

Face the Facts About Amine Foaming

Amines can be filtered free of contamination and fouling with these preventive methods.

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Amine foaming is a complex problem caused by a combination of chemical contaminants, stabilized by fine particulates, and dependent upon physical parameters and process conditions. To prevent foaming from disrupting gas plant operations, we need to know the causes and symptoms. We also need to ask some questions. What role computer simulation can play in solving the problem? What role should additives, antifoamants, corrosion inhibitors, and formulated solvents play? How does selection and operation of filtration equipment promote or reduce foaming?

The causes

Foaming is caused by changes in surface chemistry. Chemical contaminants that lower treating solution surface tension enhance foaming tendency and aerosol formation. When the surface tension is low, the solution can create a very thin film that is elastic in nature and capable of encapsulating a gas bubble or forming tiny liquid droplets (aerosols). When the surface tension is high, the solution cannot form a thin film and will not readily encapsulate a gas bubble or form an aerosol (Figures 1 and 2).

Fine particulates such as iron sulfide play a different role. Iron sulfide tends to form a quasi-polymeric layer in the film around a bubble, which increases the surface viscosity and prevents the migration of liquid from the bubble wall into the intersection of the bubbles. In short, iron sulfide simply retards drainage and thus stabilizes foam.

A clean amine solution will not form a stable foam. Contaminants in the feed gas, amine degradation products, fine particulates and chemical additives that reduce surface tension and raise surface viscosity can dramatically enhance foaming tendency and foam stability.

Contaminants

The most damaging are water soluble surfactants, that is, soaps. Many well-treating compounds and pipeline corrosion inhibitors fit this description. These contaminants are often much more problematic than liquid hydrocarbons, because soaps are readily soluble in clean amine solutions while hydrocarbons are not. Therefore, small quantities tend to significantly lower the amine solution surface tension. The gas plant operator should have the names and compositions of treatment chemicals that are commonly used by upstream processing units. Material Safety Data Sheets (MSDS) can provide a considerable wealth of information about the components in a particular compound. If no other source of information is available, ask the supplier for an MSDS. Suppliers are required by law to provide users with MSDS.

Lube oil is another common contaminant. Compressor lube oil forms a fine aerosol that easily passes through traditional inlet separators, while lube oil alone is not particularly soluble in clean amine solutions. As the amine solution degrades it becomes more soluble, and when this occurs, foaming problems are not far behind.

Oxygen contamination is a serious problem that is often underestimated. Part-per-million levels of oxygen can react with the amine to form carboxylic acids. Carboxylic acids react with functional amine and basic amine degradation products to form very soluble long-chain organic acids or fatty acids. Fatty acids increase liquid hydrocarbon solubility in the amine solution as well as cause severe foaming problems themselves. Phosphoric acid can be inadvertently released into the amine system with serious consequences. Some activated carbons are washed with phosphoric acid during the manufacturing process to remove inorganic minerals. Phosphoric acid causes

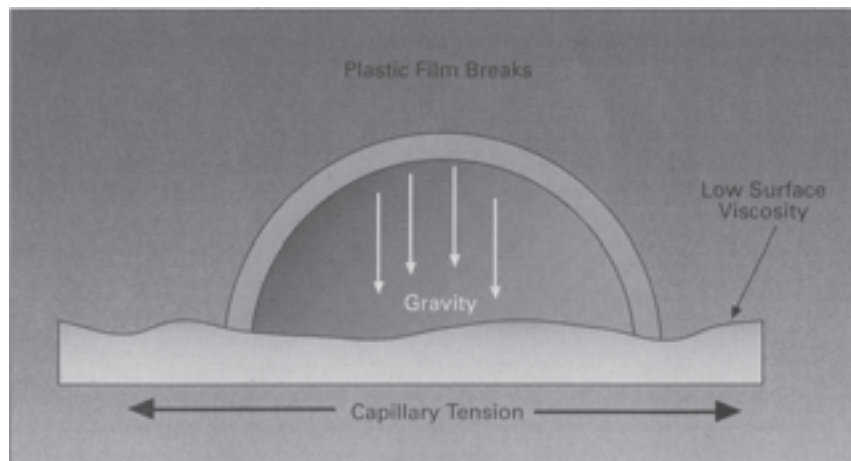
severe foaming problems. Dirt and larger solid contaminants do not adversely affect surface chemistry. Dirt, however, tends to "blind off" the available coalescing surface area of inlet filtration equipment and prematurely foul mechanical as well as activated carbon. A regularly scheduled inspection should be made to insure filter elements are not fouled or collapsed due to dirt.

Greases and oils can be introduced to the plant during maintenance. Maintenance materials should be washed to remove greases and cutting oils before being placed in the system. For example, cotton wound filter cartridges made from scrap fabric not only fail to consistently filter but can add surfactants to the amine system. The fabric is often treated with surfactants to make it waterproof or dirt resistant. When such a fabric is used in filter elements, surfactants can be washed into the amine solution and cause foaming. So, while cotton wound filter elements are relatively inexpensive, they can do more harm than good.

Degradation products

Acidic amine degradation products can be very troublesome. They are formed when the amine reacts with oxygen in the feed gas. The reaction proceeds at varying rates, depending on concentration, temperature, and pressure. Primary and secondary amines are easily oxidized. It takes less organic acid to cause problems in a tertiary amine solution because tertiary amines have inherently lower surface tension.

Organic acids also reduce the effective acid gas absorption capacity of the treating solution by forming heat stable salts. Heat stable salts are the soluble reaction products of organic acids and functional amine. A buildup of heat stable salts is a symptom of a problem in the making. If left unchecked, the same organic acids which form heat stable salts with the amine can polymerize to form longer chain organic acids which cause foaming.



■ Figure 1. Unstable foam in uncontaminated liquids.

Particulates

Hydrogen sulfide reacts not only with amine, but also with the metal-lurgy inside the plant to form iron sulfide. Over a period of time, iron sulfide will deposit through the plant. When these deposits cause restrictions in tray valves and orifices, vapor velocities increase. Higher vapor velocities can cause aerosol formation and other problems. Usually, however, once a thin layer of iron sulfide is formed on exposed metal surfaces, additional iron sulfide tends to float around the solution. Iron sulfide is a very fine particulate that tends to concentrate on the surface of the treating solution, thereby increasing the surface viscosity. The effect of this is to retard foam drainage and stabilize foam.

Ionic iron catalyzes the oxidation of MEA and DEA. Finely divided iron can then increase amine degradation, which increases the organic acid content of the solution and promotes foaming. Rust is also a fine particulate that can stabilize foam. Both iron sulfide and iron oxide particulates can prematurely foul activated carbon if not removed from solution through the carbon filter.

Chemical additives

Chemical additives such as antifoamers and corrosion inhibitors have a place in amine plant operations, but they should only be used

with a thorough understanding of the chemistry.

Most antifoamers are either silicone based or are long-chain alcohols. Corrosion inhibitors can be either inorganic metals or film-forming organic compounds. Formulated solvents are based on combinations of amines or amines to which corrosion inhibitors and/or antifoaming agents have already been added. A system already full of silicone from lube oil or the amine formulation does not usually respond well to the addition of more silicone.

Another common antifoamer is long-chain alcohol. Extreme caution should be exercised when using it. It can readily undergo oxidation to form a long chain fatty acid. A feed gas containing oxygen would provide the reactant to oxidize it to a fatty acid. Long-chain alcohols should be avoided when oxygen is present.

Corrosion inhibitors, for the most part, are organic film-forming chemicals. As such, they are surface active and would readily be removed by activated carbon until the carbon becomes saturated. When this happens the carbon begins to unload and can rapidly increase the concentration to a point which it can cause a foaming problem.

Formulated solvents pose a new challenge for the gas plant operator. The formulations are typically proprietary. The suppliers do not reveal the composition, thereby making it virtually impossible to

make informed decisions regarding supplemental additives. Even mixed amines can be a problem for the operator. If the mixture contains MEA and DEA, and the feed gas contains oxygen, organic acids will form readily. If the bulk of the formulation is MDEA, which is sensitive to small concentrations of organic acids, the solution will likely have severe foaming problems. Not knowing that the solution contains MEA or DEA, the operator may add antifoamer rather than change the carbon specification to selectively remove these organic acids.

How foaming affects the processing plant

Lost treating capacity is often the net effect of a foaming problem. When foam in the contactor becomes stable, its height increases and the void volume inside the vessel decreases. Reduced void volume increases pressure drop—the symptom. As the vapor liquid contact area is reduced (filled with foam), the effective mass transfer zone is reduced and less acid gas is absorbed. When foaming occurs in the flash tank, it reduces the surface area from which the gas evolves. Reduced surface area prevents the solution from achieving the desired semirich loading. Foam simply covers the surface and prevents gas from migrating out of the solution. If the semirich flash is below par, additional heat will be needed to generate a suitable lean loading. If the reboiler is at full rate, it may not be possible to achieve specification and the feed gas rate must be reduced.

Excessive amine losses and foaming problems go hand in hand. The contaminants that cause foaming problems also promote aerosol formation. An aerosol is made up of extremely small liquid droplets, which pass through conventional mist pads. These losses can become economically significant, particularly with high priced amines or formulated solvents.

In some cases, operators have installed overhead condensers to reduce overhead losses. The problem

is submicrometer liquid particles, not amine vapor. This procedure fails to recover the bulk of the aerosols, but instead condenses otherwise volatile hydrocarbons and returns them to the amine solution. Good design practice dictates an overhead temperature 5–10°F higher than the feed gas temperature to keep hydrocarbons from condensing into the amine solution. An effective way to reduce overhead aerosol losses is to use a fiber mesh pad rather than a wire mesh pad or chevron mist eliminator. Fiber mesh pads are effective at capturing submicrometer aerosols. Wire mesh pads and chevron mist eliminators are, at best, only effective in capturing particles 3 μm and larger.

Even in nonfoaming systems, attention to the design and operation of the mist pad can reduce chemical makeup requirements substantially. The principle of mist elimination is based on forcing droplets to hit a surface and agglomerate into larger droplets that fall into the process. When the gas velocity is too low, the droplets simply bypass the wire or fins and go overhead. When the gas velocity is excessive, particles are reentrained in the exit gas. Mist eliminators have very little turn-down. If the plant is operated at substantially reduced gas rates for extended periods, restricting the flow through the mist pad to increase the velocity through the open area is advisable.

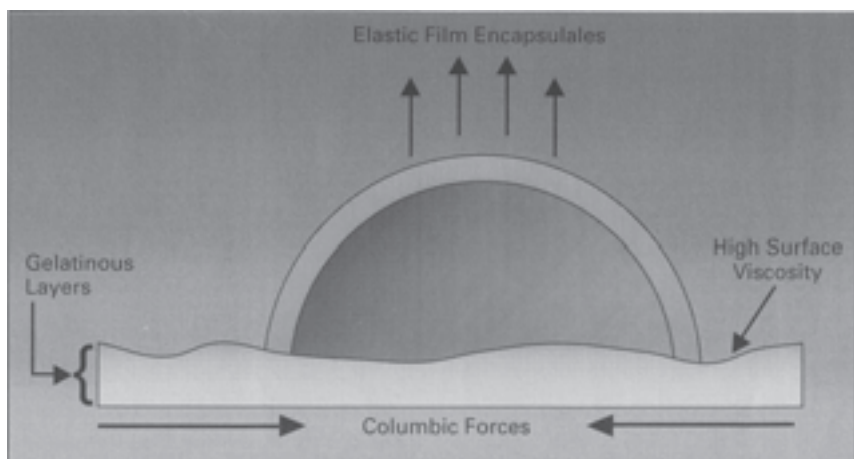
Corrosion, like foaming, is a big

problem in amine plants. Much has been written about corrosion and, for the most part, it is fairly well understood. Wet acid gases are highly corrosive; organic acids are highly corrosive; MEA solutions are more corrosive than DEA solutions which are, in turn, more corrosive than MDEA solutions. Flashing across valves and in exchangers is corrosive and erosive. While foaming does not cause corrosion, corrosion products can cause foaming problems. Iron oxide and iron hydroxide can react with amines to catalyze degradation to organic acids. Rust will increase filter duty, both mechanical and carbon.

Diagnosing a foaming problem

The amine itself is a good indicator. The color, the smell, and the ability to emulsify can easily and quickly be checked. Test the solution at several locations: the rich amine from the contactor, the semirich amine from the flash tank, the lean amine before and after the carbon filter, and the amine before and after the mechanical filter. It is also a good idea, if possible, to inspect the inlet separator and gas-liquid coalescer to insure that the elements have not collapsed or otherwise been damaged.

If the lean amine feed to the contactor has no adverse foaming characteristics, but the rich and semirich



■ Figure 2. Stable foam in contaminated liquids.

amine foams, then the problem is probably due to something bypassing the inlet filtration equipment. In this case, it has probably not yet saturated the carbon filter.

If the plant solution foams as bad on one side of the carbon filter as it does on the other, then the carbon is spent or cannot remove this particular contaminant. Keep in mind that most antifoamers are surface active and will be removed by carbon. If large doses of antifoamer have been added, the carbon is probably spent. Carbon will adsorb antifoamer until it is saturated, then begin to release it. When the antifoamer from the carbon begins to be released, the concentration builds rapidly until it becomes a foam stabilizer rather than an antifoamer.

If laboratory data show that fresh carbon of the type used in the plant is effective, then it will likely be necessary to recharge the carbon bed several times. If the contaminant is not otherwise removed, carbon consumption can be quite costly. The same tests should be run using another filter to determine whether the problem is due to particulates. Keep in mind that unless the carbon filter is protected on the inlet with a good mechanical filter, solids can plug the pours and quickly render it useless.

Beyond field testing, send a sample to a qualified laboratory for analysis. Have the solution checked for organic acids (by ion chromatography), heat-stable salts (by ion exchange), amine concentration (by gas chromatography and alkalinity), soluble metals (by atomic absorption), iron sulfide, liquid hydrocarbons, and water. These tests will provide a number of checks and balances.

Process simulation

Before any assessment can be made with regard to the operation of an amine plant, it is necessary to know the technical limitations of the equipment and the design. Computerized process simulators can provide this information.

A heat and material balance that shows the required equipment sizes

and duties for the desired gas-treating operation will quickly show if there is a process bottleneck when compared to the actual equipment sizes and duties found in the plant.

Three cases should be run. The first should simulate the design case to determine the requirements and establish a point of reference. The second should be run with the design case feed gas rate and composition, but using actual duties and equipment sizes. The third should simulate the current or target case using the actual equipment duties but with the current feed gas composition and conditions. Together, these cases will tell whether the plant was ever able to perform as designed and what it should be able to do in its present state.

When evaluating equipment and process limitations, begin with the feed gas and move through the process gathering as much information about each piece of major equipment as possible. Some of the key items include the feed gas, inlet filters, contactor, flash tank, lean/rich exchanger, stripper, reboiler, overhead condenser, carbon filter, mechanical filter, and reclaimers.

Once the process is fully simulated, mechanical problems, lost heat transfer efficiency, flashing problems and disproportionate circulation or heat input can be systematically identified. If the plant is experiencing a problem due to chemical contamination, identify

and remove the contaminants with proper filtration equipment.

Filtration equipment

For the most part, gas-treating plants are not operated by the people who design them. Consequently, designers often tend to neglect or undersize equipment needed to sustain long-term operability and make maintenance practical.

In all fairness to the design engineer, he bases the design on inlet gas conditions provided by someone else and on chemical stability data provided by the supplier. In most cases, the gas is assumed to be free of liquid contaminants, and degradation is reported as negligible by the amine supplier. Minimizing filtration equipment is then justified, and the designer reduces the initial investment. In practice, neither condition holds true. As the treating solution degrades, and becomes exposed to influent contaminants, filtration becomes increasingly important.

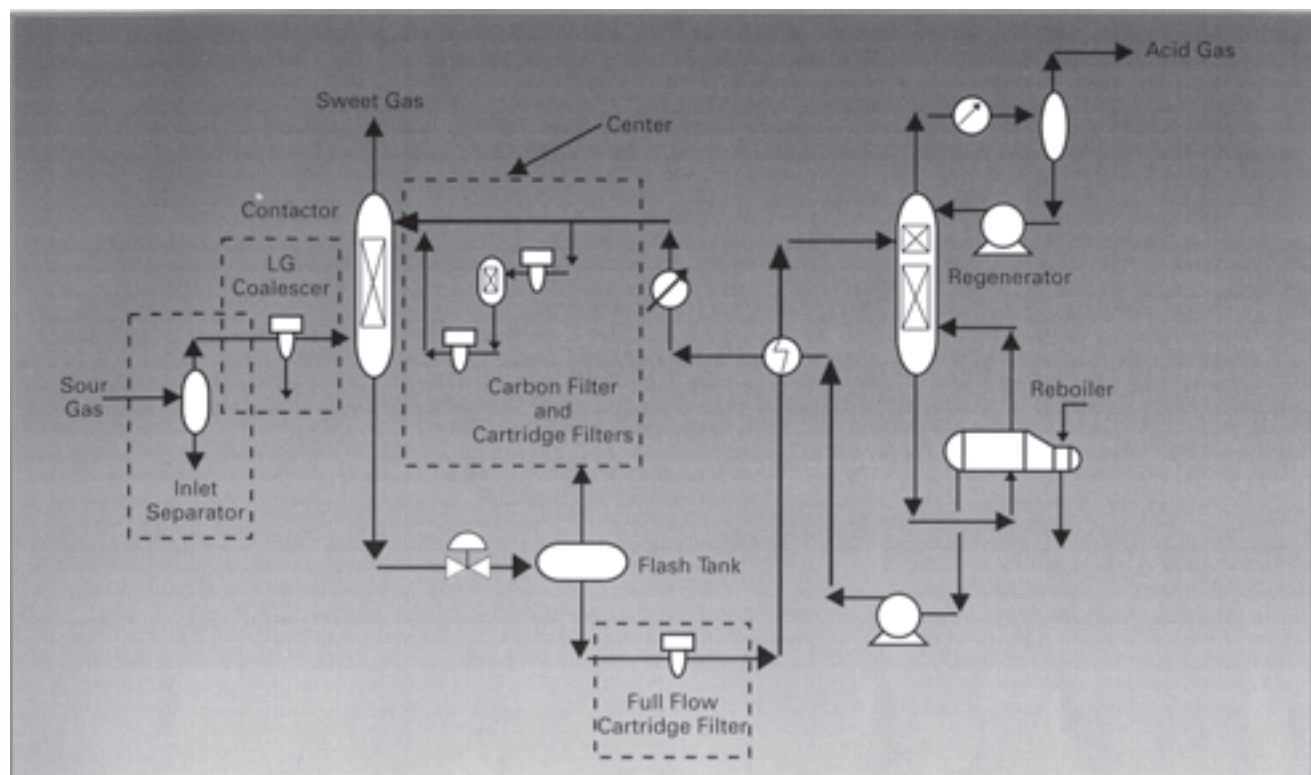
Effective solution filtration includes using a properly designed and installed inlet separator, gas liquid coalescer, solution filter, and cartridge filter (Figure 3). This point is emphasized because of the need to not only purchase the correct gas-liquid coalescer, but to properly install and operate it. It is not uncommon to find a gas-liquid coalescer installed backwards or missing elements, and empty carbon beds.

It is absolutely essential to open and inspect every filter system prior to commissioning its use.

Inlet gas separators. The best filter system is the one that prevents contaminants from entering the amine system. The inlet separator removes free liquids suspended in the gas stream. The optimum arrangement includes a slug catcher with an alarm system to announce the receipt of a liquid slug and an inlet filter separator to remove free liquids. The inlet separator should be located in the gas line downstream of any compression equipment and ahead of the gas liquid coalescer.

Gas-liquid coalescers. A filter separator does not eliminate the need

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■ Figure 3. Effective amine plant filtration scheme.

for a gas-liquid coalescer. A gas-liquid coalescer is located downstream of the filter separator (just ahead of the contactor); it catches smaller liquid particles, such as submicron lube oil aerosols that pass the inlet separator. Provide the supplier with a list of all the possible contaminants and fully describe the inlet gas. A properly specified, installed and operated gas-liquid coalescer should remove liquid droplets as small as $0.001\mu\text{m}$.

Adsorption (carbon) filters. The solution filter adsorbs surface active contaminants from the circulating amine solution. Location depends on the temperature of the stream and the source of the contaminant. Temperature affects solubility and adsorption characteristics. The most efficient filtration takes place when carried out on cooler streams. Contaminants are less soluble and more surface active. A solution filter located on the lean amine feeding the contactor would receive amine degradation products formed on the reboiler. A mechanical filter located downstream of the solution filter will keep fines out of the amine solution. A mechanical filter ahead of the

solution filter will keep dirt, rust, and iron sulfide from prematurely fouling the media.

The design of a carbon filtration system must be broken down into two sections, that is, bed design and carbon specification. The bed must be designed to insure proper contact and flow patterns. The carbon itself must be specified according to the type contaminants it is to remove.

Not all activated carbon is alike. Activated carbon that is designed to remove liquid hydrocarbons will be less effective at removing amine degradation products. Carbon that is designed to remove amine degradation products will foul prematurely if the solution contains liquid hydrocarbons and fine particulates. Similarly, the use of activated carbon with formulated products can be counterproductive. If not properly specified, carbon can remove additives which the amine supplier puts in the formulation to retard foaming (Figure 4). When this happens, the operator pays a premium for an amine containing an antifoamer which the carbon preferentially removes.

The adsorption process is dynam-

ic. Performance is based on the adsorption of liquid contaminants as the solution passes through and over the surface of the carbon. Contaminants are trapped in pores and held in place by weak physical or chemical forces. These contaminants desorb and are re-adsorbed, making their way down through the bed until breakthrough occurs.

In order to retain the maximum amount of contaminants within the bed, it is necessary to provide a suitable flow regime. If the flow rate is too high, premature breakthrough will occur. Needlessly slowing the flow rate requires a large vessel and capital investment. There is a trade-off between vessel size and performance. The rule of thumb is 4 gal/min for each square foot of surface area with a contact time of 10–20 min. A 10% slip stream is usually adequate for amine plant carbon filtration if the provided the bed is sized properly.

The liquid should flow evenly through the bed from top to bottom without dead zones. A taller, thin vessel would tend to limit distribution-related problems. Regardless, a

distributor should be used to introduce the liquid to the vessel.

The vessel should be designed for easy recharge. Larger beds should be equipped with a slurry transfer system. For recharges of 10,000 lb or more, suppliers will deliver carbon in bulk. Smaller operations should provide an easy-opening access on the bottom of the vessel and a recharge manway on top.

Whether the vessel is recharged by slurry or manual dumping, a slight vacuum should, if possible, be applied to the vessel before putting it in service. The vacuum will "degas" the carbon (remove air from deep in the pores) and increase its effective surface area. If applying a vacuum is not practical, backflush the bed with warm condensate water to remove fines and displace entrained air.

Activated carbon has a high oxygen demand. It will adsorb large volumes of oxygen. Care must be taken when entering a vessel used to store activated carbon to insure sufficient oxygen is present to support life.

Carbon beds and internals are typically constructed of carbon steel. Wet carbon should not, however, be stored in carbon steel for extended periods of time; it is quite corrosive. Carbon is much less corrosive when stored in the amine solution itself.

The pore diameter is the critical specification. Iodine and molasses numbers are empirical measurements of pore diameter. As a practical specification, carbons made from bituminous coal with high iodine numbers (900–1100) tend to be more efficient for removing degradation products in amine service. Carbons made from bituminous coal or wood charcoal with high molasses numbers (>200) are more efficient for removing liquid hydrocarbons in amine service.

An 8530 or 12540 mesh carbon is suitable for most amine plant operations. A finer mesh has a higher bulk density (pounds per cubic foot of dry carbon), but the surface area per pound is about the same. Finer mesh carbons are usually more expensive and difficult to handle, but carbon consumption (pounds of contaminant removed per pound of carbon) is about the same.

It is imperative to specify a carbon that has not been acid washed with phosphoric acid. Phosphoric acid is sometimes used to reduce the ash content, but small amounts of phosphoric acid will cause severe foaming problems.

Steam regeneration is somewhat effective in increasing the life expectancy of activated carbon in certain cases, but steam will only remove those contaminants that vaporize at or below the temperature of the steam. If the carbon is fouled with high boiling

per unit, but they cost less in the long run, particularly in sustaining overall plant performance.

Nonfixed or pressed media cannot give reproducible results, because there is no control over the fibrous structure. Cotton wound, cotton sock, molded cellulose and pressed cloth elements give nominal results. These types of elements are often dimensionally unstable. They tend to disintegrate and unload fines when subjected to heat and minor pressure differentials. Elements made from recycled fabric can contain oils and surfactants that will leach into the system and cause foaming.

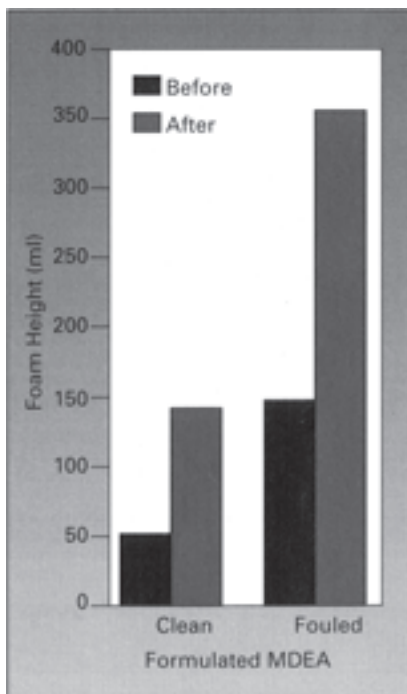
When comparing filters, it is important to understand the difference between a "nominal" rating and an "absolute" rating. Nominal ratings are assigned by the manufacturer and are not necessarily indicative of the performance. For example, a 2 μm nominal filter element does not mean that the filter will remove all particles larger than 2 μm . On the other hand, an absolute rating does give an indication of the level of performance. The absolute rating is the diameter of the largest hard spherical particle that will pass through the filter.

The most useful specification is the beta rating. The beta rating is simply the number of particles of a specified size and larger in the inlet divided by the number of particles of given size and larger in the outlet.

A filter cartridge for use in an amine plant should have a beta of 5,000 for 10 μm particles. This specification translates to a removal efficiency of 99.98% for all particles 10 μm and larger.

In conclusion

Be patient when implementing a solution. If the amine system is fouled, it may take a number of carbon charges and mechanical filter changes to clean it. Take this opportunity to work with the process simulation model in an effort to optimize the heat input and circulation rate. Eventually, the plant will respond, and in most cases it will be less expensive than changing amines or replacing tower internals. CEP



■ Figure 4. Foaming tendency (carbon filtration efficiency).

contaminants, steam regeneration will do little good. The most effective regeneration technique is to return the carbon to the supplier for reactivation.

Mechanical (cartridge) filters. The cartridge filter removes fine particulates and protects the solution filter media (carbon) from premature fouling. The better cartridges provide consistent, reproducible results. These are wound using extruded polymers that are dimensionally stable at the processing temperature. Controlling the filament diameter and winding technique yields a product that gives reproducible results. These cartridges generally cost more



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