

Understanding and responding to sulfuric acid absorption tower problems through process parameters

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A poorly performing absorbing tower can manifest in poor stack appearance, bad stick test results, bad acid emission testing results, as well as acid sulfate splashes on nearby structural steel members and grade. Absorbing towers are equipped with mist eliminator elements designed to remove acid droplets from the exiting gas stream and retain the acid inside the tower. It is easy to assume that poor demisting performance means poor mist eliminator design or condition. However, that may or may not follow. It has been said that 99% of “mist eliminator problems” are not due to problems of the mist eliminator itself. Though this percentage may not be accurate, experience suggests its order of magnitude is correct.

Compromised mechanical conditions inside the tower are often the cause of the problem. These include damaged gaskets and flanges, leaking or plugged seal cups and drains, tubesheet cracks and holes, and even wet air ingress into the downstream stack. All these conditions can produce overall system performance loss, which is often attributed to the mist eliminator elements. Acid or gas maldistribution due to packing fouling or acid distributor issues can also produce a negative effect. Since much has already been written about these conditions, the intent of this article is to address the process conditions—either from an out-of-control acid system or from faulty process data—that result in gas conditions that overwhelm the elements with mist loadings beyond the system design as well as vapor slip.

Poor performance indicators

Many of us have seen a smoky acid plant stack (Fig. 1A) as well as stick tests with heavy spotting or charring (Fig 1B).

A wet gas stack as discharged from a tail-gas scrubber may have a water vapor or steam plume based on water content in the stack gas and ambient conditions. The colder the weather, the heavier the steam plume. The steam, however, dissipates in short order. A trailing and persistent plume after the steam plume dissipation indicates opacity from acid droplets. Without a tailgas scrubber, a plume at the stack outlet indicates the presence of acid mist and compromised system performance. In many locations, stack opacity in and of itself is cause for an air permit violation. This normally draws a lot of attention from both inside and outside the plant



Fig. 1A: Stack opacity.



Fig. 1B: Spotted stick test results.

very quickly. Discolored stick test results are more of an internal matter but are still a cause for investigation.

Poor absorption tower performance can be broken down into two sources: acid mist and SO₃ vapor slip. The process may slip SO₃ gas to the stack, but this gas quickly hydrates to acid mist droplets once exposed to atmospheric moisture. From an environmental perspective, there is not much difference between vapor and mist emissions. These two sources may occur simultaneously or independently. A visible stack may occur in spite of clean absorbing tower stick test results. And a heavily spotted stick test may be obtained with a visibly clear stack.

Opacity

Stack opacity results from the refraction of visible light. The same refraction principle may be noted with a beam of light passing through a prism or sunlight forming a rainbow on a misty day. The wavelength of visible light is roughly 0.4 to 0.7 microns (or 400 to 700 nanometers, as shown in Fig. 2).

Acid droplets that fall within this range of visible light have the greatest impact on refraction and opacity. Larger acid droplets will not produce the same visible effect; and may produce no visible effect at all.

It takes a minimum droplet count in the stack exhaust to become visible. The larger the stack diameter, the greater the optical path.

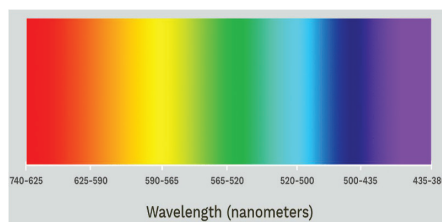


Fig. 2: Visible light spectra.

More droplets will be contained within the optical path. Hence the exhaust gas from a large diameter stack will be more readily visible than from a smaller stack with the same content of acid droplets. As larger plants with larger stack diameters have become more common, the number of opacity complaints has increased.

As noted earlier, submicron acid droplets can be formed within the process—inside the absorbing tower or downstream of the tower from SO₃ vapor slip—when mist is formed by contacting atmospheric moisture. From a practical and compliance perspective, it may not matter. But from a troubleshooting perspective, the distinction is important in identifying the root cause of the opacity.

Proper stack opacity reading requires certification per EPA methodology, described by EPA Method 9. This methodology requires: (1) the sun positioned at the observer’s back, (2) the observer being removed from the stack base by a minimum of two stack heights, and (3) the observer being certified as an opacity reader within a reasonable period of time. To be a certified stack reader, it does not matter if the cause of opacity is process generated mist or condensed acid vapor. But skilled sulfuric acid plant stack readers can bring value beyond determining compliance; they can also help determine root cause.

Some say that the shade of the plume can indicate the source of the mist. Condensed acid vapor is whiter in color, whereas process-generated mist has more of a grey hue. Some find the intensity of the sunlight has a more significant impact on plume color than the vapor vs. mist sourcing. Some say that if the plume starts with a gap above the stack outlet, then it is largely SO₃ vapor reacting and condensing in the air. Stack gas outlet velocity is normally 30 ft/s (0.9 m/s). There may be several hundredths of a second needed to mix the exhaust gas with enough ambient moisture to hydrate and form enough acid droplets needed to generate a visible plume. This travel time leaves a clear space below the plume initiation and the top of the stack. This can be observed in the stack exhaust shown in Fig. 1A. If the mist is process-generated before the stack or even inside the stack, then there is no gap, and the plume is instantly visible. Unfortunately, in many instances, the plume may be due to both mist and vapor, which can confuse the analysis.

Stack viewing is a quality check. Quantifying acid mist testing using EPA Method 8 testing supplemented with specialized equipment to separate mist loading from vapor concentration and categorize mist droplet sizes would be required for a more definitive analysis.

Stick tests

A stick test involves inserting a soft wooden stick like pine into an opening in the process gas duct exiting the strong acid tower for a predetermined duration—one to three minutes is common depending on the tower service. The stick is typically a rectangular cut 1" x 2" but other shapes and sizes have been used. There are two types of results from the stick test that are being evaluated:

1) Contact with strong acid droplets will leave a spot on the stick. The sulfuric acid is a strong dehydrating agent and will remove water from the wood's hydrocarbon-based structure, leaving black carbon spots. Spots will only be noted on the upstream surface where the impact of acid droplets occurs. The sides of the stick and the end tip may be charred by passing the stick in and out of the duct nozzle opening. This discoloration is disregarded. Only the largest droplets will leave spots that are visible to the human eye. Very small droplets (the kind that lead to the opacity noted earlier) will flow around the stick with the gas flow and not leave a visible mark. Hence, acid mist-generated opacity can occur even though the stick test is clear.

2) Contact with SO₃ vapor will result in slight browning or tanning of the stick. The more SO₃ present or the longer stick test duration, the more tanning will occur. There is always SO₃ vapor present due to vapor-liquid equilibrium. At 180°F (82°C) this may be ten to fifteen ppmv. There are no foreseen stick tests with "zero vapor." Unlike spots, tanning will occur on all exposed surfaces of the stick—front, back, and sides. Very long stick test durations likely will show signs of tanning. This would be expected with long-term exposure to the process gas.

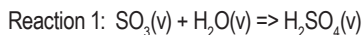
Upon completion of the test, results should be recorded quickly. A photo or several photos of the stick test details noting test date and time is a suggested minimum. This will allow future access to process data retrieval from that test period. Variables of interest would be plant rate, acid feed conditions, and mist eliminator pressure drop. Over time, the stick itself becomes less valuable. Acid spots can bleed through adjacent sections of wood, rainwater can wash away the spots, and process data will be forgotten.

A very badly performing tower may generate a completely black stick, either from many

spots or from deep tanning. Repeating the stick test with a shorter time duration is advised to allow differentiation of the spots and obtaining a "readable" stick test result.

Causes of mist formation

Gas from the converter section after two or three catalyst passes has most of the SO₂ oxidized to SO₃. This gas is cooled prior to the absorption step. Water vapor, to the extent present, reacts in the gas phase to generate sulfuric acid as follows:



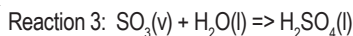
The greater the extent of gas cooling, the more acid vapor is produced.

Inlet gas temperature to the absorbing tower is maintained above the condensation point of this sulfuric acid vapor—the dew point temperature. This includes maintaining colder heat exchanger metal surfaces above the dew point temperature. As this gas cools within the absorbing tower, the sulfuric acid vapor can condense into small droplets or can be absorbed into the bulk fluid.

Condensation is noted as follows:



To the extent that droplets are produced, much of the resulting mist is submicron in size. It is not readily absorbed by mass transfer means (the irrigated tower packing). To a large degree, mist reaches the demisting section downstream of the packing. The balance of the SO₃ gas is absorbed into the bulk circulating acid in the simplified reaction as follows:



The gas inlet temperature was noted to be high enough to avoid the condensation of sulfuric acid vapor prior to entering the tower. Too high of a gas temperature can be counter-productive, as it overheats the bulk acid on a local level and vaporizes acid and water from the bulk. Effectively this reverses Reaction 2. As the gas cooling continues upwards through the tower packing, some or much of this vapor likewise condenses per Reaction 2 and forms additional submicron mist.

Both Reactions 2 and 3 are means to generate sulfuric acid in the liquid form. The design intent is to generate sulfuric acid in liquid form by Reaction 3. The hotter the gas inlet temperature and the colder the acid temperature within the tower, the greater the potential for submicron mist generation. This is often called shock cooling and is defined by the extent of Reaction 2 becoming increasingly significant relative to Reaction 3. Hundreds of milligrams of submicron mist per cubic foot of gas can be produced in this fashion.

To minimize the extent of submicron mist formation within the tower, the objective is to

minimize sulfuric acid vapor present in the inlet gas stream and tower bottom. This requires: (1) minimizing water vapor content in the incoming gas stream and (2) reducing the temperature of the incoming gas stream below 450°F (232°C); below 400°F (204°C) is preferred. In modern plants focused on greater energy recovery, the high gas temperature condition is not normally an issue.

Causes of vapor slip

The absorbing tower removes SO₃ from the process gas stream by absorbing it in strong acid.

There is a vapor-liquid equilibrium relationship between the sulfuric acid concentration and the SO₃ content of the gas phase. The absorption of SO₃ is not ever completed but is limited by: (1) vapor-liquid equilibrium and (2) the effectiveness of the mass transfer (packing) section.

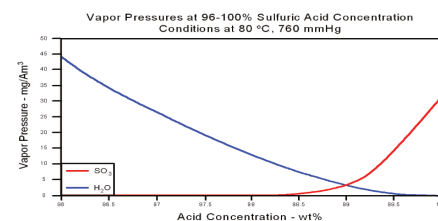


Fig. 3: Vapor pressure correlations.

The equilibrium relationships are fairly well understood. By energy and material balance from the process design, the acid inlet and outlet compositions and temperatures of the packed section are determined. The conditions at the top of the tower packing often limit the absorption effectiveness. The partial pressure of both water vapor and SO₃ with respect to acid concentration at the tower inlet can be observed in Fig. 3.

Data is plotted at 176°F (80°C). This is a normal set point and will be discussed later. Vapor pressure of water is normally present in meaningful concentrations over the designed operating range. Vapor pressure of SO₃ begins to climb to meaningful concentrations above 98.5 wt% acid. High water content in the acid at the tower top (acid concentration below set point) also means high water content at the tower bottom. Note that the water vapor pressure must also be considered at the tower bottom. High water vapor content at the tower bottom can lead to mist formation as was discussed earlier. Hence, the normal acid concentration control point for the acid feed can readily be observed here.

Contact between gas and acid streams to allow SO₃ absorption occurs in a packed bed.

The typical packing type used is three-inch ceramic Intalox Saddle. Evaluation of the tower mass transfer performance may be done using a McCabe-Thiele diagram considering: (1) the system equilibrium line with the operating line (with slope of the operating line based on L/G ratio) providing the number of theoretical absorption stages needed and (2) the height of each theoretical stage which is largely based on the mass transfer coefficient of the selected packing size and style.

The McCabe-Thiele diagram for absorbing processes can be found online and in textbooks. The number of stages required is equal to the number of steps or partial steps connecting the operating line endpoints with the equilibrium line. This diagram represents a perfect world with uniform gas and acid distribution. An example diagram is shown in Fig. 4.

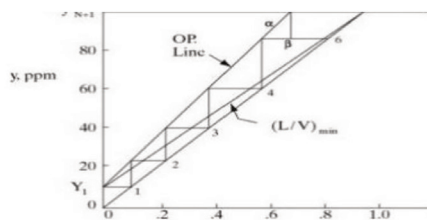


Fig. 4: McCabe-Thiele example diagram.

It is not common to produce such a drawing for each strong acid tower design. Rather, design norms and practices developed over decades lead us to where we are today in terms of process design parameters as well as distribution efficiency and required packing height. However, reverting to these first principles can be done for off-design operating conditions.

An acid temperature of 82 °C (180 °F) and an acid concentration of 98.5 wt% are common control set points to operate the top of the tower to maximize the mass transfer effectiveness, as seen in Fig. 3. With a typical L/G ratio based on controlling bottom acid temperature and acid concentration, for instance 113 °C (235 °F) and 99.5% sulfuric acid concentration, the operating line of a McCabe-Thiele diagram is established. For these conditions, two stages of mass transfer are adequate for absorption. The height of a mass transfer stage (HTU) depends on the type and size of the packing selected as well as the process conditions. Normal HTU for a strong acid tower designed to modern gas velocity and acid irrigation rates and using 3-inch Intalox saddle packing is two to three feet. Six feet of packed height is possible for a tower design and has been used. However, engineering design margins may add some additional packed height for: (1) unique design conditions, (2) real-world inefficiencies for acid or gas maldistribution, or

(3) process measurement error. Unique conditions might include higher plant site elevations and / or frigid winter operating temperatures.

Operating deviations from these optimum design conditions may be by intent, by loss of process control, or by poor instrument readings. If these deviations allow the equilibrium line to move in an unfavorable direction—closer to the operating line with higher acid inlet temperature or concentration—then more theoretical stages are required to achieve the same absorption effectiveness. Some benefit may be obtained by increasing packed height, by changing packing to something with a higher mass transfer coefficient (without being hydraulically problematic), or reducing the acid temperature to attempt to regain the expected equilibrium line given concentration changes. With an existing tower and fixed dimensions, the ability to accommodate these changes is limited. And colder acid temperatures can generate more submicron mist as was noted earlier.

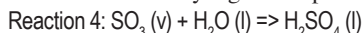
Colder acid temperatures may also adversely impact kinetics. The absorbing tower chemistry like all or nearly all reactions is temperature-dependent. Reaction rate is expressed by the Arrhenius rate equation in Fig. 5.

$$k = Ae^{\frac{-E_a}{RT}}$$

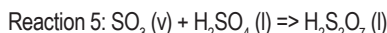
Fig. 5: Arrhenius Rate Equation

T is the temperature. k is the reaction rate. A is the Arrhenius factor which has some temperature dependency to it. E_a is the reaction activation energy. And R is the universal gas constant. This conveys the temperature dependence and shows that higher temperatures generally lead to faster reaction rates.

The simplified sulfuric acid absorption reaction is a chemical reaction with the reaction rate being a function of temperature. Whereas equilibrium is favored by lower temperatures, reaction rate is favored by higher temperatures.



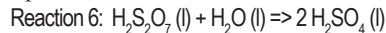
This reaction is simplified and actually occurs in two chemical steps with the first step occurring at the film surface to produce oleum. This is due to the relative scarcity of water in the 98.5% acid at the film surface. Reaction 4 may proceed simultaneously until the water is consumed. The rest of the reaction follows Reaction 5.



Oleum at the surface then diffuses from the film into the bulk solution where adequate water is found to complete the reaction. These

two reactions occur in short succession and the presence of the oleum intermediate is not long lived.

Diffusion is also temperature dependent and occurs more rapidly at higher temperatures. Once in the bulk solution the reaction is completed per Reaction 6.



As a rule of thumb, reaction rate doubles for an increase in temperature of 10°C. Following this rule of thumb, taking an acid tower designed to operate at 180°F (82°C) one can estimate the reaction rate reduction with falling temperature. The reaction rates slow to roughly half at 158°F (70°C) and roughly one-quarter the design rate at 140°F (60°C). This is a commonly observed issue during start-up when the acid temperature is not up to its design point. The exhaust gas may be opaque for two or three hours until the acid system can be brought up to temperature from absorption reaction heat and acid cooler bypassing. Bypassing acid around the acid coolers to the maximum extent possible during short plant outages has been advised. Larger operating complexes with multiple plants may transfer hot acid from an operating facility to charge the acid system with warm to hot acid for restart. This reduces or can eliminate the visible stack immediately after restart.

Conclusion

Performance problems in sulfuric acid absorbing towers are common. Initial evaluation of the issues may point to the mist eliminators. As part of the mist eliminator troubleshooting, a review of the process parameters can be expected. This review may include verification of the data through independent means as well as a systematic testing protocol to vary these parameters over a period of time in an effort to find a “sweet spot” for tower operation. Parameters of interest may include acid flow, temperature, concentration, and gas inlet temperature. One may be able to select the most probable cause from tower pressure drop data as well as stick test and stack appearance.

Failing to identify the root cause from this effort, a more intrusive tower investigation may be required, involving shutdown and tower entry to perform the classic mist eliminator troubleshooting inspections of gaskets and flanges, seal cups and drains, tubesheet welds etc., as well as acid distribution and packing. But this effort might be postponed until optimization of the process parameters has been exhausted.

For more information, please contact Walter Weiss (walter.weiss@elessentct.com) of Elessent Clean Technologies or visit the company's website at ElessentCT.com. □