CALGON CARBON CORPORATION

Gas treaters need clean amines

Cut operating costs of amine treaters by using activated carbon to restore and retain amine solution effectiveness

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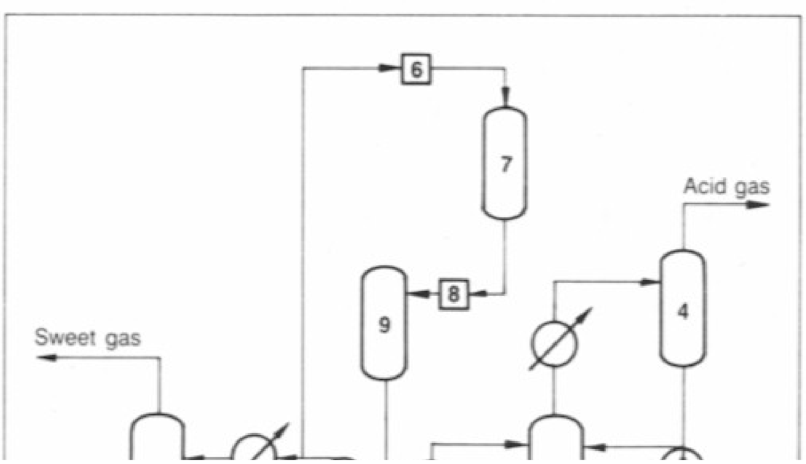
ALKANOLAMINES are used in the HPI to remove hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from gaseous streams. When the amine solution becomes dirty, operating costs increase. Then granular activated carbon can be used to clean up the dirty amine and restore effective amine treating. For example, the use of granular activated carbon at a 40 Mbpd refinery reduced amine system operating costs by $ 205,800.

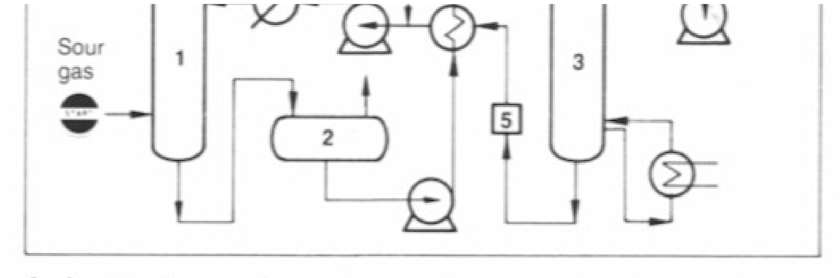
Amines get dirty. A "dirty" amine solution is one which is contaminated with hydrocarbons, organic acids or iron sulfides. It is also considered dirty if it is overloaded with antifoam agents, or is degraded chemically or thermally. When amine solutions become dirty, several operational results can occur which adversely affect the performance of the amine system. A dirty amine can cause foaming in the absorber and stripper, reduce scrubbing efficiency, and promote corrosion. As a result, operating costs are increased because of increased amine makeup, increased off-spec product and increased system maintenance.

Additionally, some problems are caused which are not normally attributed to dirty amine. For example, many refineries that have dirty amine compensate for the lower scrubbing efficiency by increasing the circulation rate. The increased circulation rate, in turn, increases steam requirements in the stripper or still reboiler.

Also, to reduce the effects of corrosion caused by a dirty amine solution, a lower than normal amine solution concentration is commonly maintained. The low amine concentration, in turn, requires a higher circulation rate to maintain acid gas removal. Higher circulation rates require higher steam usage in the reboiler to maintain stripper efficiency.

Corrosion inhibitors and antifoam agents are often added to off-set the negative effects of dirty amine. These methods can be expensive and not very effective. In fact, too much antifoam agent can cause additional foaming and add to the problem.





Amine treater receives sour gas at contactor (1). Lean amine absorbs acid gases. Resulting rich amine passes through flash tank (2) and enters amine stripper (3). From stripper overhead, acid gases are separated (4) and amine recycles. Stripper bottoms of lean amine pass through solids filter (5) and returns to amine contactor (1). A slipstream (10% of amine circulation rate) flows through 5 filter (6), into carbon absorber (7), through 10 filter (8) and to amine storage (9). Amine inventory: 6,600 gal. Amine circulation: 300 gpm. Slipstream: 30-40 gpm. Carbon online: 4,000 lb.

Using granular activated carbon. Granular activated carbon has been successfully used in many amine applications to clean up dirty amine solutions and keep them clean. The use of carbon can reduce and, in many cases, eliminate the need for antifoam agents and corrosion inhibitors. Carbon will remove degradation products that cause foaming and reduce scrubbing efficiency. It will also remove organic acids that are often the precursors for heat stable salt formation.

To get the full economic benefits of carbon, a properly designed carbon system is needed. Historically, many carbon systems in amine service have been under-designed or misapplied. This has resulted in carbon treatment being rejected because it was deemed ineffective. Carbon systems have often been improperly designed to treat the full circulating flow of amine solution at higher than recommended superficial velocity. These usually were systems designed with insufficient contact time between the amine solution and the carbon to make them effective.

Experience has shown that a properly designed carbon system should treat a 10-20% slipstream of amine solution. Systems which were designed for less than 10% slipstream frequently did not have sufficient carbon on line to maintain total inventory quality. On the other hand, systems designed for greater than 20% slipstream maintain acceptable amine quality, but may have prohibitive capital requirements.

Another common mistake is not in design, but in operation. Many refinery or gas plant operators do not understand the basic principals of carbon adsorption and leave the carbon on stream past its effective life. When carbon capacity is exhausted, or the carbon has become spent, it will no longer clean the amine. Hence, the amine stream becomes contaminated and the effects of dirty amine reoccur.

An effective carbon system for amine systems should include a properly designed and sized adsorber, mechanical filtration, and efficient carbon handling equipment. The size of the carbon adsorber should provide sufficient contact time between the amine solution and the activated carbon to achieve effective adsorption performance. Additionally, the physical configuration of the adsorber should afford adequate hydraulic capacity with respect to overall pressure drop. A minimum contact time of 15 minutes and a maximum superficial velocity of four gpm per square foot are considered a good design guidelines. This has proven to be most effective at removing the degradation products and the precursors for heat stable salt formation.

For safety purposes and to use the full carbon adsorption capacity, the carbon system should be installed on the lean side of the circulating amine stream. Experience has shown that when rich side treatment is applied, the CO_2 and H_2S that are absorbed by the amine can be released in the carbon bed. This gas tends to form "bubbles" around the carbon granules and inhibits the adsorption process.

Mechanical filtration, bag or cartridge, should be provided both upstream and downstream of the carbon adsorber. The upstream filter removes suspended solids before the amine enters the carbon adsorbers to ensure that the carbon adsorber is used to adsorb dissolved organics rather than to filter suspended solids. The downstream filter will remove any carbon fines which may exit the adsorber.

The carbon handling equipment should be designed to provide easy, efficient ways to transfer virgin carbon into the adsorber and to remove spent carbon from the adsorber. The common practice of dumping carbon from bags and drums into a manway is very dirty, labor intensive, and expensive.

Incorporating these requirements, Calgon Carbon Corp. developed a granular activated carbon system that is specifically designed for treating amine circulating streams - the CleanAmine System. It is a skid mounted, easily installed, carbon treatment system designed with special attention to providing a properly sized adsorber, effective mechanical filtration, and efficient carbon handling. These systems are in service nationwide treating monoethanolamine (MEA), diethanolamine (DEA) and the solutions of the Ucarsol and the Sulfinol processes. The amines are being used to treat fuel gas, hydrogen, natural gas, and/or tail gas.

An example. In May 1985, the first CleanAmine System was started at a major refinery in the western part of the United States. The system was installed in a DEA circulating stream which was used to treat fuel gas. The main reason for carbon treatment was to reduce a severe foaming problem in the amine contactor.

Prior to the installation of the carbon system, the amine was black and opaque in appearance. The refinery had very high operating costs due to high usage rates for: amine, antifoam agents, steam, and filter cartridges.

Operational savings. After the carbon system was installed, it was credited with saving the refinery as much as $205,000 per year. Table 1 shows an itemized breakdown of operating changes and associated cost savings. In the first year, the refinery was able to reduce the amine makeup rate by nearly 30% with a savings of $20,000. This savings was attributed to reduced loss of amine due to reduced carry over from foaming and reduced heat stable salt formation.

Additional savings resulted by reducing antifoam agent usage by 67% with a savings of $ 12,000. This resulted because the carbon treated amine did not require antifoam agent addition to maintain low foaming in the contactor.

Also in the first year, the refinery was able to reduce the circulating rate and increase amine strength which resulted in a steam savings of $2,000 pounds per hour. This resulted in a savings of almost $ 78,000.

Lastly, the refinery was able to reduce filter cartridge usage by 60% with savings of $54,000. The cleaned amine tended not to create iron sulfide (the majority of the solids removed in the filters) as readily as the dirty amine. This resulted in the reduced filter cartridge use.

During the second year of operation, the refinery continued to optimize their amine system by further reducing filter change-outs, amine make-up, anti-foam agent addition and carbon usage. The second year data indicate that total savings will be $205,800 compared to $ 147,800 for the first year.

Improved product. In addition to the direct economic benefits, the refinery has also seen a dramatic improvement in product gas quality. Pre-carbon treatment data indicated a fluctuation from 10-40 ppm H_2S in the product gas. Except for a few excursions caused by upset conditions in the refinery, the product gas quality has been running at or near non-detectable H_2S levels.

Although small upsets may not require a refinery shutdown, they often require modification of the standard operational procedures. With carbon, small upsets are smoothed out and standard operational procedures can be maintained.

A final documented benefit of using carbon to treat amine solutions is a reduction of heat stable salts formation. Heat stable salts are reaction products of the amine with strong acids such a formic, acetic, and sulfuric acids. The formation of heat stable salts results in amine losses and dilution of the amine concentration. The diluted solution has a lower activity than the more concentrated amine solution. While carbon does not adsorb heat stable salt, it will remove the precursors for their formation. In this example, heat stable salts at about 15 wt% were reduced in the first few months of carbon usage to less than half as much. Since carbon will not remove heat stable salts from the amine stream, the reduction of heat stable salts concentration in the amine circulating stream is attributed to physical losses and reduced heat stable salt formation. Heat stable salt levels continued to decline and have remained low (< 5 ppm) as a result of the carbon system.

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