



Control of Foam Formation in the Amine Gas Treating System

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Abstract: Acid gas removal by using amine gas treating system is an essential part of processes, such as coal gasification where carbon dioxide, hydrogen sulphide, carbonyl sulphides, and other contaminants need to be removed. Foaming in amine plants increases operating costs and reduces treating efficiency. Plant upsets due to foaming require immediate mitigating actions. Amine solutions foam because normal froth is stabilized into foam by contaminating surfactants. 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. Possible contaminants include not only liquid hydrocarbons and iron sulphide, but well treating fluids, amine degradation products, and other finely divided solids. The objective of controlling foaming should be to minimize level of contaminants in the amine solution. This seminar report explains how removing the foam and describes a series typical amine foaming incidents, causes, and plant responses; all with respect to the effects on the root causative agents. The most common way to control foaming has been injecting antifoaming chemicals into the recirculating solution stream to break the foam. This report will discuss the foaming problematic in chemical absorption plants.

Keywords: Amine system, foaming, plant response, foam removing.

I. INTRODUCTION

Amine gas treating, also known as amine scrubbing, gas sweetening and acid gas removal, refers to a group of processes that use aqueous solutions of various alkyl amines to remove hydrogen sulphide (H₂S) and carbon dioxide (CO₂) from gases.

During operation of an amine unit, degradation of the solvent occurs due to reaction with contaminants like oxygen, sulphur dioxide, and acids in the feed gas. Some of the tertiary amine oxidation products lead to a number of operational problems in the amine units. Amine gas treating may face problems with solvent degradation for many reasons including conditions that permit inlet contaminants. In this report, we will describe acid gas cleaning by foaming control with emphasis of the use of antifoaming methods. It provide detailed review of Foaming in amine plants causes upsets, mitigation actions have been employed to avoid its formation.^[1]

A. Amine Gas Treating System

Amine gas treating, also known as amine scrubbing, gas sweetening and acid gas removal. It is a common unit process used in refineries, and is also used in petrochemical plants, natural gas processing plants and other industries.

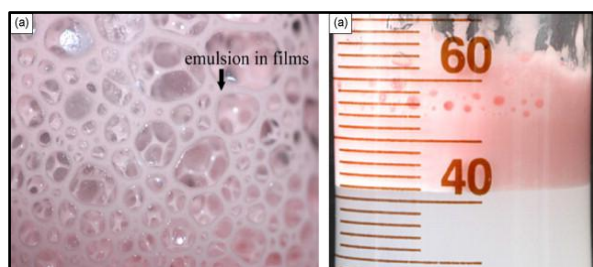
Amine has a natural affinity for both CO₂ and H₂S allowing this to be a very efficient and effective removal process.

B. Foaming

Foam is a substance that is formed by trapping pockets of gas in a liquid or solid. A bath sponge and the head on a glass of beer are examples of foams. Foaming continues to occur in amine facilities because various factors induce foaming. High capital losses occur annually due to foaming in systems. Such losses derive from the temporary loss of sour-gas processing capability and hence a reduction in sales and fuel-gas production, solvent loss of environmental regulations. Continuous antifoam injection has been the most common method to suppress foaming. Although use of antifoam injection is well known and documented, it is only recommended as a last resort and then only intermittently.

C. Foaming in amine systems

Foaming in alkanolamine solutions is the most common problem in these Liquefaction plants. Mostly it occurs in the absorber, can also be observed in the stripper. Impurities in the feed gas such as hydrocarbon liquid, organic acids, well chemicals, foam reducing agents and amine degradation products all have an effect on the ability for the amine to foam. Pure amine solutions do not form stable foams. In order to form stable foam, some other components must be present in the treatment solution. There are two Categories of contaminants, those that are added to the solution, and those that are formed within the solution. Each contaminant can have an impact on foaming tendency and foaming stability.^[11]

Fig. 1. Foam structure^[13]Fig. 2. Picture of foam formation^[11]

II. LITERATURE REVIEW

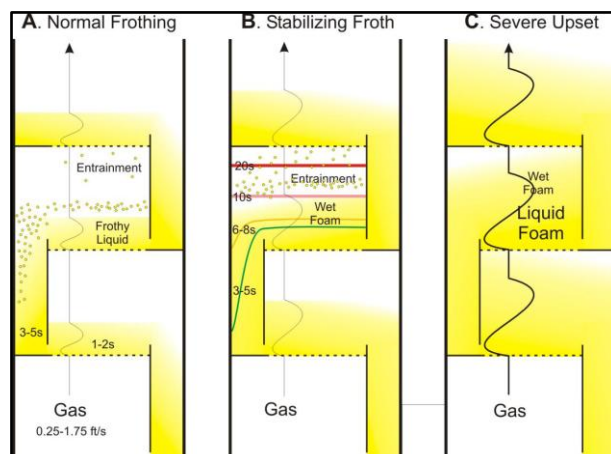
Foaming experiment has been conducted by testing three parameters, which are effect of solution temperature, effect of solution concentration and effect of impurities. Foaming is one of the famous problems that widely encountered in gas treating plants and gas absorption process as a result from process using aqueous alkanolamine solutions. Foaming has been seen negatively since its presence will lead to serious impact to industrial plant such as loss of absorption capacity, reduced mass transfer area and efficiency also carryover of amine solution to the downstream plant.

Based on plant experience, foaming usually occurs during plant start-up and operation in both absorber and regenerator. From previous study regarding research of foaming in amine solution which have been published, in 1989 Pauley found that the effect of hydrocarbon and organic acids on the foaming tendency of monoethanolamine (MEA), methyldiethanolamine (MDEA), diethanolamine (DEA) and formulated MDEA. During 1989 to 2007 scientists had studied that, in general, foaming is caused by various chemical contaminants such as suspended solids, condensed hydrocarbons, amine-degradation products, foreign matter from corrosion inhibitors, from grease or from contaminants in the water, fine particulates like iron sulphide and additives containing surface active chemicals. Such a way to prevent or reduce the foaminess problem many measures have been applied including mechanical filtration, carbon adsorption, solution distillation and antifoam addition.

III. FOAMING SYMPTOMS

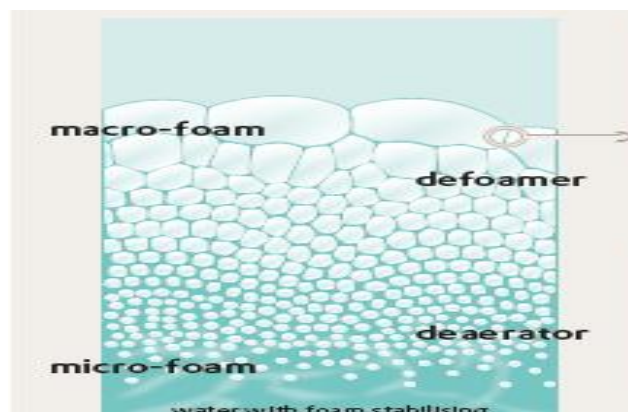
An amine system subjected to foaming exhibits the following behaviour:

- Sudden increase in the column's differential pressure.
- Foaming reduces the vapour-liquid contact area, generating a reduced effective mass-transfer zone and hence less acid gas is picked up by the amine. Unexpectedly high H₂S content indicates possible foaming.
- Amine carryover to downstream equipment.
- Loss or reduction in the rich-amine flow rate is accompanied by an abnormal level indication in the absorber column's bottom section.
- Abnormal absorber column's temperature profile can be another indicator. During foaming, the bulge temperature normally shifts from the lower trays to the upper trays, if foaming was caused by contaminated sour gas.

Fig. 3. Tower foaming, differential pressure and liquid level flux^[9]

A. Foam Stability

Drainage would be expected to completely remove the water from foam lamellas which would then collapse on their own accord. In practice, drainage comes to a halt when loss of liquid in the lamellas causes the surfactant concentration to be so high that electrostatic repulsion forces between the surfactant molecules prevent further retraction of the lamella walls. The foam lamella attains a thermodynamically stable state of equilibrium between

Fig. 4. Stabilization of the lamella by surfactants^[15]



drainage and amphiphilic molecule foam lamella micro-foam de-aerator de-foamer macro-foam hydrophobic hydrophilic water with foam stabilizing interfacial region ~ 1 nm substances gas liquid ~10 ... 100nm foam lamella.

B. Prevention of foaming

- Problems with foaming can usually be minimize by limiting the external pollutants like oil from compressors, well chemicals and rust inhibitors entering the system.
- A combination of a slug catcher, inlet filter/separator, and a gas-liquid coalesce installed in a series in the feed gas line is the best way to prevent external contaminants from entering the system.
- Conventional separator have difficulty removing aerosols 3 microns or less in diameter, while specialized high-efficiency gas-liquid coalesces can remove compressor lubricating oil droplets as small as 0.001 micron^[10]
- Amine contactors and regenerators should be supplied with a differential pressure indication and alarm to provide an early warning of foaming problems.

IV. METHODS AND MATERIALS

A. Antifoams

A common method of foam destruction is the addition of chemical antifoaming agents. Antifoam or an anti-foaming agent or de-foamer is a chemical additive that reduces and hinders the formation of foam in industrial process liquids. Commonly used agents are insoluble oils, poly-dimethyl silanes and other silicones, certain alcohols, stearates and glycols. The additive is used to prevent formation of foam or is added to break a foam already formed. Many types of antifoams are commercially available with a range of properties and varied foam destruction efficiency.

Types of antifoams:

- Oil based antifoams
- Water based antifoams
- Silicone based antifoams
- EO / PO based antifoams
- Alkyl poly acrylates

1. Properties of antifoams:

- Antifoams are insoluble in the foaming medium and has surface active properties.
- Antifoam product is a low viscosity and a facility to spread rapidly on foamy surfaces.
- It has affinity to the air-liquid surfaces where it destabilizes the foam lamellas. This causes rupture of the air bubbles and breakdown of surface foam.
- Entrained air bubbles are collect, and the larger bubbles rise to the surface of the bulk liquid more quickly.

2. Behaviour of antifoams

As already described, antifoams work by penetrating and destroying the foam lamellas. The first barrier to be

overcome when penetrating is the pseudo emulsion film. This is a thin liquid lamella between the rising antifoam droplet and the liquid surface. If the pseudo emulsion film is too stable, antifoam droplet cannot penetrate the surface and de-foaming is not possible. Once the antifoam droplet has overcome the pseudo emulsion film and penetrated the lamella. It describes the force equilibrium between the three phases the liquid to be de-foamed, antifoam and air. The antifoam droplet may spread after penetrating the lamella. If the antifoam can spread on the surface, it forms an antifoam lens at the lamella surface and displaces the surfactants at this location. As a result, the stability and flexibility of the lamella are impaired and it may collapse. The spreading process leads to flow of the lamella liquid along the direction of spreading. This phenomenon, also known as Marangoni flow, causes a local thinning of the lamella at the location of the spreading antifoam droplet and leads to further destabilization of the lamella. The penetration and spreading of antifoam droplet is illustrated.

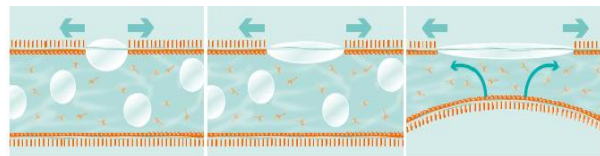


Figure 5: Penetration and spreading of the active ingredient of the antifoam^[15]

If the antifoam droplet has penetrated both sides of the lamella, a subsequent dewetting or stretching mechanism can lead to rupture of the lamella.

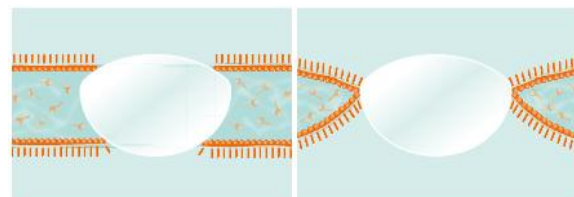


Figure 6: Film bridging during de-foaming^[15]



Figure 7: De-wetting during de-foaming^[15]

B. Equipment required for amine process

1. Feed gas separator

Before entering the absorber gas is pass through an inlet separator where entrained droplets or sludge of liquid are removed from the gas stream by impaction devices. Baffles remove a portion of liquids. Mist eliminator pads located near the gas outlet of the tank, trap the rest. Typical contaminates in natural gas streams may be liquid hydrocarbons salt water, sand well treating compounds, pipeline treating chemicals and compressor oils.



2. Tray tower absorber

The sour gas, freed of entrained liquids by the inlet separator, enter the bottom of the absorber. Usually the absorber is a tray column; although packed columns are also used. In either case, the objectives is to provide

intimate contact between the gas and the amine solvent so that the H₂S and CO₂ molecules can transfer from the gas phase to the solvent liquid phase. In tray columns, a liquid level is maintained on each tray by a weir usually 2 or 3 inches high.

Table No. I Physical properties of absorber column working^[14]

	Chemical Absorption		Physical Solvent Absorption
	Alkanolamine	Inorganic Carbonate	
Types of absorbents	MEA, DEA, DGA, MDEA, DIPA	K ₂ CO ₃ , K ₂ CO ₃ -MEA, K ₂ CO ₃ -DEA	Selexol, Rectisol, Purisol
CO ₂ absorption mechanism	Chemical reaction CO ₂ : 2RNH ₂ +CO ₂ +H ₂ O↔(RNH ₃) ₂ CO ₃ (RNH ₃) ₂ CO ₃ +CO ₂ +H ₂ O↔2RNH ₃ HCO ₃	Chemical reaction CO ₂ : Na ₂ CO ₃ +CO ₂ +H ₂ O↔2NaHCO ₃	Physical dissolution
Operating gauge pressure, mmHg	Insensitive to pressure	>10,337.76	12,922.2-51,688
Operating Temp., °C	37.78-204.44	93.33-121.11	Ambient temperature
Swing variables (temp. or pressure)	Temperature principally	Both, but pressure principally	pressure principally
Absorbent recovery	Reboiled stripper	Stripper	Flash, reboiler or steam stripper
Meets ppmv CO ₂	Yes	Yes	Yes
Selectivity CO ₂ Vs H ₂ S	Only MDEA selective for H ₂ S	May be selective for H ₂ S	Some selectivity for H ₂ S
Utility cost	High	Medium	Low to medium

3. Flash tank

In many unit the rich amine solution is sent from the absorber to a flash skimmer tank to recover hydrocarbons that may have dissolved or condensed in the amine solution in the absorber. The pressure of the solution is dropped as it enter the tank, allowing the lightest of the hydrocarbons to flash. The heavier hydrocarbons remain as a liquid, but separate from the aqueous amine, forming a separate liquid layer.

4. Heat exchanger

The rich solvent is preheated before entering the stripper. Because the lean amine exiting the re-boiler must be cooled before entering the absorber, there is an opportunity to exchange heat from the lean to the rich stream, thereby reducing the heat load on the re-boiler. This is usually done in a shell and tube lean rich heat exchanger with the rich solvent passed through the tubes, which are usually made of stainless steel.

5. Regenerator/stripper

Like the absorber, the stripper is either a tray or packed column with approximately 20 trays or the equivalent height in packing. To minimize amine vaporization loss, there may be a water wash section at the top of the column with an additional four to six trays. The preheated rich amine enters near the top of the column and flows down counter current to a gas stream of steam, H₂S and CO₂.

6. Filtration

A filtration scheme of mechanical and activated carbon filter is important in maintaining good solution control. Mechanical filters such as, cartridge filters or precoat filters remove particulate material while filters remove chemical contaminants such as entrained hydrocarbons and surface-active compounds.

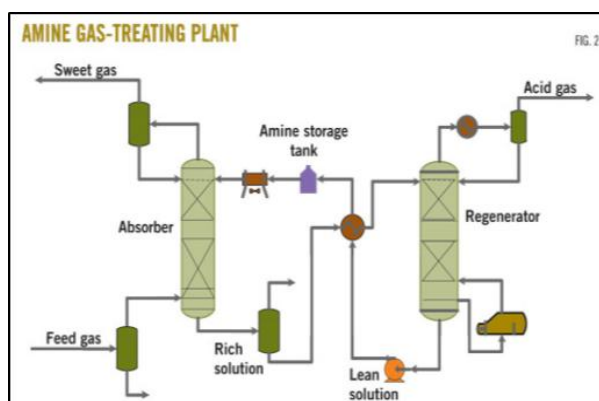


Figure 8: Sketch of typical amine based acid removal process^[11]

C. Process description

1. Sour gas enters the contactor tower and rises through the descending amine.
2. Purified gas flows from the top of the tower.



3. The amine solution is now considered Rich and is carrying absorbed acid gases.
4. The Lean amine and Rich amine flow through the heat exchanger, heating the Rich amine.
5. Rich amine is then further heated in the regeneration still column by heat supplied from there boiler. The steam rising through the still liberates H₂S and CO₂, regenerating the amine.
6. Steam and acid gases separated from the rich amine are condensed and cooled.
7. The condensed water is separated in the reflux accumulator and return to the still.
8. Hot, regenerated, lean amine is cooled in a solvent aerial cooler and circulated to the contactor tower, completing the cycle.^[4]

D. Advantages of Amine Gas Treating System

- Reduces CO₂ and H₂S levels to the required specifications
- Modular, skid-mounted system
- Reduced manufacturing and commissioning times
- Standardized and proven designs
- New equipment only
- Guaranteed performance
- Lower installation and removal cost
- Built in liquid containment to reduce environmental hazards^[2]

E. Controlling Amine Plant Foaming

1. An experienced control room operator notice that the differential pressure across one of the columns began to fluctuate. The operator to inject a chemical antifoaming agent into the recirculating amine solution. The systems differential pressure dropped to below the normal operating level within minutes. The AFA injection was noted in the daily log, and the incident forgotten.
2. 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.
3. The differential pressure beginning to rise again. Make up water was being added through the reflux drum to the regenerator.
5. The solution's surfactant concentration was slowly increasing naturally, and the foam breaking antifoam was imbalance, 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.
7. 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. 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 lines. Eliminating surfactant ingress to the plant is not practical, and is not sufficient because surfactants may be a natural by-product of amine degradation.^[7] 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 Sigma-Pure™ 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. Sigma-Pure™ is not sensitive to the type of surfactant or solvent, does not require pre-treatment.

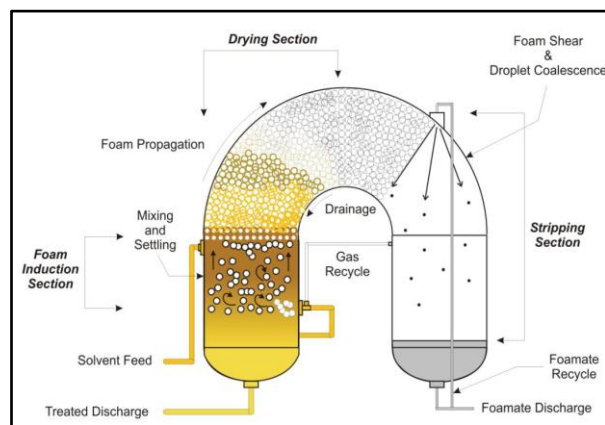


Fig. 10. Foam induction section^[9]

A slipstream of the recirculating amine stream is pumped into the Sigma-Pure™ 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.

V. ADVANTAGE AND DISADVANTAGE

A. Advantages of De-foaming Using Antifoaming Agent

1. Lower surface tension, compared to organic antifoams
2. Insoluble in most systems
3. Tends to react less with process ingredients
4. Persistence – generally performs longer
5. Can cost less to use due to its effectiveness and persistence at low use levels

B. Disadvantages of De-foaming Using Antifoaming Agent

1. It becomes defective after some time of process
2. Dosing again and again in short period is require for de-foaming
3. Its excessive use enhance the foaming in column.

VI. CONCLUSION

Amine solutions foam because air bubbles are stabilized into foam by contaminating surfactants. The most common way to control foaming has been injecting antifoaming chemicals into the recirculating solution level breaking 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 Sigma Pure process is a proven way to remove foam causing surfactants from operating amine systems.

A variety of solution impurities and operating conditions can cause air trapping bubbles to stabilize into foam. Since foaming in amine plants causes upsets, mitigation actions have been employed to avoid foam formation. The foam reducing action is normally the addition of chemical antifoam. Antifoams are intended to facilitate gas and liquid disengagement by weakening the cell structure of the air bubbles. Antifoams have no positive impurity removal properties. The tracer of these chemicals into recirculating amine solutions is common, and even regarded as necessary for normal plant operation.

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