Fuels and Chemicals

Scientific & Technical Report GDS120

Analysis of Foaming Mechanisms in Amine Plants

Presented by:

C. Richard Pauley
Pauley Gas Conditioning
Chattanooga, Tennessee

and

Reza Hashemi
Scott Caothien
Pall Corporation
East Hills, New York

to the

American Institute of Chemical Engineer's Summer Meeting
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*Filtration. Separation. Solution.*SM

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Table of Contents

1.0 Introduction

Foaming in amine plants increases operating costs and reduces treating efficiency. When foaming becomes severe, amine is often carried over into downstream treating equipment. It is commonly held that liquid hydrocarbons and iron sulfide cause foaming. Most treatments rely heavily on carbon filtration and the addition of antifoam agents to the circulating solutions. [1,2] Unfortunately, most antifoam agents are surface active, and are removed by activated carbon. Most often, after a brief improvement the problem becomes worse.

Since pure amines do not form stable foams, one or more components must be present in the treating solution in order to form a persistent foam.[3] Possible contaminants include not only liquid hydrocarbons and iron sulfide, but well treating fluids, amine degradation products, and other finely divided solids. The purpose of this work is to determine the physical/chemical mechanisms which cause foaming and offer some practical solutions to control the foaming.

2.0 Mechanics of Foam Formation and Stability

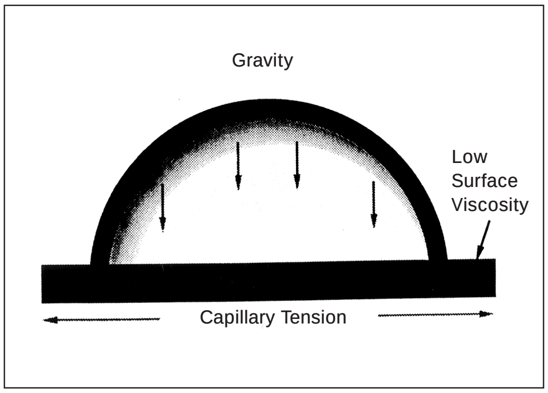
Foam is the result of a mechanical incorporation of a gas into a liquid. The liquid film surrounds a volume of gas creating a bubble. The formation and stability of the bubble depends somewhat on physical conditions such as temperature and pressure. Foam is primarily dependent on surface characteristics such as elasticity of the film layer, gelatinous layer efficiency, drainage, and surface viscosity.

2.1 Surface Tension & Foaming Tendency

The surface tension is an indication of a solution's tendency to foam. The surface tension (γ) is a force acting parallel to the surface which opposes any attempt to expand the surface area (A). The work required to expand the surface area is called the surface free energy (G) and depends on cohesive and intermolecular forces in the liquid:

Surface Free Energy, $dG = \gamma\, dA$ (EQ.1)

Figure 1A
Unstable Foam in Uncontaminated Liquids



In order to expend the surface, molecules must move from the interior of the liquid to the surface. This movement requires overcoming forces such as dipolar effects and hydrogen bonding. A nonpolar liquid with a minimal amount of hydrogen bonding would require little work to expand its surface. It follows that liquid hydrocarbons would have a low surface tension and tend to foam, while polar aqueous alkanolamine solutions would have a high surface tension and tend not to foam.

2.2 Elasticity of Film Layer & Foam Stability

Low surface tension alone does not ensure a stable foam.[3,4] The nature of the surface layer is more important to foam stability than just a low surface tension. Consider a bubble wall or film which is a dynamic system constantly stretching and contracting. After stretching, the thinner film section contains less liquid and has a higher surface tension. Liquid tends to migrate along the bubble wall to restore equilibrium carrying with it a relatively thick layer of underlying fluid which restores film thickness (Figure 1A). This ability to resist film thinning is referred to as film elasticity. Gibbs defined elasticity in terms of the surface tension (γ) and surface area (A) by the relation:

Elasticity, $E = 2A\,(d\gamma/dA)$ (EQ.2)

Antifoamers are chemicals which are designed to increase the elasticity.[5] When the chemical's migration along the surface is slower than its migration from the bulk to the bubble wall, the thinned spot will not heal. Such a foam is weak and unstable.

2.3 Gelatinous Layer Formation & Hydrocarbon Solubility

Factors which increase hydrocarbon solubility will increase the solution's tendency to foam, and factors which increase gelatinous layer formation will increase foam stability.

The gelatinous nature of the surface layer contributes enormously to foam stability. Gelatinous surface layers are plastic, i.e., they remain motionless under a shearing stress until the stress exceeds a certain yield value. The small gravitational and capillary stress acting on the surface is usually less than the yield value. Consequently, the formation of a plastic or gelatinous layer has a tremendous foam stabilizing effect. Molecules containing long unbranched hydrocarbons and small terminal polar groups form gelatinous surface layers.[3] Secondary and tertiary amines would tend not to foam; therefore, foam stability is a moot point in a clean amine solution. However, the addition of a chemical species promotes a gelatinous layer. If such a solution begins to foam, the foam will be quite stable.

The addition of liquid hydrocarbons to amine solutions has been considered the primary cause of foaming problems. However, liquid hydrocarbons will only reduce the surface tension of the solution and increase its tendency to foam to the extent that liquid hydrocarbons are more soluble in the bulk solution. Since liquid hydrocarbons are more soluble in secondary and tertiary amines, secondary and tertiary amines are more likely to foam in the presence of liquid hydrocarbons. The ability to form gelatinous surface layers also means that secondary and tertiary amine foams will be quite stable.

Any chemical species which lowers the surface tension (enhanced foaming tendency) or promotes gelatinous layer formation (enhances foam stability) can create a problem in amine treating solution. Acidic amine degradation products do both, and since acidic amine degradation products are soluble in the treating solution, small concentrations can be quite influential. Acidic amine degradation products have been observed in used MEA, DEA and MDEA solutions.[6] The rate and type of degradation products formed depends on the type of amine. MEA is quite easily degraded when compared to DEA and MDEA. MEA and DEA have labile hydrogen atoms attached to the nitrogen atom and form certain degradation products which MDEA can not. Some of the more common degradation reactions are shown in Table 1.

TABLE 1 – SOME AMINE DEGRADATION REACTIONS

Oxidation of amine to form carboxylic acids and ammonia.
Internal dehydration of amine carbonate to form HEOZD.
Simultaneous dehydration and decarboxylation of HEOZD to form THEED.
Internal dehydration of THEED to form DEP.
Double dehydration of DEA in presence of MEA to form HEP.
Condensation of two MEA molecules to form Piperazine.
Acylation of tertiary amines to form Quaternary Ammonium Salts.

HEOZD	N(hydroxyethyl) oxazolidone
THEED	Tri(hydroxyethyl) ethylenediamine
DEP	Diethanolpiperazine
HEP	N(hydroxyethyl) piperazine

2.4 Film Drainage & Foam Stability

Stable foams drain slowly. Film drainage is a process by which the liquid around the bubbles migrates from the cell wall into the intersection of the bubbles. The geometry of the bubble intersection results in capillary tension which draws the liquid into the intersections and away from the wall until the bubble ruptures. The capillary action is influenced by the external forces such as repulsive Coulombic forces, vapor velocity, and gravity. Repulsive Coulombic forces retard the formation of bubble intersections and limit drainage. Gravity tends to accelerate downflow drainage while vapor velocity tends to hold liquid up in the foam and retard drainage.

2.5 Iron Sulfide & Surface Viscosity

Iron sulfide is produced by the reaction of H_2S in the feed gas with iron found in the plant's material of construction or iron oxides brought in with the feed gas. Iron sulfide produced in this manner is extremely fine. Figure 2 is a photomicrograph of a plant solution collected on a 10 micron absolute polypropylene cartridge showing iron sulfide particles which are primarily submicron in size. Colloidal iron sulfide particles are so small that they remain in suspension indefinitely and follow Brownian movement. They will concentrate on the liquid surface forming a quasi-polymer network in the film around the bubbles. This will increase the surface viscosity and retard the migration of liquid that thins the bubble walls. In addition, the dipolar character of iron sulfide increases the Coulombic repulsion of individual foam bubbles to further retard drainage (Figure 1B).

The larger particles shown in the photomicrograph are aggregates of iron sulfide. If iron sulfide is allowed to concentrate in the solution, it can form aggregates that can become attached to vessel orifices and restrict gas flow. The restrictions caused by these aggregates increases the vapor velocity through the tower. The increased vapor velocity further limits drainage and enhances the stability of the foam.

Figure 1B
Stable Foam in Contaminated Liquids

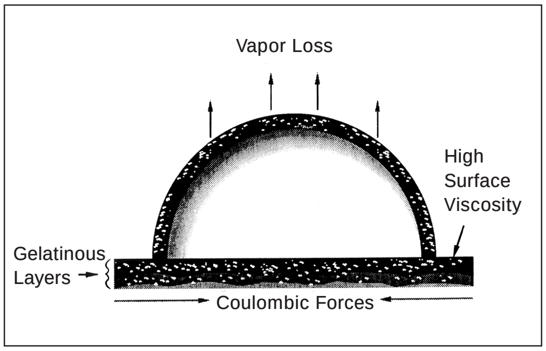
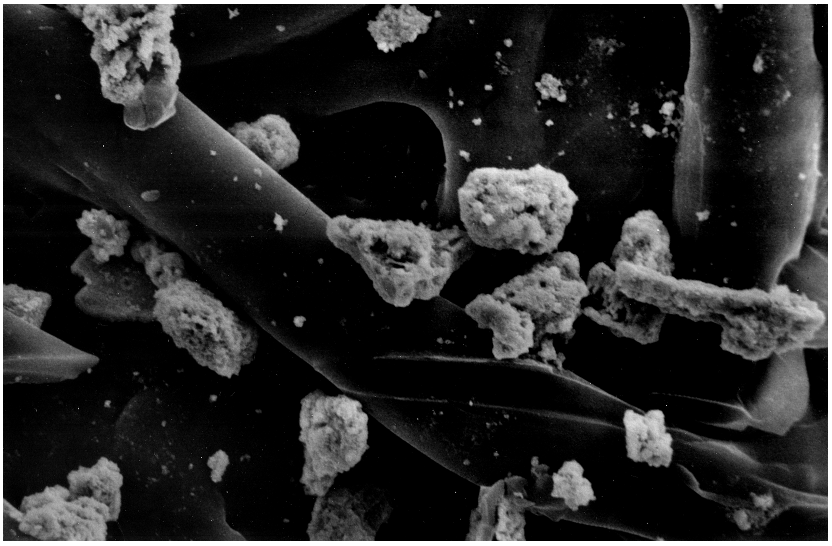


Figure 2
Collection of Submicron Iron Sulfide Particles



The surface tensions of the commercial amines were determined, at various concentrations, using the procedure described in the Appendices. The results are presented in Figure 3. The surface tension of MDEA is slightly lower than MEA and DEA, but formulated solvents have surface tensions significantly lower than MEA and DEA. The formulations must contain additives that decrease surface tension. Such additives commonly found in formulated products increase the foaming tendency and foam stability as indicated by the data in Figure 4A.

The foaming tendency (foam height) and stability (break time) of commercial amines were evaluated using the procedure described in the Appendices. The results are presented in Figure 4A. Based on the results, pure MEA, DEA, and MDEA solutions do not foam appreciably, and the small amount of foam produced is unstable. The two formulated MDEA solvents have a greater foaming tendency and produce a more stable foam than the generic MDEA solution.

Figure 3
Surface Tension of Aqueous Amine Solutions

At Ambient Temperature

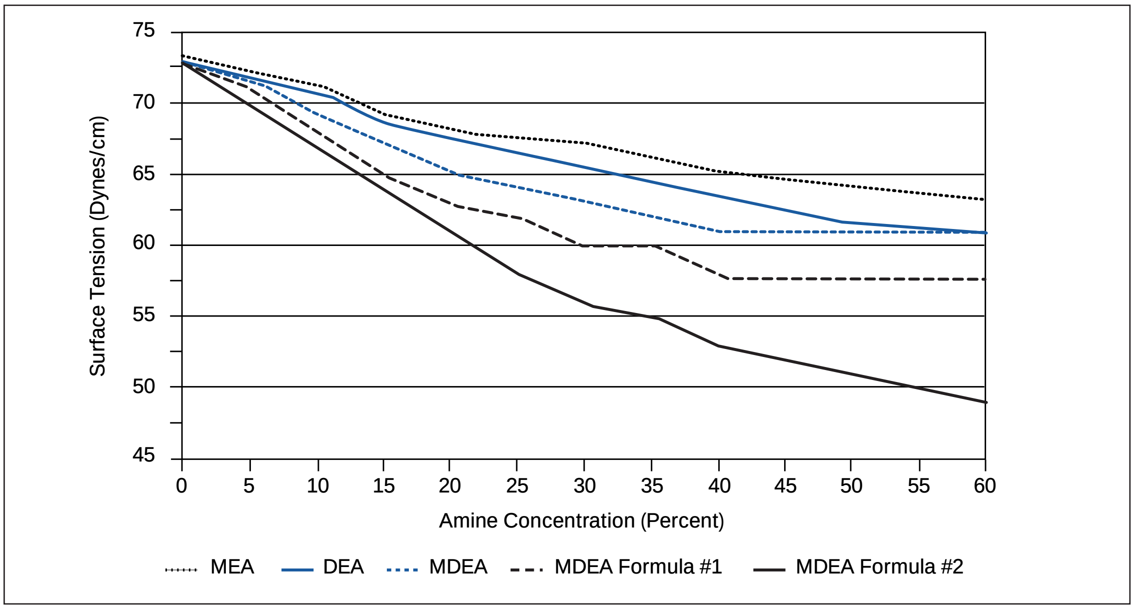
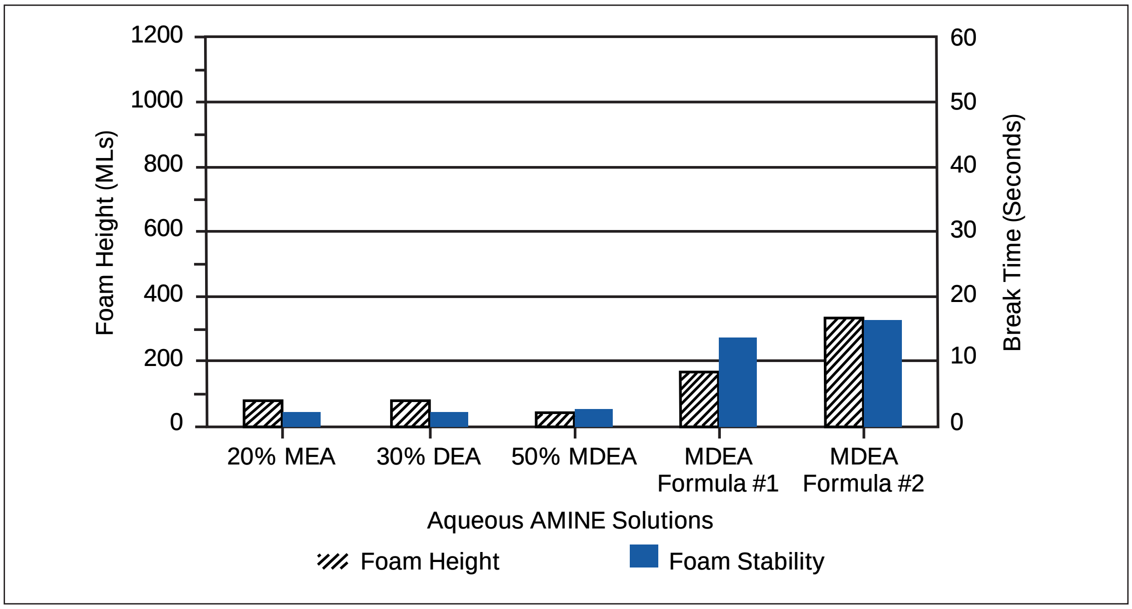


Figure 4A
Foam Height & Stability of Aqueous Amines



Several of the commercial amines were contaminated with liquid hydrocarbon. The foaming tendency and stability were again measured. The results are presented in the first three bar groupings in Figure 4B. The foaming tendency and stability of the MEA solution was not significantly different in the presence of liquid hydrocarbon, but the foam stabilities of MDEA and formulated MDEA significantly increased. The addition of a small amount of organic acid to the formulated MDEA sample enhanced both foaming tendency and foam stability by several orders of magnitude (the last bar groupings of Figure 4B).

The effect of acidic amine degradation products was evaluated by adding a series of lower molecular weight organic acids to 20% MEA solutions (Figure 5A and 5B). The effect of higher molecular weight organic acids was evaluated on 20% MEA, 30% DEA, 50% MDEA, and formulated 50% MDEA (Figure 6A and 6B). The individual data points shown on Figures 6A and 6B illustrate the proportionate difference between 20% MEA and the other amines.

Figure 4B
Foam Height & Stability of Aqueous Amines

Contaminated with 5,000 PPM Liquid Hydrocarbon

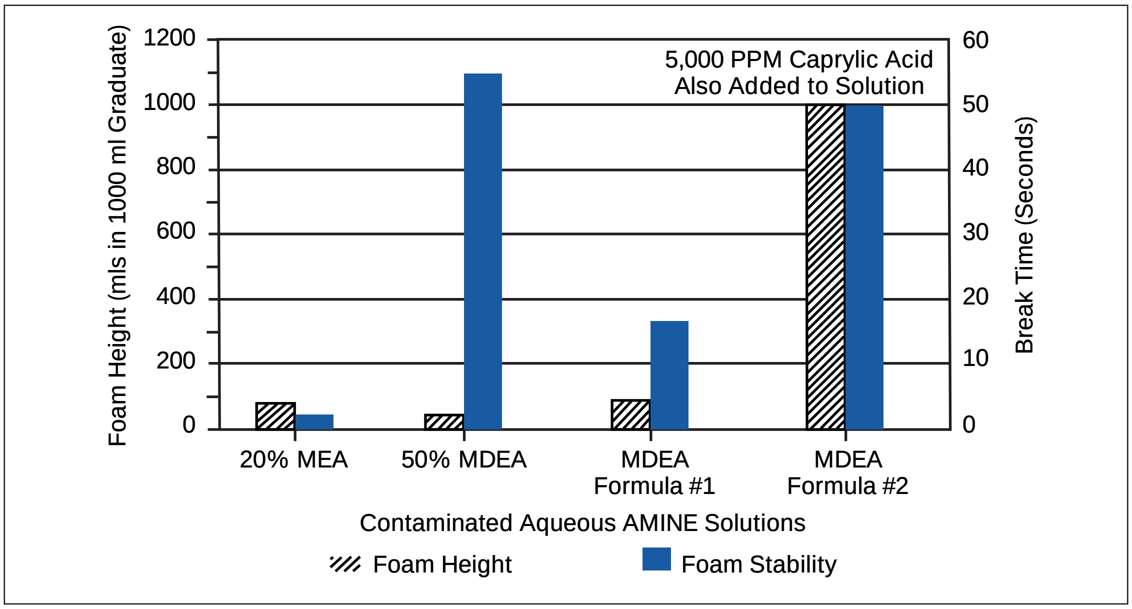
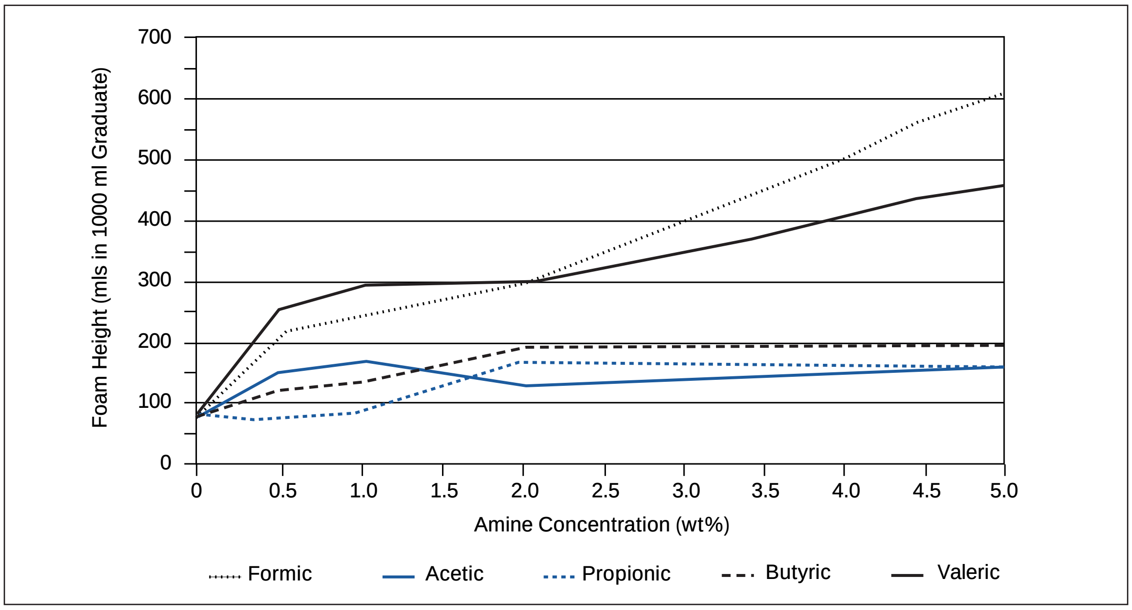


Figure 5A
Foaming Tendency of Contaminated Amine Solutions

20% MEA



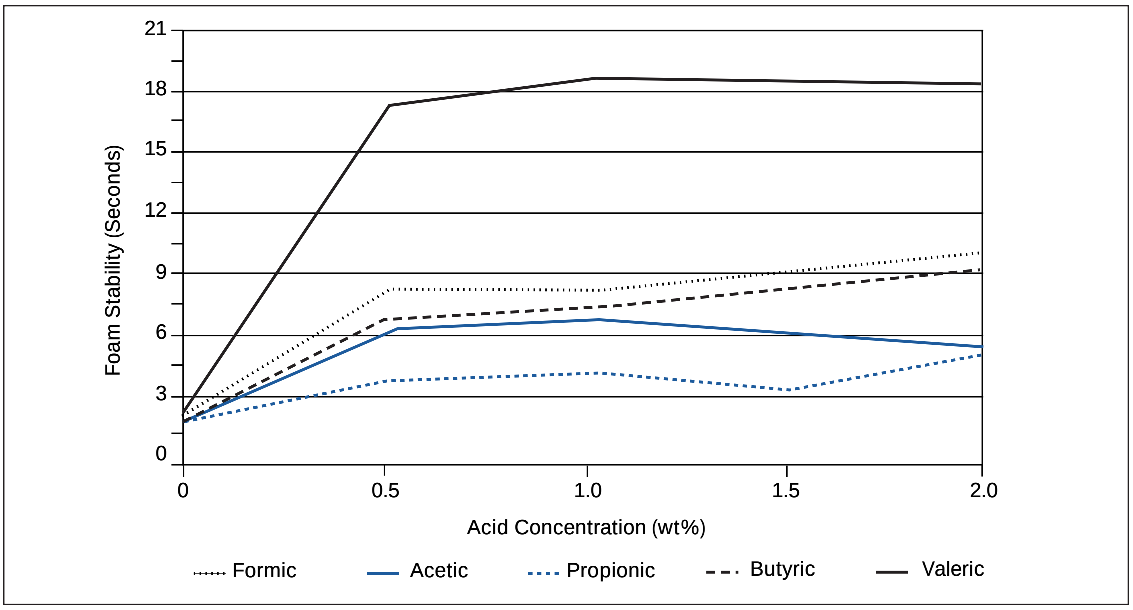


Figure 5B
Foam Stability of Contaminated Amine Solutions

20% MEA

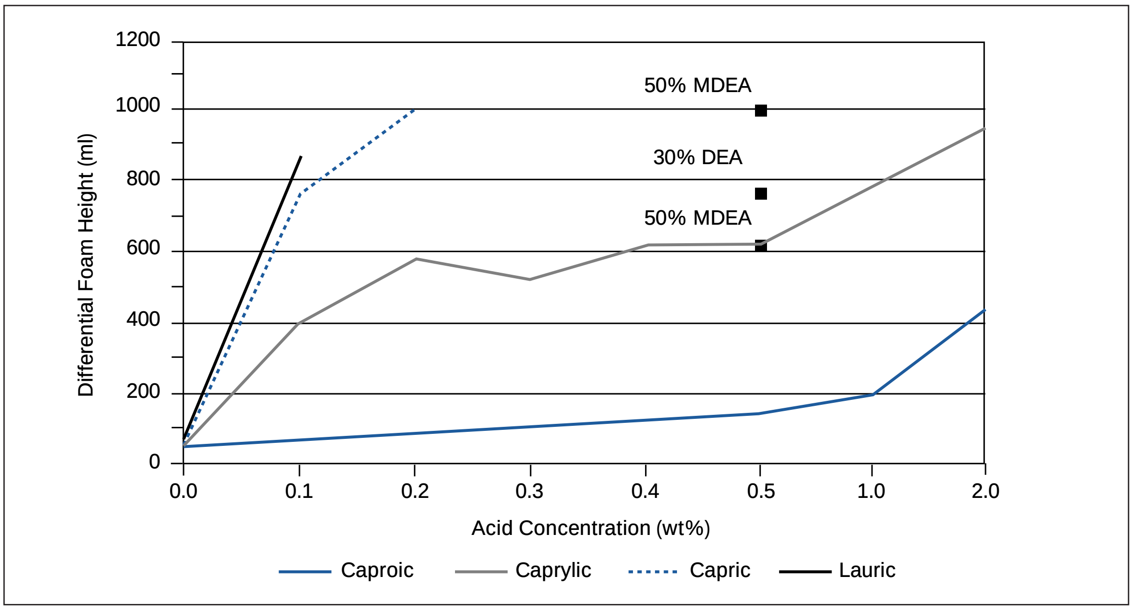


Figure 6A
Foaming Tendency of Contaminated Amine Solutions

20% MEA

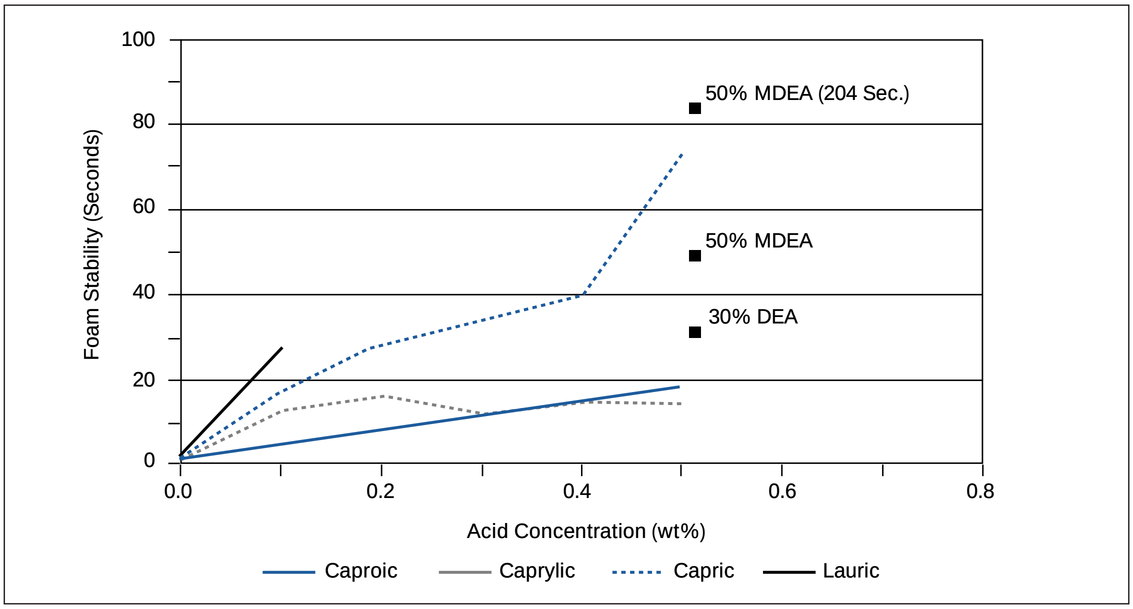


Figure 6B
Foam Stability of Contaminated Amine Solutions

20% MEA

The impact of carbon filtration on contaminated amine solutions was evaluated by filtering contaminated amines through activated carbon using the procedure described in Appendix A. The results are presented in Figures 7A and 7B. The data shows that some activated carbons are totally ineffective at removing foam promoting species.

Figure 7A
Effect of Carbon Filtration on Foaming Tendency

20% MEA Contaminated with 0.5% Caprylic Acid

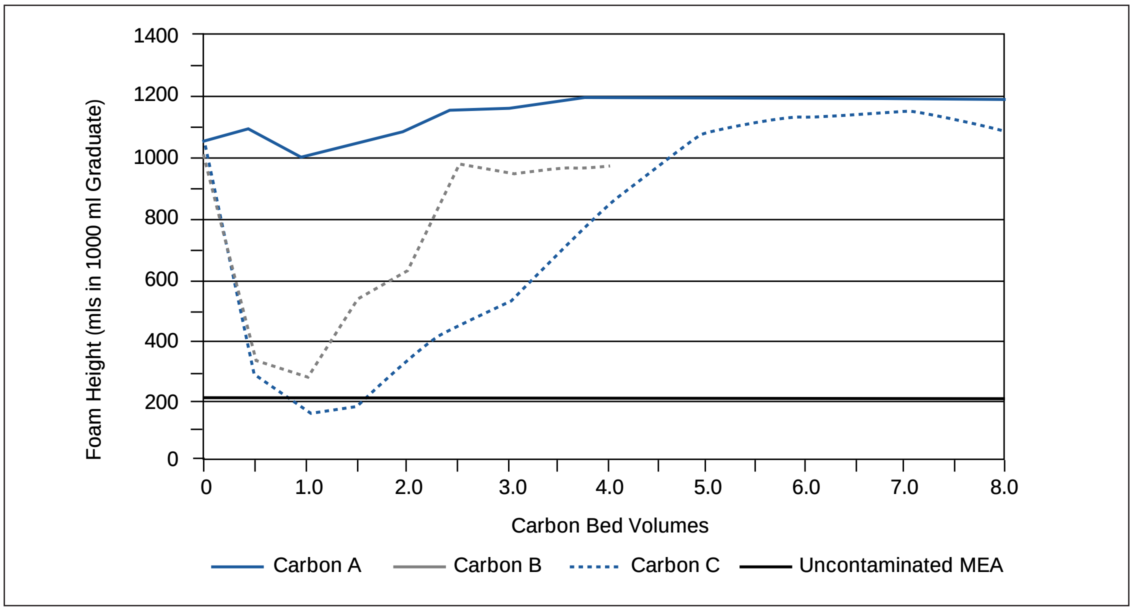
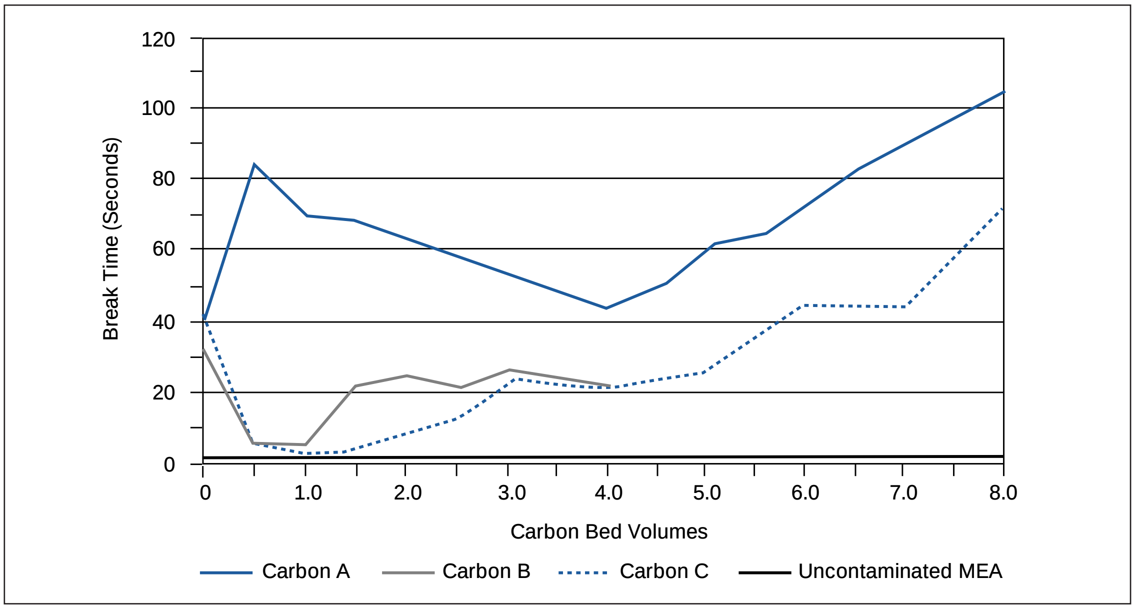


Figure 7B
Effect of Carbon Filtration and Foam Stability

20% MEA Contaminated with 0.5% Caprylic Acid



4.1 Contaminants

Pure amine solutions do not form stable foams. In order to form a stable foam, some other components must be present in the treating solution. There are two categories of contaminants, those contaminants which are added to the solution and those which are created within the solution. Added contaminants include liquid hydrocarbons, well treating fluids, antifoam agents, corrosion inhibitors, particulates, and lubricants in the form of aerosols. Contaminants created within the treating solution include basic and acidic amine degradation products, iron sulfide, and iron oxides (hydroxides). Each contaminant can have an impact on foaming tendency and foam stability.

4.2. Foam Stability as a Indication of Problematic Behavior

Foaming tendency alone is not a good indication of problematic foaming behavior. Foam stability must also be evaluated. For example, pure aqueous MDEA has a lower surface tension than the other amines and should have a greater foaming tendency (Figure 3). In fact, the opposite is true; pure aqueous MDEA has a lower foaming tendency (Figure 4A). However, the data appears to be consistent with the fact that additives increase foam stability (Figure 4B). Additives which are typically added to formulated MDEA to reduce surface tension actually increase foam stability. The subsequent addition of small quantities of liquid hydrocarbons or organic acids then have an enormously adverse effect on formulated MDEA solutions.

4.3. Factors Influencing Foam Stability

Foam stability is primarily dependent on the formation of a gelatinous layer and the addition of components which increase the surface viscosity and inhibit draining. Liquid hydrocarbons enhance the formation of gelatinous surface layers, but only enhance the solution's foaming tendency to the extent they are soluble in the solution. Small amounts of acidic amine degradation products both enhance the solution's foaming tendency and promote foam stability.

4.4. Effect of Contaminants on Foam Stability

The combination of certain contaminants can create a significant foaming problem in gas treating solutions. In order to limit foaming problems, it is necessary to remove contaminants from the inlet gas or to remove them from the treating solution. For example: Liquid hydrocarbons have a small effect on the foaming tendency of clean amine solutions, but significantly stabilize aqueous MDEA foam (Figure 4B). When both liquid hydrocarbon and organic acid are present in the treating solution, the foaming tendency and foam stability are enormously increased.

While antifoam agents reduce foaming tendency, they increase foam stability. Continued treatment with antifoamer will initially knock back the foam, but will make the solution sensitive to smaller amounts of foam promoters. The best remedy is to eliminate the need for antifoam agents by removing liquid hydrocarbons and other surface active materials from the inlet gas. Activated carbon should be used to remove amine degradation products. However, activated carbon is only effective when properly specified and monitored.

Particulates such as iron sulfide increase the surface viscosity and inhibit film drainage. Any gas stream which contains H_2S will eventually produce iron sulfide. The most effective way to eliminate this contaminant is with mechanical filtration.

4.5 Contaminant Removal

Several types of carbon were evaluated with respect to their ability to remove organic acids (Figures 7A and 7B). Based on the data, carbon with a high iodine number is more effective. (Iodine numbers are empirical values which denote the efficiency of carbon at adsorbing certain types of chemicals.) However, any activated carbon becomes ineffective when surface active compounds begin to breakthrough. A side stream reclaimer can be effective at removing some contaminants, but without a reclaimer activated carbon assumes the entire duty. Unfortunately, activated carbon will not remove every contaminant, particularly lower molecular weight organic acids. These acids tend to concentrate in the solution and will increase foam stability in high enough concentrations. Since secondary and tertiary amine processes preclude the use of a reclaimer, *effective* carbon and mechanical filtration are critically important in DEA and MDEA based processes.

The amount of carbon required and its effectiveness depends on the type and amount of contaminants to be removed. In this case, activated carbon should be selected on the basis of iodine number. A high iodine number is more effective at removing the type of compounds which promote and stabilize foam. Additives must be carefully evaluated when using activated carbon. Surface active additives will be adsorbed onto activated carbon and simply increase the carbon requirement.

Effective carbon filtration will also remove some particles. However, fine colloidal solids (e.g., iron sulfide) can pass through the bed while larger particles or aggregates will plug the bed. Cartridge filters are typically used on a side stream of the treating solution but have been used on full streams as well. These filters are supposed to remove solid contaminants from the liquid and also protect the carbon beds.

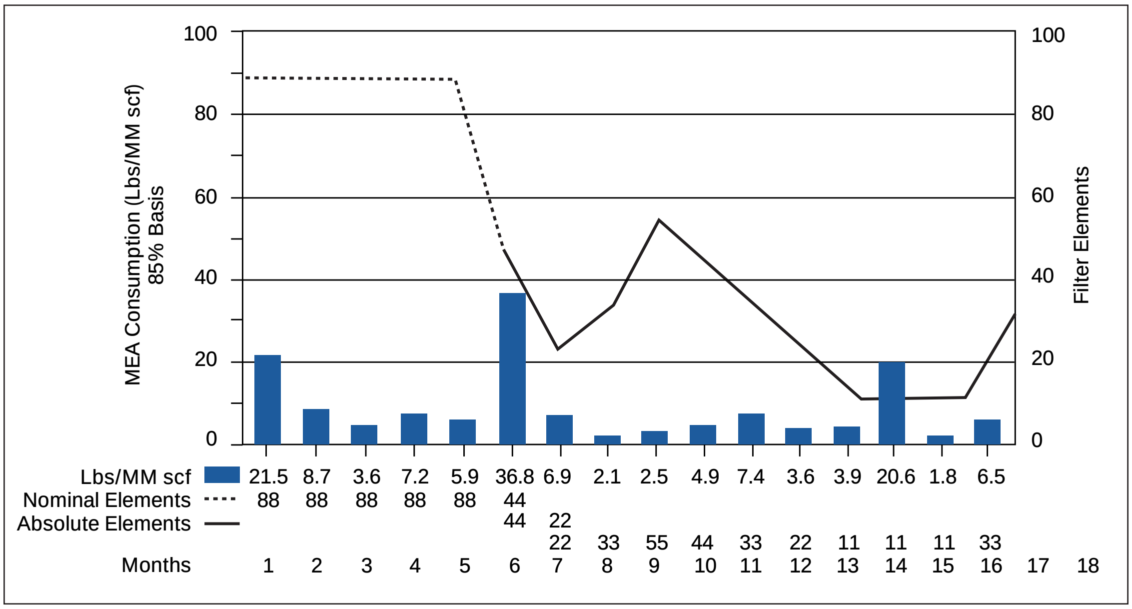
Not all cartridge filters are the same. Only selected cartridge filters can be efficient in gas plant liquid systems. Any filter will remove some contaminants, but it is the fine particles which must be removed in order to minimize surface viscosity. Nominal cartridge filters will pass such particles and are ineffective in foam control. Rather they remove the aggregates and larger solids, resulting in some apparent cleanliness. This apparent cleanliness is not necessarily a sign of troublefree operation. Colloidal particles will remain in the system and “over-contaminate” the solution which will ultimately increase surface viscosity and foam stability.

To maintain a clean system, the majority of the colloidal particles must be removed. Filtration at 0.5 micro absolute is required in order to assure sufficiently low levels of solids. Coarser filters (e.g., 10 or 20 micron absolute) are partially effective because they are also partially effective in submicron levels (Figure 2).

In a recent case study at a natural gas treating plan in Texas, 10 micron absolute filters effectively eliminated a persistent foaming problem.[7] The plant in question had experienced a persistent foaming problem in its MEA unit. The unit contained a full flow carbon filter and full flow mechanical filter. Nominal filter elements would plug frequently indicating that something was being removed, but the foaming problem persisted. Even fresh activated carbon gave little improvement. However, when the filters were replaced with 10 micron absolute elements, foaming was effectively eliminated. As a result, the amine carryover as gradually reduced (Figure 8).

Figure 8
Amine & Filter Element Consumption

27 MMSCFD
Texas Gas Plant



5.0 Conclusions

1.0 Clean amine solutions do not form stable foams.

2.0 Contaminants such as liquid hydrocarbons, well treating fluids, corrosion inhibitors, lubricants, acidic amine degradation products, and particulate matter promote the formation of foam, but more importantly stabilize foam.

3.0 Stable foams are the result of contaminants which promote the formation of a gelatinous layer, increase the surface viscosity, and inhibit drainage.

4.0 MDEA and formulated MDEA solutions tend to form quite stable foams when contaminated by small amounts of liquid hydrocarbons and organic acids.

5.0 Activated carbon can be effective at reducing foaming problems. Selection and timely replacement are important. Carbon should be selected on the basis of iodine number. A high iodine number is more effective. The carbon should be replaced when the foam stability (not foaming tendency) first begins to increase.

6.0 Additives must be carefully evaluated. The use of antifoamer should be considered a temporary treatment not a long-term solution. Surface active additives will be adsorbed onto activated carbon and simply increase the carbon requirement. Antifoam agents, which reduce the foaming tendency, can increase foam stability.

7.0 Liquid hydrocarbons play a significant role in the foaming mechanism due to their ability to promote gelatinous layer formation. A high efficiency liquid gas coalescing filter, installed ahead of the adsorber, is the most effective way to limit liquid hydrocarbon carryover into the process. (The size of liquid particles found in process gases are typically on the order of 0.1 to 0.6 microns.[8] Conventional inlet gas separators are not effective at removing liquid hydrocarbons which are less than 3 microns in size. [9, 10])

8.0 Iron sulfide, carbon fines, and colloidal iron oxides will increase the surface viscosity. Aggregates will increase the vapor rate which will retard film drainage. Fine particles can be effectively removed only by absolute rated cartridges. Experience indicates that ten (10) micron absolute is a minimum specification whereas the 0.5 micron absolute filters would provide maximum protection.

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7.0 Appendix A – Experimental Procedures and Apparatus

A.1 Determination of Foaming Tendency and Stability

Scope

This test is designed to determine the foaming tendency and resultant foam stability of pure liquids or mixtures.

Principle

Air is sparged through a measured amount of solution at a specified rate for a specified period. The difference between initial and final foam height is measured. The air is stopped and the time required for the foam to collapse is reported.

Apparatus

(1) 1,000 – 2,000 ml graduated cylinder.
(1) Gas flow meters, rated up to 5,000 ml/min.
(1) Sparger tube, either sintered glass or metal.
(1) Length of surgical rubber tubing to connect air source to flow meter and flow meter to sparger.
(1) Timer or stop watch.

Procedure

Step 1: Preset the flow meter to allow 4,000 ml/min. of air to sparge into the graduated cylinder.
Step 2: Pour 200 ml of TEST SOLUTION into the graduated cylinder, begin air flow, and start watch or timer.
Step 3: After five minutes, record the foam height then terminate air flow. Immediately reset and restart the stop watch or timer.
Step 4: Record the time required for the foam to break back to the initial level in the graduated cylinder.
Step 5: Thoroughly clean the graduated cylinder and sparger before reuse. Very small amounts of surfacant may affect the test.

Calculation & Data Handling

Report initial liquid level in milliliters, final foam height in milliliters, and break time in seconds.

A.2 Determination of Surface Tension

Surface tensions were determined at room temperature using a Fisher Surface Tensionmeter, Model 20. Apparent interfacial surface tension readings were obtained then corrected for the ring and wire used.

A.3 Determination of Carbon Efficiency

Scope

This test is designed to determine the efficiency of activated carbon at reducing foaming tendency and foam stability.

Principle

A surface active contaminant is added to an aqueous amine solution. The solution is filtered through a tube containing a measured amount of activated carbon. The effluent is caught in increments equal to the volume of carbon in the tube, i.e., bed volumes. Bed volume increments are subsequently analyzed for foaming characteristics.

Apparatus

(1) 6,000 ml reservoir and stirring device.
(1) Carbon bed: 2″ ID X 12″ L.
(1) Lobe pump calibrated to deliver 110 ml/min. of amine solution.
(1) Three way ball valve.
(1) Length of 1/4″ tygon tubing to connect reservoir, pump, ball valve, and carbon bed.
(1) Supply of 500 ml beakers.

Procedure

Step 1: Prepare a 5 liter solution while adding the ingredients to a reservoir. Begin mixing.
Step 2: Place a glass wool plug in the bottom of the carbon bed to support the carbon and charge the bed to the top and seal.
Step 3: Support the carbon bed and attach the tubing from the reservoir to the ball valve. Connect one port of the valve to the top of the carbon bed and the other port to return solution to the reservoir.
Step 4: Position the ball valve to return solution to the reservoir and establish flow. Check the flow rate calibration and catch a 300 ml sample. Mark it "0 bed volumes."
Step 5: Switch the valve to deliver solution to the carbon bed. When liquid flows from the bottom, catch the entire reservoir, 300 mls to a beaker. Label each beaker as successive one-half bed volume catches beginning with "0.5 bed volumes."
Step 6: Determine the foam height and break time of each sample using the procedure described in Section 3.1.

Calculation & Data Handling

Report initial liquid level in milliliters, final foam height in milliliters, and break time in seconds.

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New York - USA

888.873.7255 toll free in the USA
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+1 516 484 0364 fax
fuelsandChemicals@pall.com

Portsmouth - Europe

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