CORROSION AND FOULING IN SULFURIC ACID ALKYLATION UNITS

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CORROSION AND FOULING IN SULFURIC ACID ALKYLATION UNITS

I. INTRODUCTION

Causes and controls for many of the potential corrosion and fouling problems in a sulfuric acid alkylation unit are reviewed in this paper. Corrosion and fouling should not be serious problems in a plant that is well designed, operated and maintained. Process conditions that provide the best yield and product quality also tend to minimize corrosion and fouling. However, problems are not uncommon in plants operated at rates significantly above the design capacity or where maintenance and operating problems go unresolved.

The Fundamentals of Corrosion and Fouling Control

Most corrosion and fouling in a sulfuric acid alkylation unit can be minimized by following the common sense fundamentals listed below:

1. Maintain good reaction conditions.
2. Avoid high velocity or temperature in sulfuric acid service.
3. Don't let acid sit stagnant.
4. Minimize the amount of water entering the process.
5. Keep acidic streams dry and "wet" streams neutral. Use corrosion-resistant materials where they mix.
6. Maintain good treating operations.
7. Be extra alert in units pushed above design capacity.

Throughout the rest of this paper, these rules will be related to specific examples in each section of the alkylation unit.

II. REACTION SECTION

A. Reactor Corrosion

Maintain good reaction conditions.

The reaction conditions which produce the best quality alkylate at the lowest acid consumption also tend to minimize corrosion and fouling throughout the alkylation unit. Low reaction temperature, low space velocity, high isobutane-to-olefin ratio and high acid strength all favor the alkylation reaction and tend to suppress undesirable side reactions. In particular, the rate of corrosion and erosion in a STRATCO® Contactor™ reactor is minimized at low temperature and high acid strength (especially low water content). Contactor reactors in low acid strength service tend to have the highest rates of corrosion.

Reactor operation also affects corrosion and fouling outside the reaction section. Good reactor operation can minimize the formation of SO₂ and alkyl sulfates, which can overload the depropanizer feed treatment and net effluent treating systems, respectively. The formation of SO₂ increases as reaction temperature increases.
Avoid high velocity or temperature in sulfuric acid service.

In general, the acid strength in the reaction section of a sulfuric acid alkylation plant should not be allowed to fall below about 89 wt%. The overall corrosion rate of carbon steel is very low at this acid strength, so general corrosion is usually not a problem. However, some precautions are necessary to prevent localized corrosion.

Iron sulfate, a corrosion product of carbon steel and sulfuric acid, forms a protective film on the surface of the steel. This coating has low solubility in strong acid at low temperature but is soft and can be stripped away if subjected to high fluid velocity. For this reason, DuPont sizes sulfuric acid lines that are to be in continuous service such that the velocity maintains between 1-3 feet per second (0.3-0.9 meters per second) in new alkylation units. Corrosion and erosion accelerates dramatically if the velocity exceeds 3-5 feet per second (0.9-1.5 meters per second). This problem is not uncommon in older alkylation units that are being operated well beyond their design capacity. Below approximately 0.5 feet per second (0.2 meters per second), hydrogen produced from the acid reacting with iron may rise to the upper portion of the piping and cut “grooves” in the lines. At low velocities, localized turbulence may also occur in and around valves, meter stations and near the suction and discharge of pumps in acid service. DuPont therefore specifies Alloy 20 valves and piping in these areas of the unit to resist erosion and corrosion.

The stability of the protective sulfate coating also depends on temperature. This is probably the reason Contactor reactors operated at high temperatures tend to have a higher corrosion rate than reactors operated in the preferred temperature range of 42-50°F (5.6-10°C). DuPont has found that there tends to be a substantial decrease in the life of a Contactor reactor tube bundle as the reaction temperature exceeds about 55°F (13°C). With ideal reaction conditions, a Contactor reactor tube bundle may last up to 15 years. However, some refiners who operate at temperatures exceeding 60°F (16°C) have reported Contactor reactor tube bundle life of ≤ 5 years in low acid strength service and some have reported failures of new tube bundles after only one year of operation at 65°F (18°C).

Care must also be taken with the installation of heat tracing to avoid hot spots on acid lines. For this reason, DuPont recommends electric tracing instead of steam tracing in acid service and the tracing must not actually touch the surface of the metal.
Don't let acid sit stagnant.

Spent acid contains polymers and other acid soluble hydrocarbon compounds that are reactive. These compounds continue to react in stagnant acid, producing solids that can plug lines and instrument connections. Plugging in level instrument connections is prevented by periodically flushing them with net effluent from the net effluent pump. Net effluent flushing connections should be piped to all the sight glasses and level instruments in acid service. Flushing of these instruments every other week (at a minimum) will usually prevent plugging. In addition, any lines in intermittent spent acid service (such as startup lines) should be drained after use to prevent plugging.

Minimize the amount of water entering the process.

The amount of water in the Contactor reactor feed impacts the rate of corrosion as well as acid consumption. The corrosivity of spent acid depends more on its water content than the actual wt% H$_2$SO$_4$. For example, 90 wt% acid that contains 5% water and 5% hydrocarbon is more corrosive than 90% acid that contains 2% water and 8% hydrocarbon. Higher water content in the spent acid can also reduce alkylate product quality. It is therefore important to monitor the performance of the feed/effluent exchangers and the feed coalescer. The feed coalescer operating temperature affects the solubility of water in the feed. New plants are typically designed for a feed/effluent exchanger outlet temperature of 55-60°F (13-16°C). A theoretical water balance can be done on the feed coalescer based on the solubility of water in the feed at the temperatures upstream and downstream of the feed/effluent exchangers. An evaluation of the coalescer should be completed if the amount of water actually removed drops below 80% of the theoretical amount.

Operation of a sulfuric acid alkylation unit with MTBE or TAME raffinate feed can also affect the amount of water entering the process. Operation with MTBE raffinate should normally provide higher octane alkylate product with acid consumption equal to or less than operation with FCC olefin. However, some refiners have reported accelerated corrosion of the Contactor reactor impeller, wear ring, feed nozzles and tube bundles while processing an MTBE raffinate. This problem is related to the presence of oxygenates such as methanol and dimethyl ether (DME) in the alkylation unit feed. Ideally, MTBE raffinate should contain less than 500 ppm DME and less than 40 ppm methanol.

Methanol and DME in the olefin feed react with the sulfuric acid alkylation catalyst, consuming acid and producing water as a byproduct, which dilutes the acid. Typical reactions are:

\[
\text{CH}_3\text{-OH} + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{HSO}_4 + \text{H}_2\text{O}
\]

\[
\text{CH}_3\text{-O-CH}_3 + 2 \text{H}_2\text{SO}_4 \rightarrow 2 \text{CH}_3\text{HSO}_4 + \text{H}_2\text{O}
\]
Methanol and DME are also harmful because they increase the solubility of water in the hydrocarbon feed, rendering the alkylation unit feed coalescer less effective. The additional water in the olefin feed charge and that produced by the above reactions causes accelerated corrosion in the Contactor reactor mixing zone.

With good operation of the MTBE plant water wash and methanol recovery column, very little methanol should be present in the alkylation plant feed. In contrast, the water wash does not remove DME. Its concentration in the raffinate stream depends on MTBE reaction zone operation. DuPont recommends that refiners with MTBE or TAME units upstream of their alkylation unit analyze their olefin feed regularly for oxygenates. Bear in mind that the refinery laboratory gas chromatograph must be specially configured to fully detect all the DME present in MTBE raffinate. DuPont has found that refinery labs tend to underreport the actual amount of DME present.

Steps should be taken to prevent conditions or upsets which increase oxygenates in the alkylation unit feed. The use of molecular sieve dryers to remove oxygenates and water from the MTBE raffinate may be very attractive depending upon the concentration of oxygenates in that stream.

If the reactors are experiencing a high corrosion rate due to oxygenates in the feed, one possible remedy is to increase the acid spending strength up to about 92 wt%. This action will increase the acid rate through the unit and reduce the concentration of water in the spent acid.

*Keep acidic streams dry and "wet" streams neutral. Use corrosion-resistant material where they mix.*

Localized low acid concentration can occur in zones where wet hydrocarbon and acidic streams are mixed, even though the overall mixture may not be in the corrosive range. In this context, a hydrocarbon stream is considered wet if it contains dissolved water. Free water need not be present. By this definition, the olefin feed and recycle isobutane in most plants are considered wet streams. In regions where wet and acidic streams are mixed, corrosion-resistant material is substituted for carbon steel. An example is shown below in Figure 1.
To resist corrosion in the Contactor reactor mixing zone, DuPont typically uses Hastelloy C for the impeller and hydrocarbon feed nozzle. The piping wherein the olefin feed and refrigerant recycle are combined is a point at which a wet stream and an acidic stream are mixed. (In this case, the refrigerant recycle is the acidic stream because it contains a small amount of SO₂.) DuPont specifies Alloy 20 piping from two feet (610 mm) upstream of the feed/refrigerant recycle mix point to the Contactor reactor feed nozzle.

B. Contactor Reactor Tube Bundle Fouling

The tube side of the Contactor reactor tube bundle sometimes becomes fouled, especially in plants that are operated at high acid spending strength and/or above design capacity. The cause is usually acid carryover from the acid settler, which becomes viscous and coats the inside of the Contactor reactor tubes due to the lower temperature inside the tube bundle. Tube side fouling is most common in the Contactor reactor/settler system with the highest strength acid because higher strength acid is more viscous. The normal solution is to temporarily stop olefin feed, recycle isobutane, and refrigerant recycle to the affected Contactor reactor and allow it to warm up. Warming the acid film inside the tubes reduces its viscosity and allows it to be washed away when feed is once again introduced.
III. REFRIGERATION SECTION AND DEPROPANIZER

Keep acidic streams dry and "wet" streams neutral. Use corrosion-resistant material where they mix.

A. Refrigeration System

The refrigerant stream in an effluent or auto-refrigerated alkylation unit is acidic because of the presence of sulfur dioxide (SO₂) generated in the reaction section. SO₂ will not cause corrosion of carbon steel unless there is water present. Corrosion in the refrigeration system should therefore not be a problem because under normal circumstances no water should be present.

To insure against corrosion in the refrigeration section, potential sources of water must be eliminated. A potential source of water is inadequate drying of refrigeration section equipment prior to startup. Another potential source of water is a tube leak in a water-cooled refrigerant condenser. It is important for the process pressure in the refrigerant condensers to be higher than the cooling water pressure so water will not enter the process in the event of a leak.

B. Depropanizer Systems

SO₂ must be removed from the alkylation unit propane product in order to meet LPG specifications but there are different schools of thought as to where it should be removed. In a dry depropanizer system, SO₂ is removed by caustic treating the propane product. In a wet depropanizer system, it is removed by caustic treating the depropanizer feed. Since the propane product is a considerably smaller stream than the depropanizer feed, a dry depropanizer system usually requires a smaller caustic treatment system capital cost than a wet depropanizer system. However, caustic consumption for both systems should be about the same. Both the wet and dry depropanizer systems have advantages and disadvantages and both can be used successfully.

1. Dry Depropanizer System

In a dry depropanizer operation, the column is fed directly from the refrigerant accumulator. As long as no water is present, the SO₂ that concentrates in the depropanizer overhead will not cause corrosion. However, if water is present, it will also concentrate in the depropanizer overhead system and rapid corrosion can occur. When problems occur, it is often difficult to track down the source of water.
Inadequate dryout of a dry depropanizer system prior to startup can lead to corrosion. Another possible source of water is the propane product treatment system downstream of the depropanizer. In alkylation units with predominantly butylene feed, the amount of propane in the unit feed can be so small that it is difficult to maintain a continuous flow of propane product. If propane product flow is stopped, it may be possible for water from downstream treatment to back up into the depropanizer overhead system. In some refineries that send only butylene feed to the alkylation unit, a small amount of propane product is recycled to the reactor section to insure the flow of depropanizer overhead product is not interrupted.

Some refiners with dry depropanizer systems have found it necessary to use stainless steel for condenser tube bundles and the top trays of the depropanizer. Others use salt dryers on the depropanizer reflux to be certain the overhead system stays dry. One of the challenges of operating a dry depropanizer system is that there is no easy way to make certain the system is staying dry. Equipment inspection (or failure between inspections) is often the first indication something has gone wrong.

*Maintain good treating operations.*

2. Wet Depropanizer System

With a wet depropanizer system, the depropanizer feed from the refrigerant accumulator is treated to remove SO$_2$ before it is charged to the column. The treatment system, as shown in Figure 2 on the following page, typically consists of a caustic wash followed by a coalescer to prevent any caustic carryover to the depropanizer tower.

The caustic wash removes SO$_2$ via the following reactions:

\[
\text{SO}_2 + \text{NaOH} \rightarrow \text{NaHSO}_3
\]

\[
\text{SO}_2 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O}
\]

The most important parameters in operation of the caustic wash are good mixing, the ratio of caustic to hydrocarbon feed and the caustic strength.
A variety of mixing devices including eductors, mixing valves and static mixers have been used to improve contacting between the depropanizer feed and the caustic. DuPont specifies an Alloy 20 Sulzer SMV five-stage static mixer for this service. The static mixer is to be designed to produce a 300-400 micron calculated average droplet size at the outlet of the mixer. Note that this droplet size is based on Sulzer’s correlations and might not be applicable to mixers provided by other vendors. A typical differential pressure for a mixer of this type is 8-15 psi (0.6-1.1 kg/cm²). The static mixer pressure drop should be monitored with a differential pressure indicator. An unexplained reduction in pressure drop is likely to indicate damage to the static mixer. In order to avoid corrosion in the mixing zone, the piping from four feet (1.2 meters) upstream of the caustic/hydrocarbon mix point to the static mixer and the piping from the static mixer to the caustic wash drum is made of Alloy 20. The caustic circulation rate is maintained in the range of 20-30% by volume of the depropanizer feed stream.

Fresh caustic strengths above 15 wt% should be avoided. Plugging of the depropanizer feed/caustic static mixer and associated piping due to precipitation of caustic salts has been known to occur when the concentration of the fresh caustic is too high. Fresh caustic strength is normally in the 10-12 wt% range.
In batch systems, the caustic should be replaced at a minimum strength of 3 wt%, as measured by titration. The caustic solution will lose water over time to the dry depropanizer feed stream. Concentrated caustic solutions tend to emulsify and carry over, so makeup water should be added to replace the water that is lost. The simplest way to do this is to add process water as necessary to hold a constant interface level in the caustic wash drum. It is important to use water, NOT fresh caustic, to maintain the interface level. Another approach to water makeup is to add water to maintain the specific gravity of the caustic in the range of 1.10 to 1.15.

The hydrocarbon from the caustic wash drum flows to the depropanizer feed coalescer where traces of caustic from the caustic wash drum are removed with the aid of coalescing media. Fresh water make-up is added to the depropanizer feed to absorb caustic droplets that carried over from the caustic wash drum. DuPont specifies the fresh water make-up/depropanizer feed inline mixer as a 316L SS five element Sulzer SMV type static mixer with a drop size of 300-400 microns. Note that this droplet size is based on Sulzer’s correlations and are not applicable to mixers provided by other vendors. Typical differential pressure across the mixer is 8 to 15 psi (0.5 to 1.1 kg/cm²). This pressure drop should be monitored with a differential pressure indicator to verify the integrity of the mixer.

If properly maintained and operated, a wet depropanizer treating system will produce on-specification LPG product with little or no corrosion in the depropanizer overhead system. However, poor depropanizer feed treatment will allow SO₂ to break through while supplying a source of water and accelerated corrosion will result.

One of the advantages of a wet depropanizer system is that it is fairly easy to make certain the caustic wash system is effective. The primary indicator of good caustic wash operation is the pH of the water collected in the depropanizer overhead accumulator boot. DuPont recommends sampling this stream at least once a day. With adequate treatment its pH should not fall below 6-6.5. It is also wise to monitor the iron content of the overhead accumulator water and the volume of water drained per day from the boot.

C. Refrigerant Recycle Pumps

Some refiners have reported fouling of refrigerant recycle pump suction strainers with ice crystals. This problem usually occurs during startup. It is caused by the presence of water in the flash drum, which normally operates at about 16°F (-9°C). The source of this water is usually traced to inadequate drying of the refrigeration system prior to startup or to poor operation of a wet depropanizer that allows water into the flash drum via the depropanizer bottoms stream.
There are two basic responses to this problem. First, the bottoms temperature of the depropanizer can be increased to flash more water out of the bottom of the tower. Second, the flash drum pressure can be increased such that the temperature in the process is not below freezing at 32°F (0°C). The former is the preferable of the two solutions since it does not result in hotter Contactor reactor temperatures.

IV. NET EFFLUENT TREATING AND FRACTIONATION

The net effluent stream from the reaction section contains traces of free acid, alkyl sulfates and di-alkyl sulfates formed by the reaction of sulfuric acid with olefins. These alkyl sulfates are commonly referred to as “esters.” Alkyl sulfates are reaction intermediates found in all sulfuric acid alkylation units, regardless of the technology utilized. If the alkyl sulfates are not removed they can cause corrosion and fouling in downstream heat exchangers and fractionation equipment.

DuPont’s net effluent treating section design has been modified over the years in an effort to provide more effective, more reliable, and lower cost treatment of the net effluent stream. DuPont’s older designs included caustic and water washes in series. Up until recently, DuPont’s standard design included an acid wash with an electrostatic precipitator followed by an alkaline water wash. Now DuPont alkylation units are designed with an acid wash coalescer, alkaline water wash and a water wash coalescer in series or with an acid wash coalescer followed by bauxite treating.

Design modifications, retrofits and changes to operating conditions of older net effluent treatment system designs can decrease corrosion and fouling in the downstream fractionation section. In addition, operating procedures such as on-line water washing of the Deisobutanizer or Isostripper can minimize the impact of fouling caused by poor net effluent treating. Contact DuPont if you would like any additional design and operating information specific to any alkylation unit’s net effluent treating system.

Maintain good treating operations.

A. Acid Wash Coalescer/Alkaline Water Wash/Water Wash Coalescer

With the acid wash coalescer/alkaline water wash/water wash coalescer design as shown on the next page (Figure 3); the net effluent stream is contacted with fresh acid in an in-line static mixer. The mixed stream is sent to the acid wash coalescer to separate the phases. DuPont specifies the in-line mixer as an Alloy 20 five element Sulzer SMV type static mixer with a droplet size of 300-400 microns. Note that this droplet size is based on Sulzer’s correlations and are not applicable to mixers provided by other vendors. Typical differential pressure across the mixer is 8 to 15 psi (0.5 to 1.1 kg/cm²). This pressure drop should be monitored with a differential pressure indicator to verify the integrity and performance of the mixer. To resist corrosion in the mixing zone, Alloy 20 is the recommended piping material from 4 feet (1.2 meters) upstream of the net effluent/acid mix point to the acid wash drum.
Mono-alkyl sulfates (acid esters) have a much higher affinity for sulfuric acid than for hydrocarbon. For this reason, it is possible to extract most of the mono-alkyl sulfates and some of the di-alkyl sulfates from the net effluent stream with fresh sulfuric acid. The acid wash utilizes the normal fresh acid supply to the reaction zone to extract both free acid and alkyl sulfates from the net effluent stream. The acid recovered in the bottom of the acid wash drum contains acid esters transferred from the net effluent. A portion of this acid is sent to the reaction section where the reaction intermediates can form alkylate and where the stream serves as a fresh acid supply to the Contactor reactors. The rest of the acid continuously circulates to mix with the incoming net effluent. The acid recirculation rate should be 3-5% by volume of the net effluent rate. Fresh acid is pumped from storage at a continuous rate to maintain the acid level in this drum.

In earlier designs, the acid wash drum was sized based only on gravity settling and an electrostatic precipitator provided insurance against acid carryover to the alkaline water wash. In DuPont’s current design, a two stage vessel with coalescing media is used in the acid wash allowing an appreciably smaller vessel to be used without the aid of an electrostatic precipitator.

The hydrocarbon flows from the top of the acid wash drum to the alkaline water wash drum, where any residual free acid, alkyl sulfates and di-alkyl sulfates are decomposed or neutralized. Effluent from the acid wash drum is combined with the hot recirculated alkaline water and passed through an in-line static mixer before entering the alkaline water wash drum.
The following saponification, hydrolysis and neutralization reactions are examples of those that occur in the alkaline water wash:

\[
\text{Saponification} \quad (C_4H_9)HSO_4 + \text{NaOH} \rightarrow \text{NaSO}_4(C_4H_9) + H_2O
\]

\[
\text{Hydrolysis} \quad (C_4H_9)HSO_4 + H_2O \rightarrow C_4H_9OH + H_2SO_4
\]

\[
\text{Neutralization} \quad H_2SO_4 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2 H_2O
\]

In the alkaline water wash drum, the hydrocarbon and aqueous phases are separated by gravity settling aided by coalescing media. Previous designs provided only gravity settling and a larger vessel was required. With the addition of coalescing media, a smaller vessel may be installed and overall capital costs of a new grassroots facility may be decreased.

The design of the alkaline water wash system is based on the olefin feed to the unit. When alkylating propylene, the alkyl sulfates formed are more stable than those formed when alkylating butylenes and amylenes. Therefore, many enhancements are made to the treating design when processing a high level of propylene.

The specification of the alkaline water wash in-line static mixer is based on the type of olefin feed processed. For units alkylating mostly butylenes and amylenes, DuPont specifies the in-line mixer as a Hastelloy C five element Sulzer SMV type static mixer with a droplet size of 300-400 microns. Note that this droplet size is based on Sulzer’s correlations and are not applicable to mixers provided by other vendors. Typical differential pressure across the mixer is 8 to 15 psi (0.5 to 1.1 kg/cm²). This pressure drop should be monitored with a differential pressure indicator to verify the integrity and performance of the mixer. For units alkylating propylene, DuPont specifies the five element in-line static mixer to have three spacers, one before each of the final three elements. The specified droplet size and differential pressure drop specification is not modified for propylene designs. The propylene design enhancements were developed in order to increase the contact time of the alkaline water and net effluent stream. To resist corrosion in the mixing zone, Hastelloy C is the recommended piping material 4 feet (1.2 meters) upstream of the net effluent/alkaline water mix point and Alloy 20 is recommended downstream of the static mixer to the drum.

The operating temperature of the alkaline water wash also depends on the olefin feed type processed. When processing butylenes and amylenes, DuPont designs the alkaline water wash to operate at a temperature of 120°F (49°C) to facilitate decomposition of the remaining alkyl sulfates. However, DuPont designs the alkaline water wash to operate at 160°F (71°C) for units processing a high level of propylene. Hot alkylate product is used in the alkylate/alkaline water exchanger to maintain this temperature. Low pressure steam can be used in the stress relieved circulating alkaline water heater to supplement the required heat addition.
Upstream of the alkylate/alkaline water exchanger, process water is added to the circulating alkaline water stream. Spent alkaline water is withdrawn and replaced by process water to control the conductivity of the alkaline water between 5,000 and 8,000 µmho/cm. Conductivity is a function of total dissolved solids (TDS) concentration. Excessive TDS (>10,000) can cause a tight emulsion that can result in carryover. Caustic is added continuously to the circulating alkaline water to maintain an alkaline water pH of 12 ± 1. The alkaline water recirculation rate should be 20-30% by volume of the net effluent rate.

The design caustic and process water makeup rates for the unit depend on the olefin feed processed. Units processing propylene are designed with twice as much process water makeup and caustic makeup to account for the increased difficulty encountered in treating operations. DuPont’s design values for these rates are very conservative, even for butylene or amylene operation.

The hydrocarbon from the alkaline water wash flows to the water wash coalescer where traces of caustic from the alkaline water wash drum are removed with the aid of coalescing media. Fresh water make-up is added to the net effluent to absorb alkaline water droplets that carried over from the alkaline water wash drum. DuPont specifies the fresh water make-up/net effluent in-line mixer as a 316L SS five element Sulzer SMV type static mixer with a drop size of 300-400 microns. Note that this droplet size is based on Sulzer’s correlations and are not applicable to mixers provided by other vendors. Typical differential pressure across the mixer is 8 to 15 psi (0.5 to 1.1 kg/cm²). This pressure drop should be monitored with a differential pressure indicator to verify the integrity of the mixer.

B. Bauxite Treating

Another type of treating available for net effluent involves the use of a bauxite treater as seen on the following page (Figure 4). The bauxite treater uses alumina (bauxite) as an adsorbent to remove all sulfate contaminants. Bauxite treating can operate as a stand-alone unit or in conjunction with an acid wash. It is generally accepted that an upstream acid wash will unload the bauxite treater resulting in fewer regenerations of the bed, which will give longer cycle times. Because acid carryover will cause pressure drop problems in the bauxite bed, an acid coalescer should be installed upstream of the bauxite treaters for protection. After the acid coalescer, the effluent stream flows down one of the bauxite treaters where the remaining acid and sulfate bearing materials are adsorbed onto the activated alumina.
Depending on a plant’s preference, regeneration of the bauxite beds can be timed strictly on the basis of pressure drop through the bed or may be set on a designated cycle length. In the regeneration of a bed, the spent bed is taken off line and its parallel twin is placed in service. The spent bed is drained of hydrocarbon and depressurized to the suction trap and flare. Initially, copious amounts of water are flushed into the bed to begin regeneration.

Because bauxite absorbs water, there is an initial heat of reaction that tends to heat the bed. In addition, water is heated by steam injection to slowly raise the water temperature. Elevated temperatures are required to enhance the removal of the organic sulfate contaminants from the bauxite adsorption sites.

As the bed regenerates, the organic sulfates are hydrolyzed to alcohol and sulfuric acid. After the water washing, the water that was absorbed by the alumina must be removed with a drying cycle. Either natural gas or vaporized isobutane can be heated and used to dry the bed, which reactivates the alumina sites. The bed is then cooled to ambient conditions and filled with net effluent awaiting its turn in the cycle.
A bauxite treater competes economically with a traditional aqueous treating system amidst several advantages and disadvantages when evaluating each system. Although it is believed that bauxite treating is superior in removing contaminants from the effluent stream, the real advantage is that water or caustic streams are no longer in contact with the reaction effluent at any time. Therefore, the streams are dry so that corrosion and fouling problems in the unit are virtually eliminated. In addition, free water in the recycle isobutane stream is eliminated which results in lower acid consumption and a slight increase in octane. Finally, operating with a dry system eliminates tight emulsions in alkaline water systems due to contaminants and prevents consequent tower fouling from salt and entrainment in the tower.

Other advantages exist for bauxite treating over the more common aqueous treating. For example, when bauxite treating is used, aviation fuel copper strip problems, due to inadequate effluent treating, are eliminated. Failures in the copper strip test typically result from trace sulfur dioxide that forms as a result of inadequate treating in the effluent stream.

Disadvantages also exist when comparing the bauxite system to the aqueous system. One disadvantage is that the bauxite system is a batch system and more labor intensive. Secondly, the regeneration of the beds creates a surge in the water treating system demand. Based on DuPont’s calculations, the total amount of water used during regeneration is approximately equal to that used for the alkaline water wash in a continuous system. The rate of water from the alkylation unit is much higher during the short washing cycle, which puts a higher load on the waste water treating system. However, the rate drops to nearly zero when regeneration is completed. Additionally, energy costs for regeneration increase the overall unit costs slightly. Also, the regeneration water is hot and has a low pH, which may lead to corrosion. Finally, the bauxite must be replaced sometime after 35 to 50 regenerations and topped off after every four regenerations.

C. Deisobutanizer Tower

The main purpose of the various net effluent treating systems is to prevent corrosion and fouling in the fractionation section. In most sulfuric acid alkylation units, the first tower in the fractionation section is the deisobutanizer (DIB). If alkyl sulfates are allowed to stay in the DIB feed, the high temperature in the bottom of the tower and the reboiler can cause them to react, forming solid "tars" and releasing SO₂. The solids can foul the DIB reboilers and lower trays. The SO₂ goes to the overhead system of the tower where it combines with water to cause corrosion. DIB reboiler fouling and corrosion in the DIB overhead system are some of the most common problems in sulfuric acid alkylation units.

The primary indicator of the effectiveness of the net effluent treatment system (except for bauxite treating systems) is the pH of the water collected in the DIB accumulator boot. With good net effluent treatment, the pH of this water should not drop below 6-6.5. DuPont recommends checking the pH of the DIB overhead accumulator at least once per day. It is also wise to monitor the iron content of the accumulator water and the volume of water drained per day from the boot.
Some refiners have taken steps to make up for inadequate net effluent treatment. Ammonia or some type of amine is sometimes added to the DIB overhead system to control pH and reduce corrosion. Filming agents are also used for corrosion control. The solids that foul the reboilers and lower trays are water soluble and some refiners have developed on-line water washing procedures for the column. These measures, while useful for extending run times and equipment life, are weak substitutes for good reactor and net effluent treatment operations.

Another common source of DIB fouling is aqueous carryover from the net effluent treatment system. The water vaporizes inside the tower leaving behind salt deposits, usually in the region of the feed tray. This problem can occur 1) if the TDS level in the water wash or alkaline water wash is not properly controlled, 2) if the water wash drum is undersized for the current throughput, or 3) if the water wash mixing device produces too many very fine droplets.

In the short term, this problem can be addressed by water washing the tower. In the long run, it is better to correct the problem in the net effluent treatment system. If the water wash or alkaline water wash drum is undersized, the usual remedy is to add a coalescer or electrostatic precipitator to eliminate the carryover. In addition, coalescing media can be added into the water wash drum to increase water removal from the hydrocarbon phase. In DuPont’s latest designs, a water wash coalescer is installed between the alkaline water wash drum and the DIB tower.

Contamination of the alkylation unit feed with aromatics can also cause water to carry over from the water wash. The aromatics are sulfonated in the reactors and can react with caustic to produce "soaps," which cause tight emulsion in the water wash. The only sure remedy for this problem is to keep aromatics out of the alkylation unit feed stream.

Most treatment problems are related to inadequate mixing of the organic and water (or organic and acid) phases. However, it is important to note that problems can also be caused by mixing that is too intense, forming an emulsion that will not separate in the drum. This can lead to caustic or water carryover that can foul the trays in the top of the DIB or may cause acid carryover from the acid wash that can cause severe corrosion.

In one alkylation unit, the mixing in the acid wash static mixer was too intense, causing acid carryover, while the mixing in the alkaline water wash was inadequate. Interestingly, pH control in the alkaline water wash appeared to function normally. The acid was apparently so finely dispersed in the net effluent that the alkaline water wash could not remove it. The problem was uncovered when the DIB feed line failed after less than two weeks of operation. Subsequent inspections also uncovered substantial corrosion of the alkaline water wash drum in the region of the interface. The problem was eliminated by correcting the intensity of mixing in the two treaters and by adding an electrostatic precipitator to the acid wash.
V. **ACID BLOWDOWN SECTION**

*Don't let acid sit stagnant.*

Stagnant acid is a potential source of fouling problems in the acid blowdown system. Level taps must be flushed periodically to prevent plugging and false level readings. It is also advisable to run the spare acid blowdown pump regularly to prevent solids from plugging the pump suction and discharge lines.

*Keep acidic streams dry and "wet" streams neutral. Use corrosion-resistant material where they mix.*

A sulfuric acid alkylation unit requires two relief systems. Wet, non-acidic vents and reliefs can go directly to the refinery flare but a separate system is required for acidic reliefs from the reaction section, the refrigeration section and the acid wash drum. A constant sweep of dry fuel gas or nitrogen on the acid relief system is advisable to prevent stagnation.

In current designs, the acid blowdown drum is the common collection point for the acid relief system. As shown in Figure 6 on the following page, the vent gas from the acid blowdown drum is sent to the blowdown vapor scrubber where it is scrubbed with caustic to neutralize acidic components (i.e. SO₂). Vapor from the blowdown vapor scrubber goes to the refinery flare.

The blowdown vapor scrubber is a carbon steel tower typically equipped with six trays. To prevent localized corrosion at the vapor feed nozzle, a section of the vapor feed line is constructed of Alloy 20 and equipped with a spray nozzle to begin neutralization of the vapor stream before it enters the scrubber. Caustic is recirculated from the bottom of the scrubber to the top tray and the inlet spray nozzle by the scrubber circulating caustic pump.
The acid blowdown drum receives spent acid continuously when the unit is in operation and is also the destination for spent acid from the Contactor reactors and acid settlers during shutdowns. Since the acid strength in the acid blowdown drum should not be below about 89 wt% for most units, corrosion of the carbon steel vessel should not be a serious problem. However, it is important to ensure that the spent acid remains dry. Potential sources of water must be eliminated through good design and operating practices.

The acid blowdown system should be dried thoroughly before it is put into service. Water could potentially enter the acid blowdown drum via the blowdown system from the reaction section because water and caustic connections are included for neutralization and flushing of the Contactor reactors and acid settlers during a shutdown. It is important for the water and caustic connections to be blinded when the acid blowdown drum is in operation and for the spent acid line to the blowdown drum to be blinded when water and caustic are in use.

It is also important to be aware of unusual sources of water. In most plants the acid knockout pot on the suction trap is connected to the acid blowdown drum. This should be fine in normal operation but in one unit, while alkylate was being recycled during startup, some water got into the suction trap because of a distillation upset. This water was sent to the acid blowdown drum, which became hot to the touch due to the heat of dilution. In other plants, sight glass drains from the reaction section are routed to the acid blowdown drum. Water could potentially enter the acid blowdown system via these drains during maintenance.
In another unit, water got into the acid sump drum after purging acid lines with water during unit startup. After acid was drained from the startup acid lines through the strong acid sewer, the acid mixed with water in the sump drum. The result was catastrophic failure of the drum.

Another potential source of water to the acid blowdown drum is reverse flow of caustic and water from the blowdown vapor scrubber. It is important for the vapor line from the acid blowdown drum to the blowdown vapor scrubber to be routed and sloped so that reverse flow of liquid caustic cannot occur. DuPont recommends to design a loop seal in this vapor line, elevated above the hydrocarbon relief header, so caustic would overflow preferentially to the flare knockout drum instead of to the acid blowdown drum in the event the blowdown vapor scrubber is flooded with caustic. The dry nitrogen or fuel gas sweep on the acid relief system should help prevent reverse flow of wet vapor from the scrubber, which could occur when the acid blowdown drum is being pumped down.

VI. **CONCLUSION**

Most corrosion and fouling problems in sulfuric acid alkylation units can be controlled by adhering to the fundamentals presented at the beginning of this paper. Many problems can be avoided by careful monitoring of operating parameters such as feed coalescer performance, treating system performance and the pH of water collected in distillation column overhead accumulators. Particular caution is warranted in plants operated significantly above design capacity. Corrosion and fouling should be considered as part of any plant expansion study.