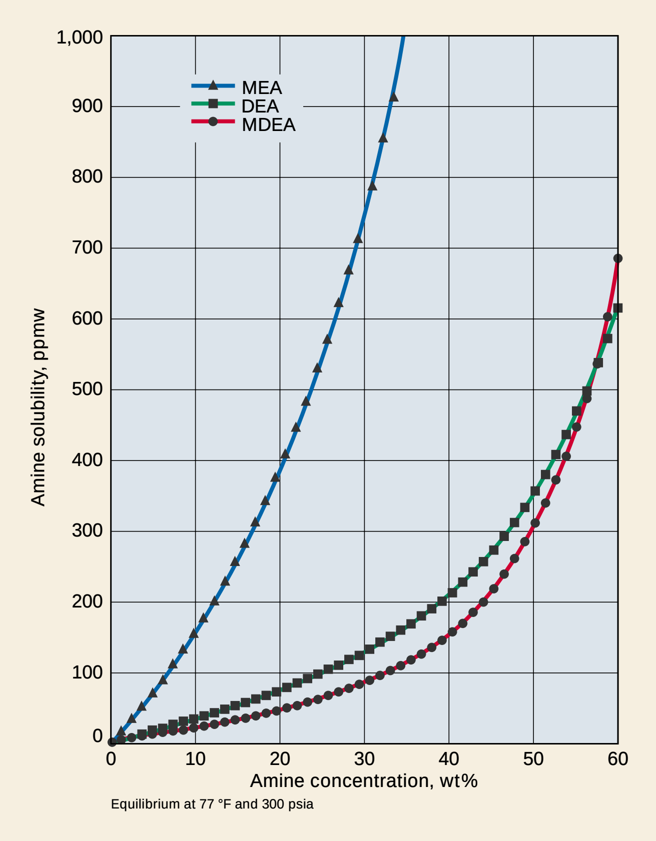

Fig. 6. Amine solubility in propane.

These graphs were developed using theoretical liquid/liquid equilibria based on Universal quasi-chemical functional group activity coefficient (UNIFAC) parameters. The theoretical predictions correlated closely with laboratory data. These graphs were developed with typical liquid treater conditions of 300 psia and 77°F.[3, 4]

The graphs show the strong effect amine concentration has on amine solubility in hydrocarbons. For a liquid polishing unit operating independently from gas treaters, operating at a reduced amine concentration is normal since amine-acid loading is low and solubility losses can be reduced. In liquid treaters operating with a regeneration system in common with a gas treating unit, a very low amine strength may cause high loading or gas absorber circulation problems. In this case, a compromise must be

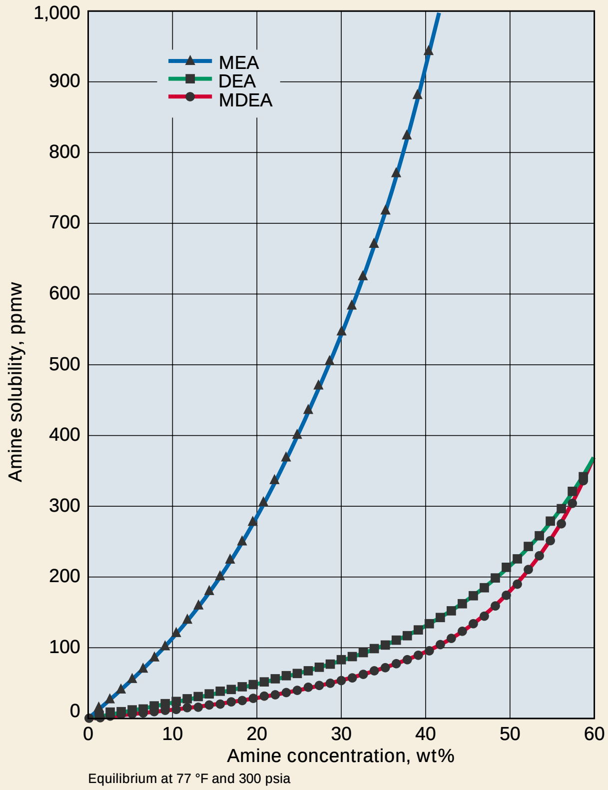

Fig. 7. Amine solubility in butane.

made. For solvents that typically operate at 50% concentration, such as MDEA and diglycolamine (DGA), we recommend a concentration of 40%. Operating liquid treaters above 40% results in substantial solubility losses.

In addition to reducing operating amine concentrations, solubility losses in liquid-treating systems can be controlled by water-wash systems. As with water-wash systems on gas treaters, the concentration of amine in equilibrium with the treated hydrocarbon is reduced. Amine in the hydrocarbon phase establishes equilibrium with the water-wash phase. This new equilibrium moves the amine back into solution for return to the main system.

The counter-current, water-wash vessel design (Fig. 8) and the co-current, water-injected, in-line static mixer design (Fig. 9) are both successful in reducing solubility losses. The counter-current water-wash vessel has a hydrocarbon retention time of 2 to 3 min. The outlet amine concentration in the wash is less than 3 wt%. A similar amine concentration can be recovered in the static-mixer system. The type of system chosen is cost dependent on the hydrocarbon flowrate and operating system pressure. Initial equipment cost can be recovered from amine savings.

With vaporization and solubility losses, the amount is set by the amine type and plant operating conditions.

Table 3. Typical entrainment sources

- Undersized tower diameter for gas flow
- Operation of tower below design pressure
- Trays operating at or above flooding
- Plugged or damaged trays
- Undersized or plugged amine distributor
- Damaged mist eliminator pad
- Damaged knockout vessel

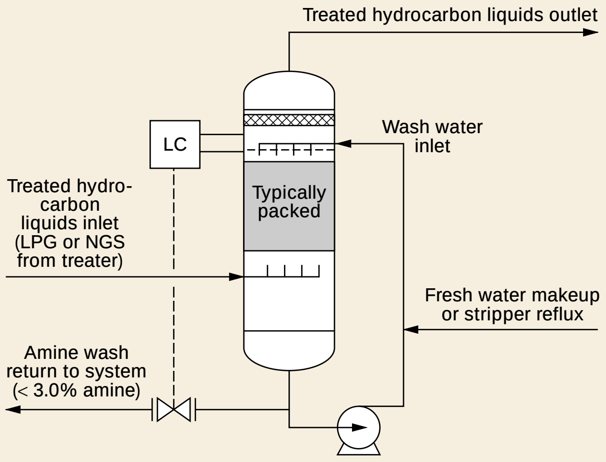

Fig. 8. Counter-current water-wash system.

Some losses in these two areas will always be present. Vaporization losses are relatively low until low-pressure or high-temperature conditions are present. However, liquid treater solubility losses are typically high. Control systems for both losses are water-wash systems. While vaporization and solubility losses are set by the physical properties of the amine and operating conditions, entrainment, degradation and mechanical losses center around the equipment, operations, conditions and contaminants.

ENTRAINMENT (GAS TREATERS)

These losses can be defined as the physical carry-over of amine solvent into treated or acid-gas streams. Entrainment can be described as a mist or spray, depending on droplet size for liquid-in-gas dispersion. It can be described as foaming for gas-in-liquid dispersion. This is strictly related to gas and liquid hydraulics in the absorber. Foaming typically results from a combination of contamination, solids and gas hydraulics in the absorber or stripper.

Liquid-in-gas dispersion (entrainment). This results from the formation of small amine droplets. Diameters from 0.1 to 5,000 microns are typically formed and carried by the gas up the column. Opposing forces acting on the droplet are gravity versus upwards gas pressure against the droplet's surface. As the amine-droplet volume decreases by radius cubed (r^3), the surface area decreases by radius squared (r^2). At some droplet size, its weight is insufficient to overcome the force of gas moving up the tower. Therefore, at smaller droplet sizes, the gas velocity must be reduced to prevent entrainment.[5]

There are several symptoms of heavy entrainment losses in gas systems. First is overloading of downstream gas knockout vessels. Even though the knockout vessel is designed to remove a normal amount of entrained amine, high levels of entrainment will overload the knockout system. Second, if knockout equipment is damaged or droplet size is small, entrained amine will move past knockout devices and collect in dehydration equipment and low places in gas transmission lines. Dehydration contamination can be checked in glycol units by pH and solvent analysis. These are all common symptoms of a high amount of entrainment, but identifying the source is important. Table 3 lists typical entrainment sources in gas treaters.

To control these entrainment losses, maintain low gas velocities where only small droplets can be carried by the gas. Small droplets will not remove a great volume of solution from the system. High entrainment losses are often attributed to operating an absorber above design gas rates or below design pressure. The Sauders-Brown equation (Eq. 1) can be used to evaluate superficial gas velocity for separation of entrained liquid in a 5-ft separation space above the top tray or with a mist eliminator. The diameter design equation (Eq. 2) uses this superficial velocity for evaluating tower design.[5–7]

$$V = K\left[\frac{\rho_L - \rho_g}{\rho_g}\right]^{1/2} \qquad (1)$$

$$\text{Then } D = \left[\frac{4G}{\pi V}\right]^{1/2} \qquad (2)$$

where V = superficial gas velocity, ft/s
D = vessel diameter, ft
G = gas flow rate, ft^3/s
r_L = amine density, lb/ft^3
r_g = gas density, lb/ft^3
K = empirical factor, 0.167 for 5-ft space above top tray or 0.35 for wire mesh separator.

In addition to gas velocity, tray design should be evaluated to determine percent flooding and slot velocities. Operating trays near or above flooding can cause an increased formation of droplets. Tray design evaluations are supplied by the vendor. Amine distributor design should also be checked as a possible source of mist formation. If mist eliminator or knockout equipment is present, their capacity and design should also be verified.[7, 8]

Mechanical damage to a well-designed system is a common source of spray. Equipment inspection can best determine if damage or plugging has occurred to trays or distributors causing the formation of a spray or mist. In addition, any damage to the mist eliminator and knockout equipment can cause normally-handled entrainment to become a high-loss problem.

Normal equipment solutions to liquid-in-gas dispersion take advantage of droplet mass and tower gas flow force. The most common solution is to insert mist-eliminator pads in the tower's top and install separate downstream knockout vessels. The basic principle of these pads is to provide a tortuous course for the gas to travel and a large surface area for droplet impingement. Forward momentum of the droplets is used to carry them onto the mist-eliminator surface as the gas makes a turn. Amine collects on the surface, forming larger drops that fall back onto the trays or the bottom of the knockout vessel. A few examples of these separation devices are shown in Fig. 10. Wire-mesh mist pads are the most common, but are normally designed for a narrow range of gas flows. If absorber gas rates change, consider replacing the mist pad for the new gas flow.

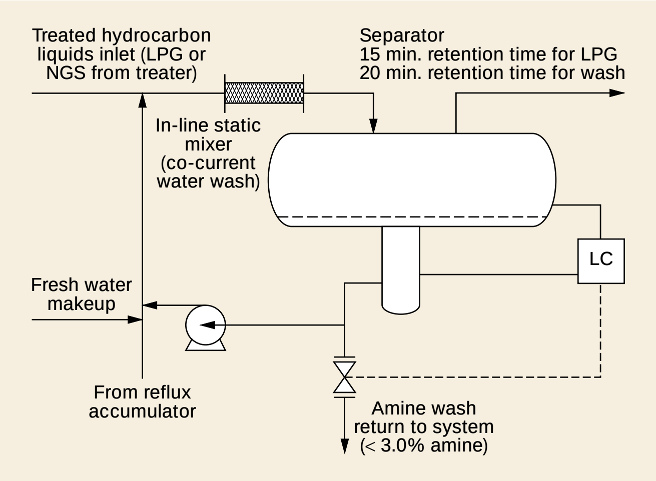

Fig. 9. Co-current water-wash system.

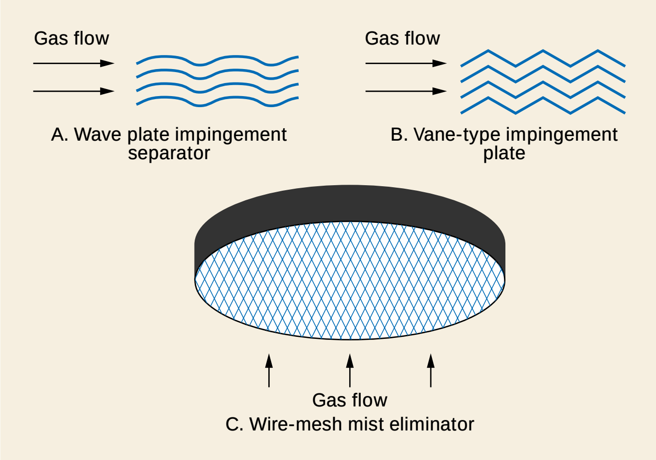

Fig. 10. Examples of mist/spray elimination devices.

Gas-in-liquid dispersion (foaming). This results from the formation of stable bubbles that build to a foam. The surface area to weight ratio for these stable bubbles is high, allowing the gas to carry the foam overhead. A certain amount of foam or froth on each tray is normal in alkanolamine treating. But this foam is not stable and quickly breaks down into solution. A foaming incident occurs when a stable foam builds on one tray up to the bottom of the next tray. This foam will move up the tower and carry over into downstream equipment.

Table 4 summarizes symptoms that identify a foaming problem. Foaming can be verified by an onsite shake test or by a rigorous bubbling test of 200-ml solvent with methane/nitrogen through a bubbling stone. In both tests, foam height and time required for the foam to break down into solution are measured.

Foaming can be attributed to three main parameters in alkanolamine systems:

- A contaminant acting as a foaming initiator
- Solids stabilizing the foam
- High gas velocity forming the foam.

One or more of these parameters is needed for foaming. Amine contaminants such as condensed hydrocarbons, organic acids, water contaminants and well-treating chemicals can be checked by laboratory analyses. Iron sulfide particles and other solids are foam stabilizers.[9]

Remedies for eliminating foaming focus on identifying and preventing solution contamination, and filtration to

Table 4. Foaming symptoms

- Overloading downstream knockout equipment
- High or erratic differential tower pressure
- Decrease in outlet CO_2
- Solution level bouncing in tower
- Solution level bouncing in flash tank
- Erratic stripper feed

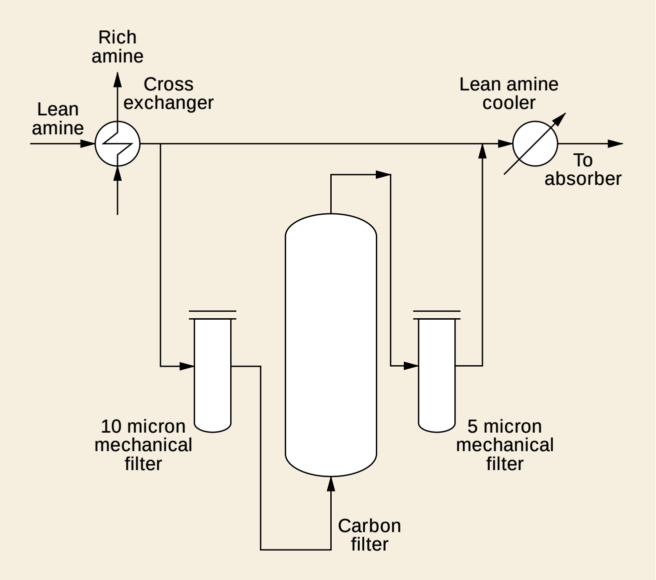

Fig. 11. Lean amine carbon filter scheme.

maintain solution quality. Table 5 lists some typical foaming agents and sources.

Many process unit operations have been successful in preventing contaminants from entering an amine system. Several refineries use water-wash systems on inlet gas streams to remove organic acids formed in cracker units. Porous-media filters on inlet gas streams are used for iron sulfide removal in sour-gas systems. Often, the process contaminant can be removed by repair or modification of existing equipment. Oxygen can enter a feed-gas stream through vapor-recovery units and through amine storage without a gas blanket. By modifying operation or equipment, oxygen contamination can be greatly reduced.

In addition to separation systems to prevent contamination, amine solution quality should also be maintained by mechanical and carbon filtration. An activated-carbon filter will remove many foaming agents in an amine system, like condensed hydrocarbons, amine-degradation products and organic acids. However, the carbon filter can also introduce solids to the system in the form of carbon fines. In a normal design, a mechanical filter is included on the outlet to remove any fines before they can enter the circulating solution. A common design for a carbon-filter system is shown in Fig. 11.

Carbon-filtration systems can be placed either on the rich or lean amine loop. They usually handle from 10% to 100% of the circulating solution. Placement of the carbon filter on the rich side is aimed at removing heavy contamination before the amine can foam in the stripper and degrade in the reboiler.[10, 11]

Table 5. Foaming agents and sources

Organic acids	Cracked hydrocarbon Inlet gas Makeup water
Condensed hydrocarbons	Rich natural gas Lean amine cooler than inlet gas
Water contaminants	Process or city water
Iron sulfide solids	Inlet gas from sour well formation
Amine degradation products	High reboiler temperature Oxygen contamination

Mechanical filtration is used to remove solids. Solids are not generally foaming agents, but will stabilize a foam once it is formed. An amine system may have a foaming initiator present but the foam breaks down into solution too quickly to cause operational problems or losses. However, when solids are introduced to this system, the foam stabilizes, causing treating and loss problems. A high level of solids can also cause erosion damage to equipment in high velocity areas. Mechanical filters from 0.5 to 25 microns are used to handle 25% to 100% of the circulating solution. These filters can be placed in lean or rich service areas.

Some high-level system contaminations can not be fully controlled by mechanical and carbon filtration. Anti-foam agents are then used to control foaming. The most common types of agents are polyglycol or silicon based. High molecular weight alcohols also perform well in amine systems. Anti-foam changes the amine's surface tension to inhibit bubble formation. Typically, anti-foam has a two-ended molecular design. One end is attracted to the aqueous phase, the other to the hydrocarbon phase. Thus, operation of the anti-foam at the solution's surface is maintained.[12]

Next month: **Part 2** of a two-part series. How to identify and prevent losses caused by entrainment in liquid treaters, degradation and mechanical leaks. Also included are two case histories to demonstrate the method's effectiveness.

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The authors

Erik Stewart *is a senior research engineer for the Dow Chemical Co., Texas Operations. He has five years of experience with acid gas treatment technologies in the natural gas, ammonia and refining industries. Mr. Stewart has worked extensively on developing environmental technologies for SO_2 and NO_x removal. He holds a BS degree in chemical engineering from the University of Washington.*

Al Lanning *joined the Dow Chemical Co. in 1982 and worked in engineering and production before moving to the GAS/SPEC Technology Group in 1987. He currently works in GAS/SPEC sales for Dow, Houston, Texas. Mr. Lanning has written several papers on H_2S treatment using liquid redox systems, been deeply involved in the successful introduction of the SulFerox process and has worked extensively on geothermal H_2S abatement technology. He graduated with a BS degree in chemical engineering from Lamar University in 1982.*

PART 2

Reduce amine plant solvent losses

A systematic technical approach will identify and quantify losses into five categories

E. J. Stewart and R. A. Lanning, Dow Chemical Co., Freeport, Texas

A systematic approach to reducing amine plant solvent losses begins by measuring current loss rates and ranking them according to loss category. The five areas of losses are: vaporization, solubility, degradation, entrainment and mechanical. Part 1 discussed the method to systematically reduce alkanolamine losses. It also included sections on how to identify and reduce losses due to entrainment (gas treaters), vaporization and solubility.

ENTRAINMENT (LIQUID TREATERS)

This has the same concepts as gas entrainment but is described as an emulsion. Because the higher density liquid hydrocarbon can exert a greater force on amine droplets, formation of small droplets will cause much higher losses in liquid treaters. Consequently, treaters are designed for low velocities for both phases to avoid small amine-droplet formation. A common symptom of entrainment losses is the presence of amine in low places in liquid lines or in downstream equipment, such as filters. An obvious emulsion 'rag' layer between hydrocarbon and amine phases in the liquid contactor is an indication of small-droplet formation.

Table 6 lists general liquid-treating design velocity parameters. Important parameters in amine entrainment are amine-distributor orifice velocities, redistributor orifice velocities and superficial velocities for both phases.[13]

Solving entrainment loss in liquid-treater systems requires a careful evaluation of treater design specifications and inspection of internals. High contactor velocities due to poor design or damage should be corrected. If entrainment persists, downstream separation equipment for liquid hydrocarbons is required. Since the liquid density is close to the amine, impingement devices are effective only on large droplets. Gravity separation of liquid entrainment is much more successful.

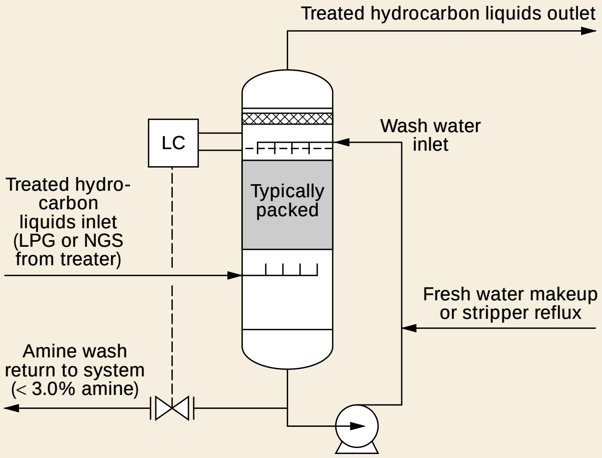

Fig. 8. Counter-current water-wash system.

Table 6. General liquid treating design parameters

Design parameter	Design criteria
Column diameter	15 gpm/ft^2 max. (total flow)
Packing material	Steel or ceramic
Amine distributor orifice velocity	170 ft/min max.
Amine superficial velocity	60 ft/hr max.
Hydrocarbon superficial velocity	130 ft/hr max.
Hydrocarbon disperser orifice velocity	1.00 to 1.25 ft/s

Gravity separation is commonly used with a 10 to 20 min. hydrocarbon retention time at low velocities. This occurs either above the absorber interphase or in a separate downstream vessel. A coalescer can work well in tandem with a low-velocity separator to improve gravity separation of larger amine droplets. Coalescer pads provide a large surface area for the amine droplets to collect and drop out of solution. Separators/coalescers with short hydrocarbon retention times are not as effective because the amine droplet momentum along a tortuous path in the coalescer does not differ greatly from the hydrocarbon. Finally, the water-wash systems used for solubility losses are very useful in removing entrained droplets as well. Figs. 8 and 9 show a good separation scheme for removing entrained and soluble amine from a treated liquid hydrocarbon stream.

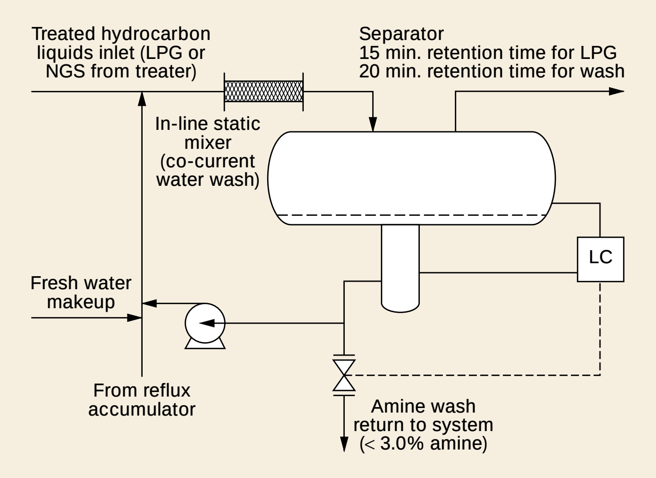

Fig. 9. Co-current water-wash system.

Table 7. HSS species common in amine systems

Nitrate	NO_3
Nitrite	NO_2
Formate	CHO_2
Oxalate	C_2O_4
Acetate	$C_2H_3O_2$
Sulfate	SO_4
Sulfite	SO_3
Phosphate	PO_4
Thiosulfate	S_2O_3
Thiocyanate	SCN

Estimation of entrainment losses in gas and liquid systems is difficult. If knockout equipment is present, carryover caught by the equipment can be determined by closing the dump-system valves and measuring level versus time. Detailed field analyses of entrainment in gas can be made using portable gas-testing labs, but a slip-stream water-wash system can be used for rough estimations. By taking a measured slip stream of the treated gas or liquid through a water wash, the amine collected per volume of gas/liquid can be measured by titration. This value will be a combination of entrained and vaporized/soluble amine. The ratio of each type of amine can be determined by using the previous graphs.

DEGRADATION

Amine-degradation losses are difficult to define in most alkanolamine systems. A broad definition of degradation is the chemical change of active alkanolamine. Amine does not leave the system but is no longer available for removing CO_2 and H_2S. Since degradation would include chemical breakdown of the amine into molecules that can and cannot carry acid gas, not all degradation is an active-amine loss. These degradation losses are often hard to determine because the alkalinity titration for amine concentration counts all basic material in solution as amine. Heat-stable-salt (HSS) formation is another form of active-amine loss. The amine and an acid form a salt that cannot be regenerated in the stripper.[14, 15]

Determination of exact levels of degradation and HSS products requires a laboratory analysis of the operating solution. Various test methods can be used. Gas chromatography will determine amine-degradation products and concentrations. HSS titration with ion chromatography will determine the concentration and type of amine tied up as a non-regenerable salt.

The chemical reactions of HSS formation have been well documented. The basic principle is a reaction of acid with amine to form an amine salt in solution which cannot be regenerated under normal stripper operation. H_2S and CO_2, by contrast, form amine salts in solution that can be regenerated in the stripper. Table 7 shows a number of HSS species that are commonly found in amine systems.

A rough species balance on the amine system is sufficient to estimate how fast active amine is degraded or complexed as an HSS. With current levels of degradation products and HSS in the operating solution, assume that current system losses are providing a purge at the rate of formation. Then, from actual loss rates obtained by inventory analyses, active amine loss by degradation is calculated from the purge rate. For example, if 2 wt% HSS and degradation products is maintained in the system with a 1 lb/hr solution loss rate, then 0.02 lb/hr degradation is occurring to the active amine.

Solutions for chemical degradation focus on two areas. First, preventing the contaminant from contacting the amine by upstream separation or contaminant reduction at the source. For example, mechanical troubleshooting of vapor-recovery units can significantly reduce oxygen levels in feed gas streams. Oxygen contamination will cause high degradation in all alkanolamines. Another example is the removal of organic acids, typically a refinery problem, with water-wash units on the inlet gas streams. By reducing the organic acids contacting the amine, HSS formation decreases.

Even with separation techniques, some amine contamination will continue. The choice of amine and reclaiming options becomes important for each application. MEA systems typically require thermal reclamation. This boils the amine overhead and concentrates salt ions in a sludge to be purged. Because DEA and MDEA are higher boiling-point amines, they cannot easily be thermally reclaimed without degrading the amine. For MDEA solvents, preferential removal of HSS from the amine system is done with technologies including ion exchange resins, electrochemical cells and vacuum distillation units. In each case, much of the complexed amine is restored and returned to the system. However, in clean natural gas service, reclaiming DEA and MDEA is not required.[16, 17]

Caustic treatment of amine has been used for HSS problems, but this is only a temporary solution. By adding a stronger base than the amine, caustic substitutes in the HSS and frees the amine. However, this method can create many additional problems. The caustic treatment can form sodium salts, some with low solubilities, and some very corrosive. These salts may deposit as solids throughout the system. Therefore, only one or two applications of caustic treatment can be done before the amine solution must be disposed of and replaced.

In addition to HSS formation and chemical degradation, thermal degradation of alkanolamine can reduce treating capacity. Because all treating alkanolamines show accelerated degradation above 350°F, thermal degradation results from high skin temperatures on reboiler tubes or thermal-reclaiming tubes. We recommend a reboiler operation with an amine bulk temperature below 260°F. With hot oil and steam heating systems, risk of thermal degradation is low since the heat media is usually not operated at high temperatures. However, in fired-reboiler operation, the temperature of amine on the tube's surface can easily exceed 350°F.

In fired reboilers, forced circulation is often used to maintain low skin temperatures. The rule of thumb is to maintain amine skin temperatures between 300°F and 325°F, and not exceed 350°F. For these temperatures a conservative design heat flux of less than 8,000 Btu/ft^2 of tube area is recommended. If thermal degradation is suspected in a fired reboiler, carefully evaluate fluid hydraulics and heat flux in the reboiler to determine the cause and location of high skin temperatures.

MECHANICAL

In the sample ranking of a natural gas and liquid-recovery plant, mechanical losses were the largest source of amine loss. Mechanical losses are defined as the physical removal of solvent from the closed circulation loop in the amine system. This occurs at the solvent operating concentration. Therefore, operation of higher-concentration solvents will incur higher amine losses unless the volume of mechanical loss is reduced. Symptoms of mechanical losses are visible as a drip or a spray from equipment. Table 8 shows a partial list of equipment areas where mechanical losses can occur.

Table 8. Mechanical loss areas

- Pipe flange/gasket connections
- Pump seal flushes or leaks
- Pressure gauge/sample line purge
- Frequent filter change-outs
- Filter cartridge elements
- Overhead fan cooler tubes
- Water cooler tubes

Loss estimation in this category is the difference between actual plant losses and the estimation of vaporization, solubility, entrainment and degradation loss. Individual mechanical losses must be identified by a plant inspection and operation procedure review. Measurements of these losses are made by bucket and stopwatch or by titration and sump-flow measurements.

Remedies for mechanical losses focus on equipment correction. They should be addressed by engineering and plant personnel or the equipment vendor. Operational changes include rewriting job procedures for methods of returning amine to the main system. For example, all filter change-outs should include a drain of the filter casing for return of amine to the main system. The solution flush for pump seals should also be returned to the amine system. This is often accomplished with a dedicated amine sump.

Case study 1. This is based on a liquid treating facility in Canada designed to process 22,000 bpd of ethane liquids. Current operating losses are estimated at 2.8 gpd on a 100% MDEA solvent basis. The low loss levels are due to a downstream water-wash system for the treated liquid stream. This system is similar in design to that shown in Fig. 9.

By completing a species balance for the wash system, recovered amine from entrainment and solubility in the liquid contactor can be calculated. Water-wash operating conditions are in Table 9.

Table 9. Water-wash operating conditions

Ethane rates	22,000 bpd	27,000 bpd
Water-wash rate	44 gpm	44 gpm
Amine concentration	0.3 wt%	0.4 wt%
Fresh makeup rate	3.52 gpm	3.52 gpm

The amine recovered at the 22,000 bpd rate is about 126.8 lb/d, i.e., 14.4 gal of 100% amine. This loss in a well-designed new plant gives an indication of the high levels of entrainment and solubility losses a liquid treater can have. For operation at 27,000 bpd, amine recovery increases to 169.1 lb/d because a greater amount of entrainment occurs at the higher hydrocarbon rate.

Most of the remaining 2.8 gpd loss is attributed to mechanical loss, such as pump seal flushes. On a yearly basis, the water wash system reduces amine plant losses from 53,004 to 8,624 lb/yr. For a liquid treating plant, this level of loss control is excellent.

Case study 2. This involves a large Louisiana refinery. This refinery is an integrated system with multiple gas absorbers and a liquid-treating unit. Historical solvent losses with MEA and MDEA were both in excess of 600,000 lb/yr. Conversion to MDEA increased the operating cost associated with this level of amine loss.

The initial loss ranking identified entrainment for both liquid and gas treaters as the largest loss category. Mist eliminators were placed in each absorber and a water-wash system was installed on the treated liquid stream. The loss rate was reduced from 640,000 lb/yr to 175,000 lb/yr. The water wash recovered much of the amine loss due to solubility in the liquid hydrocarbon stream.

End of series. **Part 1,** May 1994, p. 67.

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The authors

Erik Stewart *is a senior research engineer for the Dow Chemical Co., Texas Operations. He has five years of experience with acid gas treatment technologies in the natural gas, ammonia and refining industries. Mr. Stewart has worked extensively on developing environmental technologies for SO_2 and NO_x removal. He holds a BS degree in chemical engineering from the University of Washington.*

Al Lanning *joined the Dow Chemical Co. in 1982 and worked in engineering and production before moving to the GAS/SPEC Technology Group in 1987. He currently works in GAS/SPEC sales for Dow, Houston, Texas. Mr. Lanning has written several papers on H_2S treatment using liquid redox systems, been deeply involved in the successful introduction of the SulFerox process and has worked extensively on geothermal H_2S abatement technology. He graduated with a BS degree in chemical engineering from Lamar University in 1982.*

INEOS LLC
Head Office
2925 Briarpark Drive, Suite 870, Houston, TX 77042
713.243.6200 main 866.865.4747 customer service
www.ineosllc.com