Filter Media Selection in
Amine Gas Sweetening Systems

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Abstract

Amine system particle filtration is an accepted part of gas plant and refinery sour gas sweetening and plays a key role in maintaining operational efficiency by preventing fouling of the system hardware, reducing incidences of particle stabilized foaming, and promoting a clean gas-liquid interface. While much has been written about target removal efficiencies and the pros and cons of depth versus surface filtration and absolute versus nominal filters, scarce attention has been paid to one of the most important features of any filter at all, and the first question the amine system operator should ask – What is the filter made out of?

Polypropylene and cellulose, the latter in the form of pleated paper or cotton string, are the predominant players in the industry, and the two are as different as night and day. The oil-wetting properties of polypropylene enhance its particle removal capability in hydrocarbon-infused amine beyond its stated micron rating, enabling it to capture particles far smaller than its pore structure would suggest, keeping the circulating fluid clean while better resisting plugging which prolongs filter life. Cellulose, on the other hand, degrades in amine, setting the stage for oxygen sepsis and the generation of heat stable salts. The paper will present data showing that open grade (40 micron absolute) meltblown polypropylene microfiber media can reduce incoming amine total suspended solids by over an order of magnitude. Additionally, data will be provided that indicates cellulose-based media contributes to the formation of oxygen-derived heat stable salts, including those of formate, sulfate, and oxalate.

Introduction

Chemical reagents known as alkanolamines are commonly used to remove hydrogen sulfide (H_2S) and/or carbon dioxide (CO_2) from the light end hydrocarbons (C1 through C4) that are produced in refineries and gas plants. H_2S and CO_2 are considered "acid gases" and will react with the basic amine to form amine salts. Some of the H_2S and CO_2, however, may react with water to form respectively hydrosulfuric and carbonic acid, both of which are highly corrosive to the metal surfaces comprising the gas processing system hardware. This corrosion produces sulfides, oxides, and hydroxides of the alloying elements of the various system components, the byproducts of which are mostly solid phase in nature having particle sizes between 1 and 150 micron. For this reason, amine systems must be actively filtered for removal of solid corrosion products and other contaminants that would otherwise foul the system components and reduce the refinery or gas plant operational efficiency, negatively affecting plant productivity and profitability. Proper selection of a high-efficiency, high-capacity particle filter is essential for achieving optimum performance and cost effectiveness, and the specific filter materials of construction are a critical part of the selection process. This latter consideration is often overlooked but it can be the most important factor separating a smooth-running, trouble-free amine operation with one that is beset with operational difficulties.

Background

Refineries and gas plants have as an essential part of their operations gas sweetening amine systems whose primary function is to remove H_2S and CO_2 from butane and lighter gas products that are generated in volumes often exceeding hundreds of millions of cubic feet per day. The amine system is a closed loop wherein sour gas (hydrocarbon gas with some concentration of acid gas) enters a reaction tower and passes through the liquid amine in a counterflow direction which strips the acid gases from the hydrocarbon gases allowing sweet gas (hydrocarbon gas largely devoid of acid gases) to exit out the other end of the reaction tower. The amine is recirculated through a series of vessels that serve to separate out the acid gases captured in the reaction tower along with other solid and semi-solid contaminants that have gotten into the amine, including corrosion products that may have formed as a result of reactions between acid gases and ferrous-metal surfaces. The acid gases are removed from the amine system in a stripper, or regenerating tower, by addition of heat in the form of steam – this reverses the chemical reaction that occurred in the absorber and frees up the amine to be used again. Solids, semi-solids, and parasitic non-amine liquids, many of which are hydrocarbons heavier than butane, are removed by a variety of separation vessels. These include the flash tank, rich and lean side particle filters, and carbon bed. Figure 1 shows a typical amine system with the reaction tower, also known as a contactor or absorber, on the left and the regenerator or stripper on the right.

Contamination

Although considerable effort is devoted to keeping the amine system free of contaminants almost every plant ends up dealing with three common forms of intrusion. These are: 1) Entrained hydrocarbons that condense out of the sour gas stream in the absorbing tower; 2) Solids in the form of corrosion products from internal metal hardware surfaces; 3) Heat stable salts that form from the reaction of amine with oxygen and acids stronger than H_2S and CO_2. Each of these is dealt with in a different way by the operations people in the plants, from taking measures to prevent their initial incursion to removal once they have found their way in, and each carries with it associated costs and other demands upon plant resources.
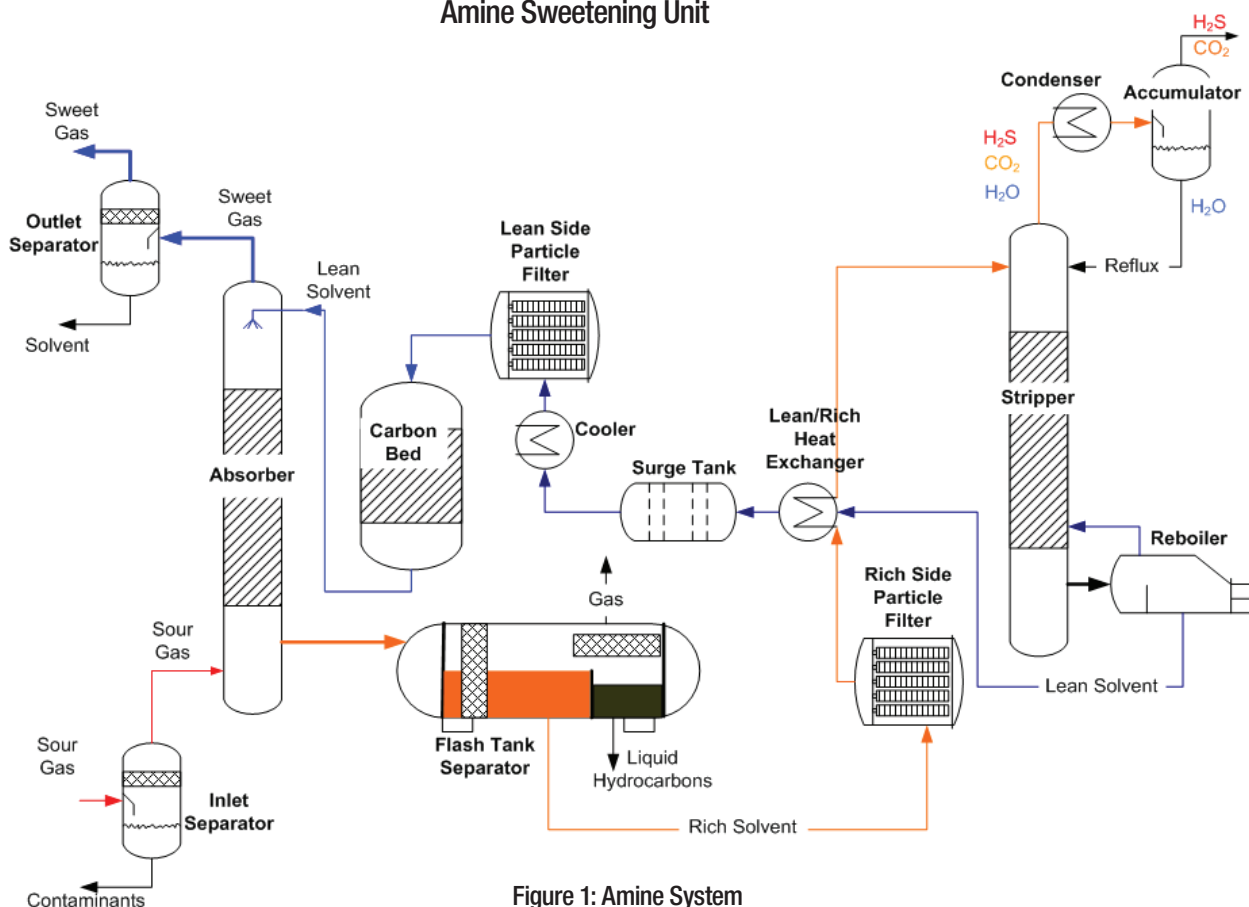
Amine Sweetening Unit

Figure 1: Amine System

Hydrocarbons

In a perfect world the only thing the system hardware would see after the inlet separator – other than the amine-water solution itself - is C4 and lighter hydrocarbons, all of which would pass as sweet gas out the top of the contactor, and then whatever H_2S and CO_2 came in with the sour gas until such time as these principal acid gases are swept from the system in the regenerator overhead. Unfortunately, hydrocarbons heavier than C4 can infiltrate through the inlet separator, sometimes in gross slugs during upsets or unintentional releases from other plant processes, more often as aerosols too small to be effectively captured by coalescing filters intended for that very purpose. Regardless of their manner of entry, hydrocarbons heavier than butane may condense out of the sour gas and flow out the bottom of the contactor along with the rich amine, where they may or may not be removed by the flash tank separator on the rich side or the carbon bed (typically) on the lean side. Emulsified hydrocarbons are especially difficult to remove and may even make their way through an otherwise active carbon bed. Moreover, because carbon beds are filtering only a slip stream of the total amine flow some considerable portion of entrained hydrocarbons that have made it through the flash tank can be expected to flow back to the contactor. The presence of even trace amounts of liquid hydrocarbon in the contactor can be disruptive as it will change the surface tension of the lean solvent that is cascading downward through the trays of the absorber, resulting in foaming. "Foaming is the most common cause of upsets in an amine plant, usually resulting in excessive amine losses, off-specification treated gas and a reduction in treating capacity. All of these affect operating costs and revenue." [1] Clearly, minimizing or eliminating hydrocarbons from the circulating amine is a primary consideration in maintaining a properly functioning amine system.

Solids

Solids are more easily prevented from entering the gas sweetening process through elimination via capture at the point of entry, as inlet separators are concerned primarily with vapors and so as a rule employ much tighter filtration media than would be feasible to use in the liquid amine. Rather, it is the solid particles that form as hardware corrosion products that are the bane of many amine unit engineers. Iron sulfide is typically the chief component indicated in an x-ray fluorescence analysis of suspended solids samples taken from gas plant or refinery amine (Table 1) and although oxides and hydroxides of iron and other alloying metals can be detected it is the reaction between iron and hydrogen sulfide that produces the fine black particles that give the greenish tint to unfiltered - or as is more often the case, inadequately filtered - rich-side amine samples. The simplified reaction is as follows:

$$Fe + H_2S > FeS + H_2$$

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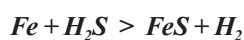
It should be pointed out that the presence of iron sulfide on internal metal surfaces is not only inevitable in sour gas treatment facilities but in fact is viewed as a good thing. "If the FeS scale is strong enough, it will adhere to the piping surface, forming a protective or passivating film. Unless removed this film prevents further corrosion of the pipes and vessels and can result in extremely long life spans for that part of the amine plant." [2] Unfortunately this passivation layer does not always stay put; it may be removed mechanically by abrasion or erosion, or chemically by reaction with hydrogen cyanide (this is more specific to refineries), or simply dissolved in the amine solution itself. The former can occur when hard particles circulate within the amine, literally abrading or knocking the iron sulfide loose from the underlying steel. These particles will tend to be relatively large and visible to the eye as discrete entities in solution. They are also the easiest to remove by mechanical filtration.

Hydrogen cyanide that enters the amine system will dissociate to form cyanide ion (CN-) and this will react with the passivation layer as shown:

$$FeS + 6CN^- \ > \ Fe(CN)_6^{4-} + S^{2-}$$

Removal of the passivation layer exposes raw steel that can be attacked further by H_2S and CO_2, and the end result of this ongoing corrosion cycle of passivation-chelation-passivation is blistering and/or pitting of internal metal surfaces. Chelated iron may return from the regenerator still bound up with the cyanide, but if the cyanide ion reacts with amine to form one of a number of heat stable salts (these will be covered in a later section on **Contamination**) then the iron may return to the contactor as soluble iron carbonate where it will quickly react with any H2S in the sour gas and precipitate out as iron sulfide. These precipitated particles will be extremely small, on the order of one to two microns, and are generally difficult to remove with mechanical filters.

Table 1: X-Ray Fluorescence Analysis of Solids in Used Filter from Refinery Amine System

Element Name (Symbol)	Semi-Quantitative XRF Results (reported in mass percent [%])			
	Sample #1: Used Filter Media		Sample # 2: Control	
	Average	Deviation	Average	Deviation
Carbon (C)	30.6	0.8	96.1	1.9
Nitrogen (N)	7.56	0.26	ND	ND
Oxygen (O)	32.1	1.7	0.244	0.091
Magnesium (Mg)	0.0028	0.0008	ND	ND
Aluminum (Al)	0.0094	0.0003	0.0116	0.0026
Silicon (Si)	0.0690	0.0028	0.0045	0.0009
Phosphorus (P)	0.0029	0.0002	0.0020	0.0002
Sulfur (S)	8.34	0.92	3.62	1.83
Chlorine (Cl)	0.0059	0.0016	0.0003	0.0001
Potassium (K)	0.0058	0.0005	0.0007	0.0001
Calcium (Ca)	0.0104	0.0005	0.0041	0.0011
Chromium (Cr)	0.0031	0.0004	0.0005	0.0002
Manganese (Mn)	0.0129	0.0009	ND	ND
Iron (Fe)	21.3	1.4	0.0008	0.0002
Nickel (Ni)	0.0025	0.0005	0.0002	0.0001
Copper (Cu)	0.0044	0.0003	0.0003	0.0001
Zinc (Zn)	0.0016	0.0003	ND	ND

Particles smaller than about 5 micron do not present an overt plugging threat to hardware and do not possess enough mass to contribute greatly to mechanical erosion of the passivation layer but they can exacerbate foaming by contributing to foam stability. "Colloidal iron sulfide … 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." [3] For this reason it is desired that even the smallest particles be removed from the amine as quickly as possible.

Semi-solids: Combined hydrocarbon and solids

Hydrocarbons and solids do exist as separate entities in amine, but it is their combined form that presents the biggest headache for operators and unit engineers. It was stated earlier that there were three common forms of intrusion upon amine systems but the combination of hydrocarbon and suspended solid matter arguably represent a fourth distinct contaminant. When occurring together the water-wet solid particles will tend towards an association with the lower surface energy presented by the organic liquid to form "a black shoe polish-like material consisting of iron sulfide bound with hydrocarbon and polymerized amine." [3]   (Figures 2a and 2b)
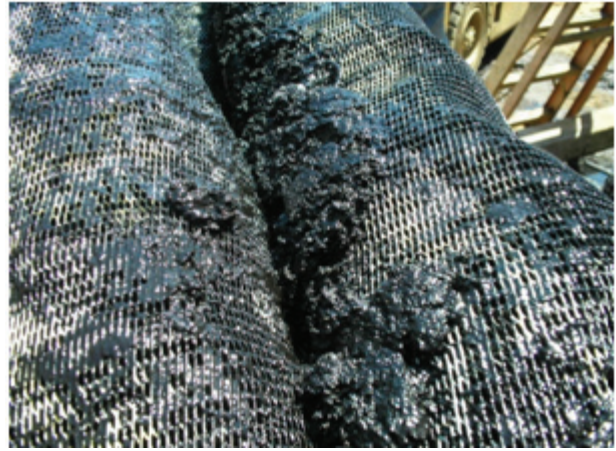
Figures 2a & 2b: Examples of "shoe polish" Contamination

The complexed mixture forms a semi-solid that has high natural adhesion properties, making it prone to stick to almost anything else that it comes in contact with, including other semi-solid particles. In this way the semi-solids agglomerate relatively quickly into larger particles, growing from several microns to several tens of microns in diameter. While these larger particles are easier to trap within the pore structure of mechanical filters they are equally prone to hanging up in hardware components of the amine system, and it almost becomes a question of which "filter" captures the particle first. Unless the semi-solids are removed in their early stages of development they are as likely to be filtered out by the internal structure of a cross-flow heat exchanger or the packed beds or trays of an absorbing tower as they are by the specific matrix of whatever cartridge or bag filter has been deployed for the same purpose. When this set of conditions exists the gas sweetening unit shown in Figure 1 will appear to the circulating amine more like the one shown below in Figure 3.

Amine Sweetening Unit With Circulating "Shoe Polish" Contamination
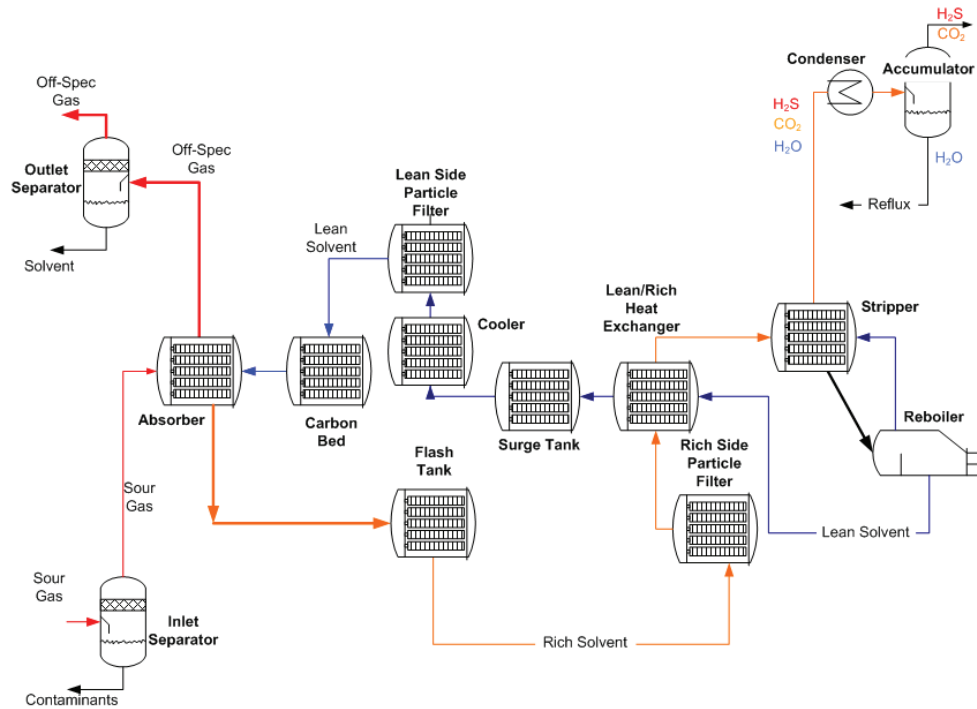
Figure 3: Amine System with Inadequate Filtration – Every Piece of Hardware Becomes a Filter

Heat Stable Salts

The acid gases H_2S and CO_2 are readily removed from rich amine by addition of heat in the stripper column but there are other feed components that can come in with the sour gas feed which react with and form strong enough bonds with the amine that the heat of the regenerator is insufficient to separate them. The compounds formed by these reactions with other gases are referred to as heat stable salts, and include ammonium salts of formate (CHOO-), thiocyanate (SCN-), acetate (CH_3COO-), oxalate ($[C_2O_4]^{2-}$), thiosulfate ($[S_2O_3]^{2-}$), and others. The heat stable salts remain in the system where they tie up amine so that it cannot react in the reaction tower, reducing the acid gas absorption capacity. In addition, heat stable salts contribute to corrosion of the system hardware, problematic foaming of the amine, amine loss, and increased energy consumption. All of these debilitating properties of heat stable salts are well understood in the industry and so anything that might contribute to their formation beyond what might reasonably be expected from normal operations should be actively avoided by unit personnel. In particular, inadvertent incursion of oxygen is to be avoided as it plays a role in the formation of both formate and acetate, two heat stable salt anions often found in highest concentration. Heat stable salts are primarily an issue in refineries where the product streams tend to contain a large number of strong acids; natural gas plants treating an oxygen-free feed stream should have very low heat stable salt formation.

Filtration

Current amine filtration best practice suggests that 10 micron absolute filtration is necessary to ensure acceptable removal of iron sulfide and other solid particulates from a circulating amine solvent mixture. "Acceptable removal" can be defined as that which maintains the level of total suspended solids in the amine at a concentration that does not allow for deposition of solids in the system hardware or negatively impact the sour gas absorption capacity of the solvent. The 10 micron specification is based on the predication that most of the iron sulfide and other solid particles that reside in the amine are in a size range that will permit effective capture by 10 micron absolute rated filter media. As it turns out in actual practice this is often not the case, and the result is that filters either do an inadequate job of removing enough particles to satisfy the above definition of "acceptable removal" or filters plug so rapidly that associated costs for replacement, labor, and disposal are unacceptably high. This dilemma can be solved by choosing a filter media that does not rely solely on pore size for capture of solids but rather combines the effects of mechanical entrapment and surface wetting to provide both a clean effluent and long filter life. Field-generated data confirms that pleated polypropylene microfiber rated 99% efficient from 25 to 40 micron meets this requirement.

Filter Media

There are multiple types of filter media for an amine unit engineer to choose from and it is not the intention of this paper to address the pros and cons of all of them. Some, like metal strainers or wedge-wire baskets, have such a poor track record that they hardly bear mentioning. Others, like polyester and nylon, present compatibility concerns that should preclude their use entirely. Polyester filter media, including blends of polyester, can hydrolize in a reversal of the condensation reaction that formed the original polymer, causing it to partially or completely dissolve in the amine. Nylon, on the other hand, will absorb water into the polymer, causing swelling of the fiber matrix and shortening filter life accordingly. Swollen cartridges can also present a significant removal problem for operators.

The two most common types of filter material found in amine systems today are cellulose, in the form of stringwound cotton and pleated paper, and polypropylene, usually as pleated microfiber but also as crystalline meltblown. Due to hydrogen bonding forces both cotton string and cellulose paper are water wettable, whereas polypropylene, lacking the electronegative oxygen atom found in the first two, is hydrophobic. Once water-wetted the natural polymers have no special affinity for hydrocarbon, while polypropylene will readily wet with hydrocarbons in the presence of water. Cotton stringwound and pleated paper filters rely on mechanical entrapment and pore occlusion for capture of solids and semi-solids in an amine solution, and they are unable to remove hydrocarbons to any measurable degree. Particles smaller than the average pore structure can be expected to migrate through the filter matrix. Conversely, as hydrocarbons adhere to the fibers in polypropylene filter media, particles significantly smaller than the pore structure are removed due to symbiotic capture of the oil-wetted semi-solids. This phenomenon is demonstrated in Figures 4a and 4b below showing filter inlet and outlet samples from a refinery's rich-side amine using 40 micron pleated polypropylene microfiber media. In this case inlet total suspended solids were reduced from 217 ppm to 6.2 ppm in a single pass.

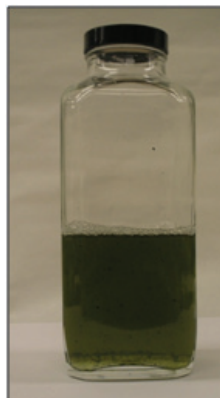Figure 4a: Unfiltered Inlet Sample
217 ppm suspended solids

Figure 4b: Effluent from 40 Micron Polypropylene
6.2 ppm suspended solids

This particular refinery had been using polypropylene media absolute rated (99% efficient) at 5 microns and, while the amine was being kept adequately clean, filter life was on the order of 12 to 14 hours. A switch to absolute rated 40 micron polypropylene media was recommended and filter life consequently extended to 21 days. The amine samples in the photos were taken about two weeks after the change to the more open filters. While polypropylene in general will exhibit oil-wetting properties a filter's ability to take up oil will depend on the wettable surface area available to it. As such, a preferred filter design will maximize the micro-surface at the fiber level and the macro-surface in the structure of the finished filter body. Large diameter fibers such as those found in spunbonded and felted polypropylene have orders of magnitude lower surface area than meltblown polypropylene fibers and become too-quickly saturated with hydrocarbons to form an effective filter "net" for future incoming solids. A filter media combining the mechanical properties of the spunbond or felt with the far greater oil-wettable surface of the microfiber is the preferred embodiment at the fiber level; various pleating techniques and filter geometries may then be employed to situate an optimum amount of this media in a given space.

The importance of keeping oxygen out of amine was discussed earlier in the section on Contamination. The cellulose molecule contains oxygen ($C_6H_{10}O_5$) and any degradation of filters constructed of cellulose may reasonably be expected to contribute free oxygen to the amine. A study on samples of pleated cellulose fiber (paper) media exposed to monoethanolamine (MEA) was conducted and compared to a control sample (no filter media) of MEA and another with polypropylene media in MEA. All samples were soaked for 24 hours at 135°F at a media-to-solution ratio of 1/100. Ion chromatography analysis results of the MEA from each are shown in Table 2.

Table 2: Anion concentration (mg/L) in MEA exposed to various filter media samples

Sample	Formate	Chloride	Sulfate	Oxalate
Control	206 ± 15	< 0.4	< 1	8 ± 2
Polypropylene	560 ± 38	0.50 ± 0.05	< 1	9.1 ± 0.4
Cellulose 5	10660 ± 1190	1.0 ± 0.6	1.5 ± 0.5	560 ± 27
Cellulose 4	6930 ± 940	3.1 ± 0.4	0.7 ± 0.2	277 ± 12
Cellulose 3	4495 ± 375	3.4 ± 0.4	3.3 ± 1.2	113 ± 10
Cellulose 2	11645 ± 1390	6.4 ± 0.8	3.5 ± 1.3	950 ± 12
Cellulose 1	5400 ± 600	2.3 ± 0.2	2.8 ± 1.2	243 ± 8

Elevated levels of formate and oxalate in the cellulose samples over that observed in either the control or polypropylene sample indicate some level of oxygen incursion from the paper. It is possible that fugitive oxygen from the phenyl-formaldehyde (phenolic) resin binders used in paper-making may also be responsible for the elevated formate and oxalate concentrations. Both cellulose (Figure 5) [4] and phenolic resin (Figure 6) [5] contain the requisite oxygen atom and it may be that either or both is infecting the amine. Further study is needed to determine the root cause of the higher anion levels.

In addition to providing a possible avenue of entry for oxygen into the amine, pleated cellulose media can leach color bodies into the solution turning it yellow to dark brown. "The chemical reaction between an amino acid and a reducing sugar, in the presence of heat, is well-documented (Maillard effect). In this reaction, a form of non-enzymatic browning, the carbonyl group of the cellulose reacts with the amino group of the alkanolamine to produce various unstable compounds, such as N-substituted glycosylamines and ketosamines. These compounds eventually break down to form complex mixtures called melanoidins (brown nitrogenous polymers and copolymers). These melanoidins are what give the amine the yellow to brown color, and are tell-tale indicators that the cellulose media is indeed breaking down and leaching into the amine solvent." [6] Weight
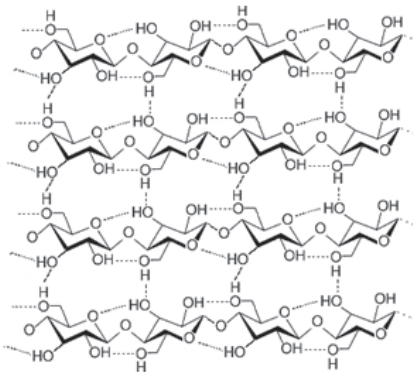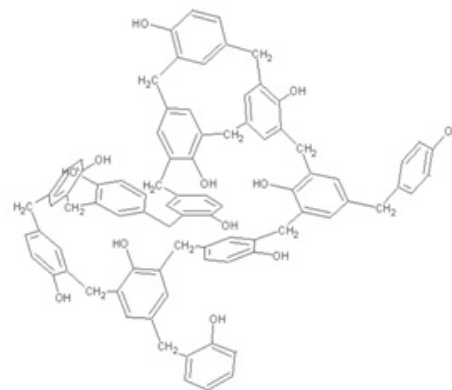

Figure 5

Figure 6

loss in rinsed and dried samples of amine-exposed cellulose confirm that an extraction of the media takes place. Figures 7a and 7b show the effects of a 2-gram sample of pleated cellulose media in 200mL of a 50% MDEA solution before and after 24 hours in a shaker bath at 135° F.

Weight loss in this particular sample was measured at 6.9% of the original dry mass of the cellulose media. Weight loss in other samples tested ranged from 1.6% to 5.3% of the original mass.

Amine samples exposed to cellulose media also exhibit increased foam retention compared to control samples and samples exposed to polypropylene. In lab experiments the difference in measured foam break times ranged from 15 to 30 seconds for control and polypropylene samples to greater than thirty minutes for some cellulose samples, and while the mechanism for foam retention isn't firmly established it is likely that the cellulose degradation products contribute to a lowering of the amine solution surface tension. In this regard these breakdown products act as surfactants in the amine.
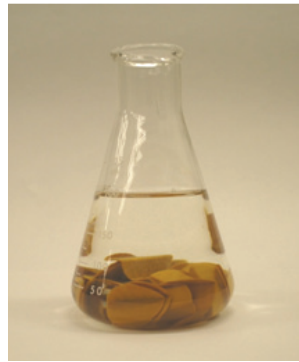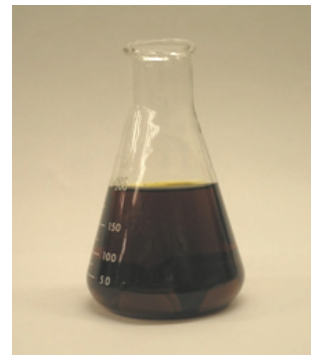
Figure 7a   Figure 7b

Conclusions

Filter media materials of construction is a frequently overlooked aspect of filter design in the selection of particle removal filters for amine systems. The oleophilic surface wetting properties of polypropylene give it a distinct advantage over stringwound cotton and cellulose paper by allowing for the use of a more open pore structure (higher micron rating) than is required by the hydrophilic medias to capture the same size particles. A direct result of a more open pore structure is longer filter life. Cleaner amine streams are also afforded by polypropylene media due to its ability to capture fine iron sulfide particles in their early stage of existence by the mechanism described in detail above. Cellulose media, conversely, must rely almost entirely on mechanical entrapment for the capture of solid particles, and is also suspected of contributing free oxygen and other degradation products that adversely affect amine quality.

Acknowledgements

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