



Control of Foaming in Amine Systems

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ABSTRACT

Amine solutions foam. Solution foaming causes plant upsets. It is the “disengagement”, or break time that differentiates normal, desirable froth from undesirable foam. Plant upsets due to foaming require immediate mitigating actions. A variety of solution contaminants and operating conditions can cause froth to stabilize into foam. Mitigating actions include adding chemical antifoaming agents, altering operating conditions, and removing foam causative agents. A series of typical amine foaming incidents, causes, and plant responses are presented. The upsets and responses are explained in terms of root causative agents. This paper explains how removing the contaminants that stabilize the froth into foam is the only efficient way to control amine system foaming.

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INTRODUCTION

Any liquid will produce froth or foam if gas is introduced into the liquid faster than the two phases disengage. The “*disengagement*”, or “*break time*” differentiates froths from foams in amine treating processes. Free liquid captured between the gas bubbles begins to drain as the bubbles rise past the bulk gas – liquid interface. The free liquid will drain from around the gas bubble until the gas pressure inside the bubble is greater than the liquid wall’s surface or interfacial surface tension. At this point the bubble will either break or combine with other surrounding bubbles (coarsening). The more stable or elastic the bubble wall, the more resistant the bubble will be to breaking. If bubbles are being formed faster than the existing ones are breaking, they will accumulate as foam. When the formation and break time are equal, a stable foam column is formed. Anything chemical or environmental that affects free liquid drainage, or bubble wall elasticity will directly affect the resulting foam’s break time.

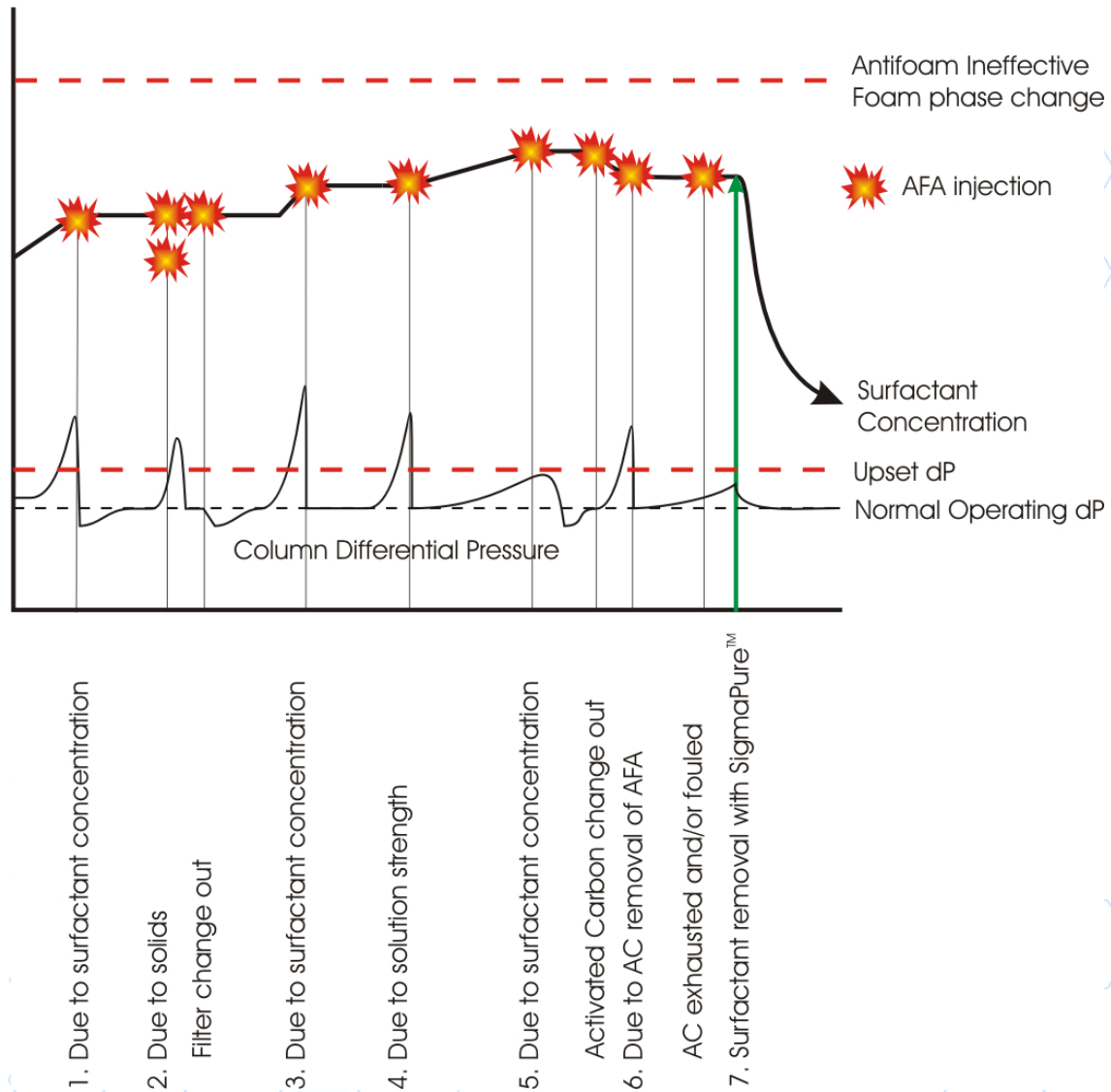
Amine process towers with trayed internals are especially prone to foaming upsets because they are designed to produce froth by violently bubbling gas through the treating solution contained on the trays. The bubble walls in the froth act as mass transfer area for the removal of the gas borne contaminants. The froth bubbles break quickly enough for the treating liquid to pass down to the next tray in the column before the gas flow is restricted. If anything increases the gas/liquid disengagement time, the froth will remain in the vapor space of the tray, and the gas flow will be restricted. This hydraulic restriction is detected as a differential pressure above and below the froth in the vapor space. This condition is described as solution foaming. A variety of solution contaminants and operating conditions can cause froth to stabilize into foam.

Since foaming in amine plants causes upsets, mitigation actions have been employed to avoid its formation. The first mitigation action is normally the addition of chemical antifoam. Antifoams are intended to facilitate gas and liquid disengagement by weakening the cell structure of the bubbles. Antifoams have no positive contaminant removal properties. The injection of these chemicals into recirculating amine solutions is common, and even regarded as necessary for normal plant operation.

This paper describes a series typical amine foaming incidents, causes, and plant responses; all with respect to the effects on the root causative agents. We also present a new strategy for actually addressing amine solution foaming: causative agent removal.

Controlling Amine Plant Foaming

Figure 1 Typical amine plant foaming upsets and responses



1. An experienced control room operator noticed that the differential pressure across one of the columns began to fluctuate. The operator's first thought was *solution foaming* so a request was radioed to the unit's outside operator to inject a chemical antifoaming agent into the recirculating amine solution. The system differential pressure dropped to below the normal operating level within minutes. The operator watched the differential pressure slowly rise back to normal and stabilize over a few hours. The AFA (antifoaming agent) injection was noted in the daily log, and the incident forgotten.

This common scenario is played out in amine plants every day. A foaming upset was averted. Notice that the surfactant concentration remained unchanged with the addition

of antifoaming chemicals. Adding antifoam to the system broke the foam, but had no effect on the surfactants dissolved in the solution. At this point the foaming tendency of the solution is in equilibrium with the solution's antifoam concentration. If the foaming tendency of the solution should increase even slightly the solution will foam again.

2. A few hours later the operator noticed the differential pressure beginning to rise again. There are a variety of contaminants and operating conditions that can cause the solution to start foaming again since there is an existing concentration of surfactants in the solution. Injecting more antifoam didn't have an immediate effect so the operator decided to shoot the plant again, and have the mechanical filters changed out. Antifoam was becoming less effective. (See, *Why does antifoam appear to become less effective over time?*)

Changing filters affects solution foaming in both positively and negatively. First, solids increase the solution's tendency to foam by inhibiting liquid from draining from the foam structure. The foam stays wet longer. Antifoam droplets can't incorporate into the foam bubbles' walls unless they are squeezed between two bubbles that have drained. In other words, antifoam can't work if the foam stays wet. (See, *How does froth turn into foam?*) Mechanical filters can also make antifoams less effective by coalescing the small AFA droplets into larger ones, or removing it completely from the flow stream.

In this case, the surfactant concentration of the solution did not increase before the foaming upset started. Solids affected the foaming tendency of the solution by increasing the stability of the froth, but also by disarming the AFA through agglomeration. Small solids suspended in the solution will stick to the AFA bubbles. The antifoam becomes increasingly less effective as solid particles are agglomerated with it. These AFA-solids agglomerates also prematurely plug mechanical filters and activated carbon beds.

It is not uncommon for antifoam to be injected after changing filters just to make sure the unit doesn't start foaming due to the changeout. In this case, the board operator noticed that the differential pressure across the column dropped below normal after the filter changeout. However, there was no correlation made between the antifoam injection and lower than normal operating differential pressure. Antifoams have the same affect on normal froth as they do on foam (stable froth). An over injection of AFA can affect the towers ability to generate froth mass transfer area.

3. The differential pressure beginning to rise again. An upset had been reported in an upstream unit which sent some surfactant containing liquids into the amine plant. Contaminating surfactants either form in the amine naturally due to degradation or ingress from outside the process. Most extraneous surfactants come in with the gas to be treated, or in make up components. An antifoam injection had to be made to maintain the equilibrium with the solution's foaming tendency.

4. Make up water was being added through the reflux drum to the regenerator. The amine solution strength went down to a point where the solution began to foam. Amine

solution strength appears to affect foaming in two ways. Lower strength solutions have higher surface tensions which do not favor foaming. However, higher water content can increase the solution solvency which can increase its surfactant concentration which favors foaming. Foaming due to higher water concentration normally involves a second less soluble contaminant that contains surfactants, like some liquid hydrocarbons. The insoluble fraction of the hydrocarbon acts like a weak antifoam. Any amine soluble fractions in the contaminating hydrocarbon increase the solution's surfactant concentration.

Higher strength solutions have higher viscosities which inhibit foam drainage, and therefore favor foaming.

5. The solution's surfactant concentration was slowly increasing naturally, but was now accelerated due to the hydrocarbon ingress from the upstream process upset. The equilibrium between the foam causing surfactants and the foam breaking antifoam was imbalanced, so another AFA shot had to be made.

6. Lab analyses confirmed the presence of liquid hydrocarbon contamination. The activated carbon obviously needed to be changed out. Like mechanical filters changes, some plants have learned to inject AFA after a carbon change out. Shortly after the activated carbon changeout, the differential pressure started to rise again.

Activated carbon is a remarkable substance. Its primary purpose in most non-amine process applications is to adsorb dissolved organic molecules. Its use in treating amine solutions should be no different. It is also generally used in a fixed bed format. Like most fixed bed media; i.e., catalysts, sand, ion exchange, etc., activated carbon is notoriously good at mechanically removing particles; including bubbles of insoluble antifoam and antifoam-solids agglomerates. In this case, the activated carbon removed a small amount of antifoam, so the solution began to foam again. It could also have been that the bed wasn't rinsed well enough, and small carbon solids agglomerated enough of the antifoam to create the imbalance in foaming equilibrium, or the fine carbon particles collected in the froth, stabilizing it into foam. It may have been a combination of all three.

Many of the surfactants that cause foaming in amine solutions are adsorbed by activated carbon. However, many are not. Activated carbon prefers some organics more than others, and will adsorb one species until something it likes better comes along. It is known to selectively desorb previously adsorbed compounds when this happens. This fact makes activated carbon a good general solution maintenance device, but not reliable for controlling amine solution foaming.

7. The column's differential pressure began to increase slowly. Plant operations had been injecting AFA, changed filters, and changed the activated carbon. It was becoming increasingly more difficult to maintain the plant's stable operation so it was decided to try something new. The device was installed which removed foam causing contaminants

from a slip stream off of the recirculating amine stream. Operations was instructed to add antifoam only on an “as needed” basis. The plant’s operating differential pressure remained at normal, and no antifoam was injected as long as the device was on line.

There is only one way to effectively treat against, or control amine plant foaming, and that is to remove the foam causing surfactants from the solution. Eliminating surfactant ingress to the plant is not practical, and is not sufficient because surfactants may be a natural byproduct of amine degradation.

The only method currently available that removes surfactants from a recirculating amine stream, is not solvent or contaminant specific, and generates little waste, is the SigmaPure™ process. This method only requires that the solution have a slight tendency to foam. In fact, the plant does not even have to be experiencing foaming symptoms for this method to work. SigmaPure™ is not sensitive to the type of surfactant or solvent, does not require pretreatment, or the use disposables of any kind, i.e., mechanical filters, carbon, or chemicals. SigmaPure™ removes the foam causing and stabilizing agents without affecting the solution’s non-foam causing fractions.

FREQUENT FOAM CONTROL QUESTIONS

Why does antifoam appear to become less effective over time?

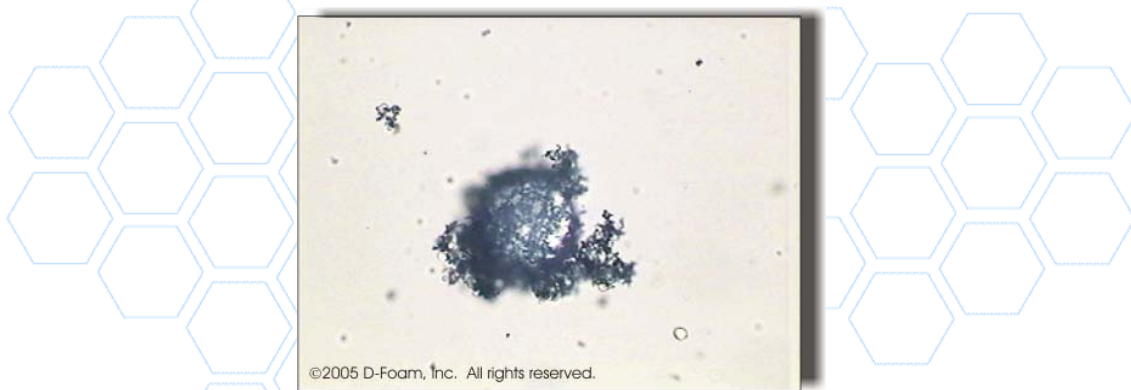
When operators have to inject antifoaming chemicals into a recirculating amine solution, it almost always has to be used again in the near future. Antifoams are not soluble chemicals. They do not become part of the amine solution, but rather are suspended as immiscible droplets or bubbles. They have to remain in suspension to be effective. (See also, *How does froth turn into foam*)?

Antifoams may become ineffective in a variety of ways. First and probably most common is their removal. Activated carbon and tight mechanical filters can remove antifoam from the amine stream. Even more open mechanical filters become more efficient as they plug, and may remove or coalesce AFA. Antifoam may not be completely removed by the filters. The larger droplets may extrude through the filters due to the differential pressure after the coalescence of many smaller 1-10 micron droplets.

Second, AFA droplets will coalesce with each other as they touch, particularly at high concentrations. This is especially true at higher regenerator temperatures. Once coalesced into larger droplets they are incorporated into the foam structure less efficiently, thus are less effective at breaking foam. Mechanical filters tighter than 25 microns can easily coalesce the more viscous antifoam bubbles suspended in the amine solution. Silicone antifoams are especially sensitive to becoming inactive due to concentration and coalescence, even on the micelle level.

Third, antifoams are also known to become ineffective due to agglomeration with suspended solids. These antifoam/solids agglomerates not only inactivate antifoam, but also prematurely plug activated carbon beds and mechanical filters.

Figure 2 Antifoam - solids agglomeration



How does froth turn into foam?

The tendency for a solution to produce foam is a complex function of chemistry and environment. Surface active chemical compounds (surfactants) naturally adsorb to gas/liquid interfaces due to polar and non-polar chemical groups at each end of the molecule. *See figure 3.* If present in the amine solution, surfactant molecules adsorb to the gas bubbles as they pass through solution. *See figure 4.* Their presence at the gas/liquid interface changes the surface properties of the interface. Surfactants reduce the surface tension, and increase the elasticity of the amine solution/gas interface; thereby producing a more stable interface than an uncontaminated amine solution of the same chemistry and strength.

Foam becomes more stable with bubble wall thickness. This means that anything; chemical or environmental, that inhibits liquid draining from the walls increases its stability. Increases in surfactant species and concentration chemically stabilize foams. Increases in solution viscosity inhibit drainage; therefore increase stability. Small solid particles produce local pools of liquid in the cell walls, and increase solution viscosity, therefore, also increase bubble stability. Lower solution sensible heat favors increased viscosity, therefore, stability. In the case of amines, higher solution concentration favors stability. System temperature and solution strength probably affect solution solvency more than the viscosity effects. This is especially true if mixed solubility contaminants like liquid hydrocarbon are present.

Surfactants may enter recirculating amine systems in two ways. First, they can be generated by amine degradation, i.e., organic acids. Surfactants may also enter with fluids like feed gas, make up water, and chemical additives. Regardless of how they enter, surfactants are responsible for turning froth into foam.

Figure 3 Surfactant molecules stabilize froth into foam by coating the gas – liquid interface.

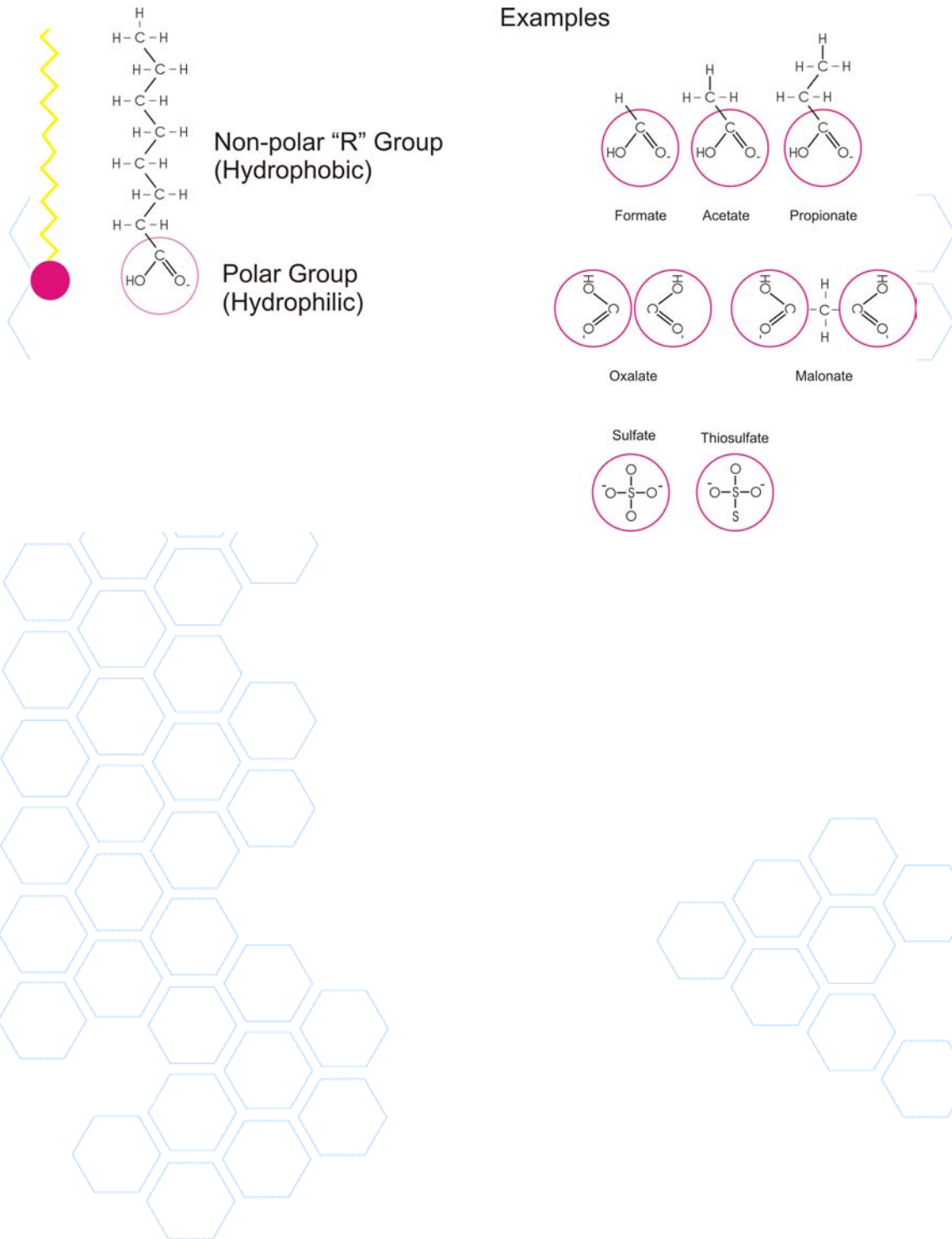
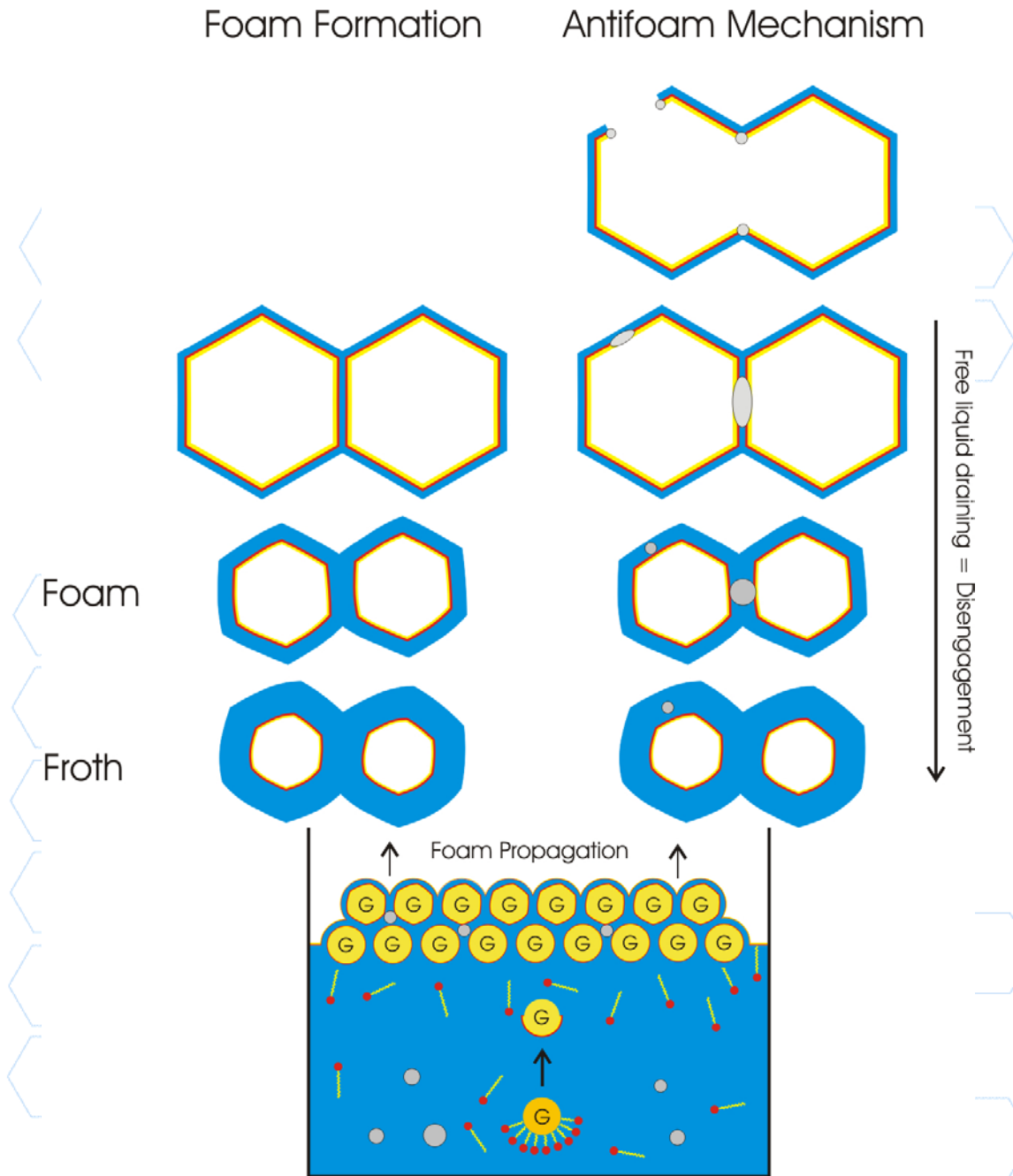


Figure 4 Foam formation by surfactants and antifoam mechanism.



What are the most common foaming symptoms?

Diagnosing process foaming can be difficult because some hardware problems yield the same symptoms. The two most common symptoms of amine process foaming are column differential pressure (*see figure 5*), and liquid level fluctuations in column bottoms and reboiler (*See figure 6*).

Think of foam in an operating column as a sponge. Gas will pass through a dry sponge with little restriction to flow. Dry sponges are also hydroscopic (love water). When liquid touches them it is absorbed, and the sponge swells. As the sponge absorbs liquid it also becomes more resistant to gas flow.

Figure 5A depicts a normal trayed column with free and frothy liquid on the trays. Gas flow direction is shown by the arrow. A normal operating differential pressure is created as the gas is forced up through the liquid on the tray. The normal differential pressure magnitude is shown by the wave in the gas flow line.

During normal operation (see *figure 5A*), froth is produced as the gas passes through the free liquid on the tray. The froth volume is greater than the free liquid alone, so it spills over the tray weir into the downcomer. This is normal froth height. Froth disengages into its gas and liquid fractions within 1-2 seconds, so most of the liquid entering the down comer is free liquid. The same is true of the gas fraction passing into the vapor space and next tray. There is some normal liquid entrainment in the gas produced by bubble wall fragments from breaking froth bubbles.

If the froth bubbles fail to disengage the froth height will increase farther into the vapor space. *Figure 5B* shows how froth height and disengagement rate (break time) relate to the level in the vapor space. As the froth height increases with break time, liquid entrainment in the gas flowing to the next tray increases. The froth's restriction of gas flow also increases as shown by the gas flow arrow.

The froth's density increases with volume due to liquid hold up between the froth bubbles. The liquid flow through the column will begin to hold up in the froth; thereby affecting the liquid level at the bottom of the column. At this point, the froth is converting into foam. If the gas – liquid disengagement time of the froth is longer than 3-5 seconds it will begin stacking up in downcomer. The differential pressure across the column will continue to go up, and the bottoms inventory goes down as the froth's disengagement time increases. It has been the authors' experiences that amine solutions which produce froth disengagement times greater than 20 seconds under laboratory test conditions produce upset level foaming conditions in most amine columns.

Figure 5C represents severe foaming upset conditions in an amine process column. The differential pressure across the column is several inches of water higher than normal. The vapor space above the trays is almost completely filled with foam, holding substantial amount of liquid. The column's bottom inventory of free liquid is reduced, but may, in fact, be high density wet foam rather than gas free liquid. If the level indicator is based on fluid density it will show low liquid level. See *figure 6*. In some cases, pumps located down stream of the column may also show signs of cavitation.

Figure 5 Tower foaming, differential pressure and liquid level flux

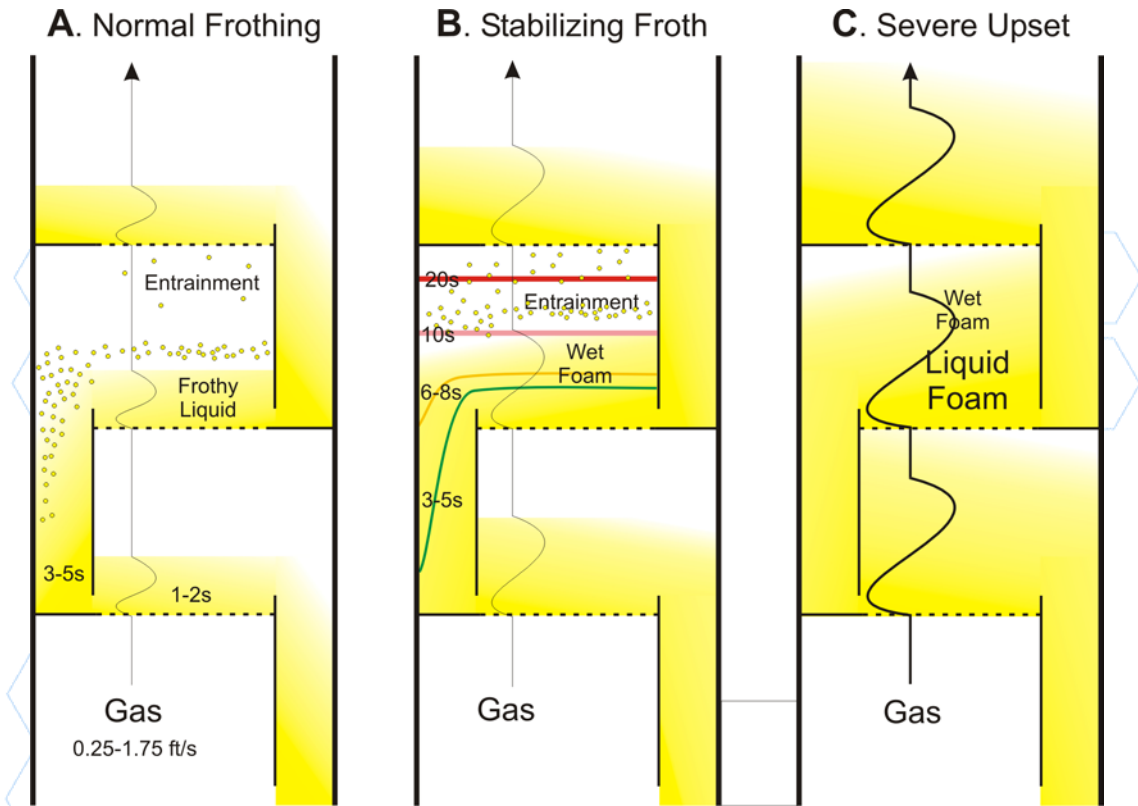
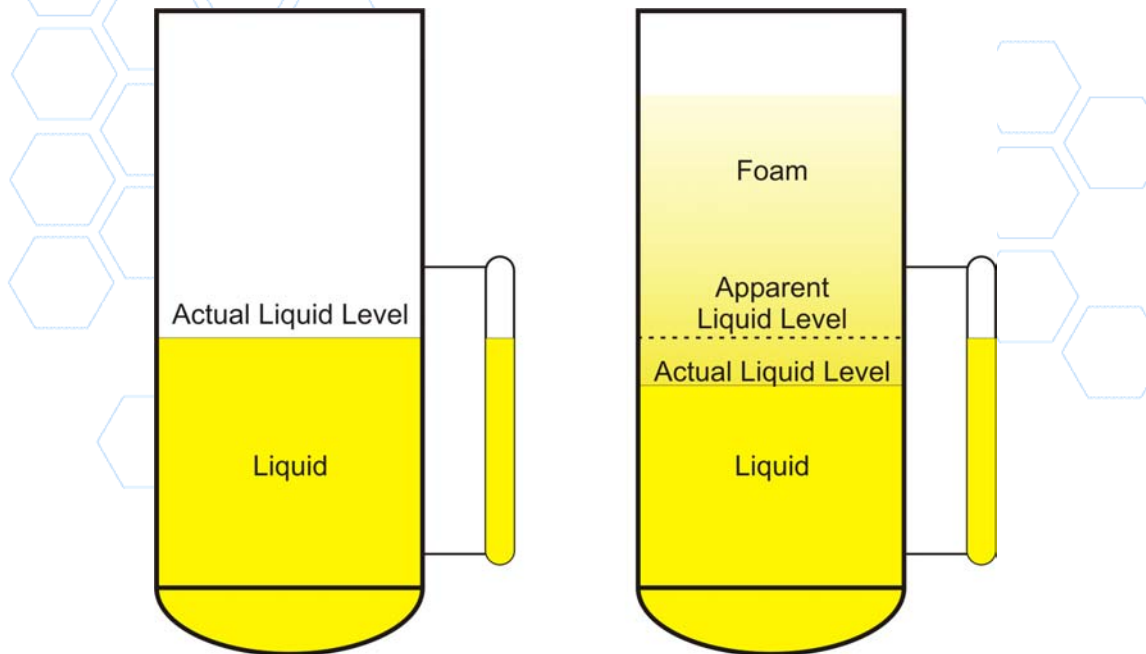


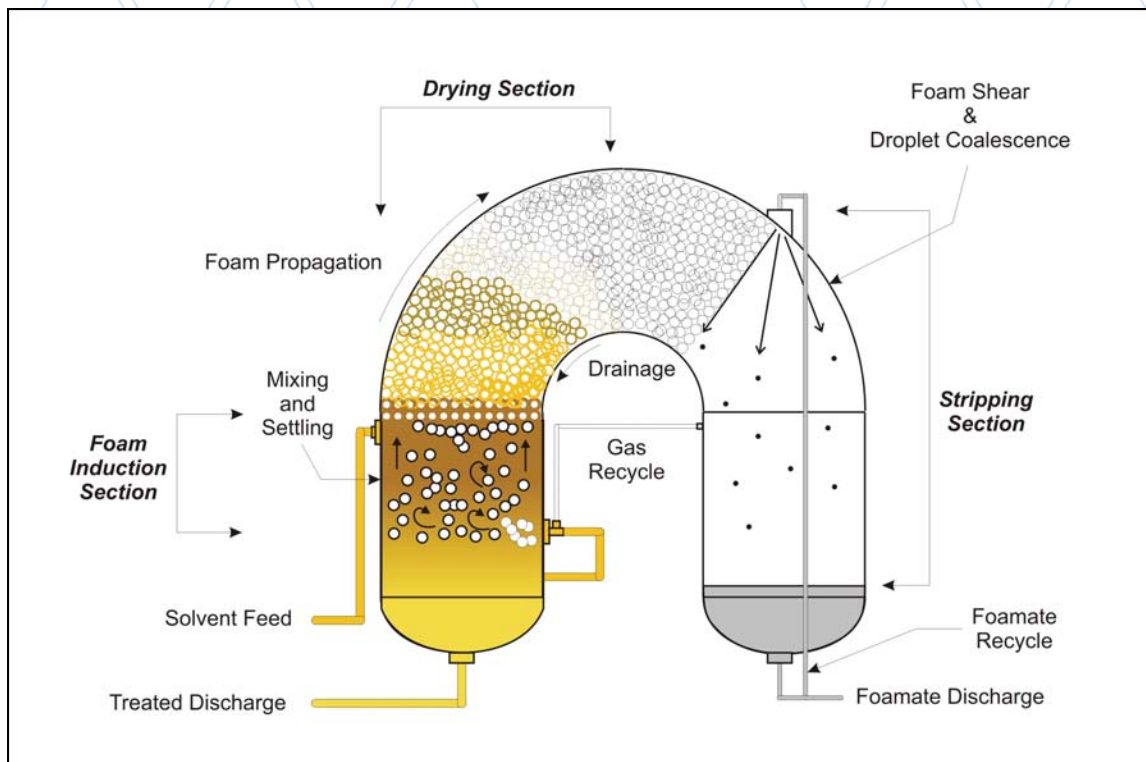
Figure 6 Solution foaming and liquid level fluctuation



Removal of Foam Causing Agents from Amine Systems

The SigmaPure™ process controls amine foaming by taking advantage of the fact that the causative agents of foaming are incorporated in the foam's structure. Thus, if the amine is made to foam and the foam separated from the solution, the contaminants that caused or enhanced the foaming are also removed. (See *figure 7* below)

Figure 7 SigmaPure™ process for amine foaming control



A slipstream of the recirculating amine stream is pumped into the SigmaPure™ process's foaming column (shown on the left). Non oxidizing gas is injected into the solution to adsorb soluble contaminating surfactants, and carry them to the bulk gas/liquid interface. The surfactants are incorporated in the foam above the gas/liquid interface, and removed from the bulk solution as it propagates up into the drying section. Free liquid drains from the foam as it moves through the drying section and into stripping section of the process. The gas and liquid fractions of the foam are separated by breaking the foam with a stripping spray (normally make up water). The foam causing contaminants contained in the liquid fraction of the foam are coalesced with the stripping spray and collected as foamate waste, while the gas fraction of the foam is recycled back to the foaming column for reuse.

This process has been successfully used to control foaming in a variety of hydrocarbon sweetening process worldwide. These processes include: LNG, Natural Gas, Refining; and Chemical plants. Further, it has been used to control foaming in a wide variety of sweetening solvent solutions which include: DEA, MDEA, DGA®, DIPA, and

FLEXSORB®. The SigmaPure™ process is not plant, process, or solution specific. Further, use of the SigmaPure™ process has not been found to negatively affect the sweetening solutions in any way. If the solution can be made to foam, it can be controlled with this portable process.

Conclusion

Amine solutions foam because normal froth is stabilized into foam by contaminating surfactants. The most common way to control foaming has been injecting antifoaming chemicals into the recirculating solution stream to break the foam. The efficiency of antifoams can be reduced in a variety of ways; therefore, are unreliable as a long term control solution. The only way to actually control amine foaming over the long term is to remove the foam causing surfactants. The SigmaPure process is a proven way to remove foam causing surfactants from operating amine systems.

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