Sulfuric Acid Mist Control After Thermal Oxidation: Operational Insights from Candle Filters and WESP Systems

Andy Olds

Envitech, Inc., San Diego, CA

Abstract

Petrochemical plants and small refineries often use thermal oxidizers to manage hydrocarbon liquid or gaseous waste. When the waste contains sulfur, thermal oxidizers often require wet scrubbers to neutralize and remove sulfur dioxide (SO_2). However, the flue gas also contains sulfur trioxide (SO_3), which reacts with moisture in the gas to form sulfuric acid (H_2SO_4). Sulfuric acid generated from the reaction of sulfur trioxide with water forms a submicron aerosol that can pass through downstream wet scrubbers.

With new regulatory focus on PM2.5 and sulfuric acid emissions, some facilities that use thermal oxidizers to combust vents containing sulfurous hydrocarbons are now required to add control equipment to address sulfuric acid.

This paper presents operational history from a small refinery thermal oxidizer system where a candle filter was installed downstream of the wet scrubber. While the candle filter exceeded the capture efficiency required for sulfuric acid, the refinery encountered substantial operational issues due to unanticipated fouling. These issues and their implications will be reviewed in detail. Wet electrostatic precipitators (WESPs) with integrated packed bed absorbers will be explored as an alternative technology for simultaneous sulfur dioxide and sulfur trioxide removal.

Introduction

Refineries convert hydrocarbon feedstocks into useful products, such as fuel and oil, or monomers for other petrochemical products. The feedstocks often contain sulfur, an impurity that must be separated from the hydrocarbons for beneficial use. Refineries use hydrodesulfurization to release the sulfur from the feedstock, producing a vapor stream containing hydrogen sulfide (H_2S). Most refineries convert the hydrogen sulfide to sulfur via a sulfur recovery unit (SRU) and tail gas treament unit (TGTU).

In some cases, small vent streams containing hydrogen sulfide or sour hydrocarbons are not economical to recover sulfur. In those cases, it is common to divert the sour gases to a thermal oxidizer prior to atmospheric discharge. A thermal oxidizer combusts the hydrocarbons to yield an offgas containing carbon dioxide (CO_2), water and sulfur dioxide (SO_2). If emissions requirements for sulfur are not met, facilities employ caustic scrubbers to remove sulfur dioxide, generating liquid waste containing sodium sulfite. Reaction of sodium sulfite with dissolved oxygen forms non-toxic sodium sulfate, safe for discharge.

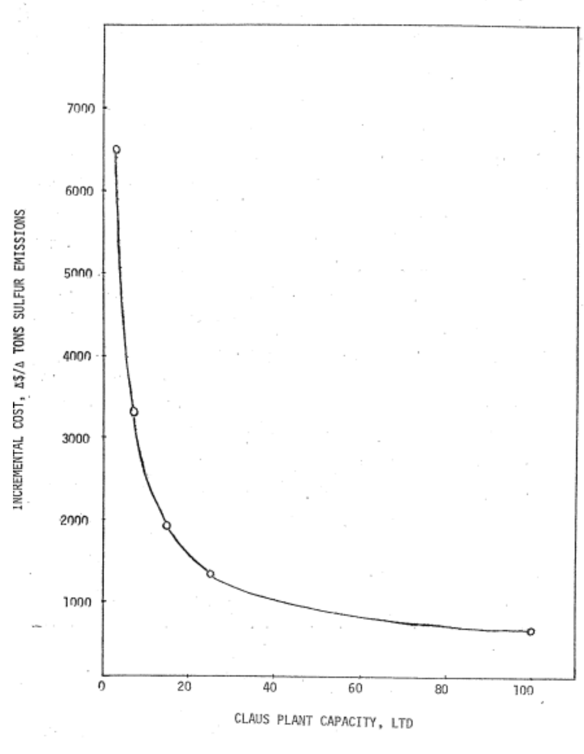
One troublesome byproduct of the thermal oxidation of hydrogen sulfide by oxygen is the formation of sulfur trioxide (SO_3). Sulfur trioxide reacts with water vapor to form sulfuric acid (H_2SO_4), a strong, corrosive acid. Further, with a dewpoint well above 212 °F (100°C), sulfuric acid condenses and passes through the caustic scrubber as a sub-micron particulate. Local regulatory bodies have begun to limit sulfur trioxide and sulfuric acid emissions, primarily through PM2.5 attainment requirements.

This paper focuses on the results from a small refinery where a candle filter was installed to address sulfuric acid emissions. While the candle filter exceeded the capture efficiency required to meet the regulatory requirements, the refinery encountered unanticipated operational issues with fouling. This paper discusses the results, possible causes of fouling, and an alternative technology for sulfuric acid capture that the refinery is currently evaluating.

Background

Sulfur is a pernicious contaminant of hydrocarbon feedstocks. Chemically similar to carbon and abundant in Earth's crust, sulfur forms a willing carbon-substitute in hydrocarbon bonds. Refiners refer to crude oil as sweet or sour; sweet crudes (<0.5% sulfur) are easier to refine, while sour crudes require extensive desulfurization and can only be refined by large, complex refineries. These refineries use hydrodesulfurization to liberate sulfur from the carbon chain and generate hydrogen sulfide (H_2S). Most refineries use the Claus process as part of its sulfur recovery unit (SRU) to convert the hydrogen sulfide to elemental sulfur, which is exported to make sulfuric acid for a wide range of processes.

Figure 2.1. Incremental Annual Cost vs. Plant Capacity



Small, simple refineries and lube oil refiners often do not generate sufficient sulfur to justify the capital and operating cost associated with an SRU. The EPA added amendments to the Clean Air Act in 1977 to define a small refinery to account for the additional hardship of installing the Claus process for sulfur recovery. The EPA based its decision on the figure to the right, which shows the dramatic cost increase to implement the Claus process for small refiners, shown in 1978 dollars.[1] The EPA used the inflection point of 20 long tons per day to establish the criteria defining a small refiner, and the EPA relaxed standards for sulfur release.[2] Some of these small refineries combust off-gases with a thermal oxidizer and use a wet scrubber to capture sulfur dioxide emissions.

One small refinery generates a variety of hydrocarbon gases from process heaters, flux tanks, storage tanks, and vacuum distillation columns and used a thermal oxidizer to combust vents from its processing units. Stack testing showed significant amounts of sulfur

---

[1] "Standards Support and Environmental Impact Statement Volume II: Proposed Standards of Performance for Petroleum Refinery Sulfur Recovery Plants," EPA-450/2-76-016-b, (January 1978)

[2] Standards of Performance for New Stationary Sources, 40 C.F.R. § 60.102a (2016)

dioxide and sulfur trioxide. New source rules related to ground level sulfuric acid drove a requirement for very low acid emissions at the stack, and the regulating body determined the refinery was non-compliant for both sulfur dioxide and sulfuric acid emissions. The refinery chose to install a packed bed absorber downstream of its existing thermal oxidizer for sulfur dioxide control and a candle filter for sulfur trioxide/sulfuric acid mitigation.

Combustion

When combusted in a thermal oxidizer, hydrocarbons containing sulfur form two significant sulfur based acid gases: sulfur dioxide (SO_2) and sulfur trioxide (SO_3). Sulfur dioxide is a noxious chemical, more acidic and corrosive than carbon dioxide. Sulfur trioxide reacts with water to form sulfuric acid (H_2SO_4). It is very corrosive, requiring exotic metals when long life is required. Up to now, regulatory agencies have focused on the emissions of sulfur dioxide, the major form of sulfur exiting the thermal oxidizer. The use of wet gas scrubbers has provided a reliable method to meet sulfur dioxide emission requirements with uptimes exceeding several years with appropriate redundancies.

Regulatory agencies have begun to shift their attention to sulfur trioxide and the resulting sulfuric acid emissions, which are reported as particulate in a stack emissions test. Once in the atmosphere, it contributes to air pollution as PM2.5 and acidifies public waterways.

The relative concentrations of sulfur dioxide and sulfur trioxide formed from combustion depend on the operating characteristics of the thermal oxidizer. Thermodynamically, most of the sulfur forms sulfur dioxide in the thermal oxidizer, with 1% to 5% of the sulfur forming sulfur trioxide. Trioxide formation increases at lower temperatures; hence, waste heat boilers or catalytic oxidation can increase the amount of trioxide generated.

Sulfuric Trioxide/Sulfuric Acid Aerosol Mitigation Technologies

While regulation of sulfur trioxide/sulfuric acid aerosol is relatively new to the petrochemical industry, it has a longer regulatory history in the mining and metallurgical processing industry as well as in the manufacture of sulfuric acid. In these industries, two technologies have dominated control of emissions: candle filters and wet electrostatic precipitators. Both are very efficient at capturing aerosols and sub-micron particulate with significant advantages and disadvantages.

Candle Filters

A candle filter is a randomly oriented, dense bed of small-diameter fibers installed between an inner and outer cage. Gas flow through the candle filter can either be outside-in or inside-out, with the direction of flow affecting the mechanism of collecting and draining the captured aerosol. Units can either hang on or be supported from a tube sheet in a pressure vessel. Depending on the configuration, candle filters can either self-drain or empty into liquid traps. The photo to the left shows a top-down view of an inside-out, top mounted candle filter, bolted to the bottom tube sheet and removable by crane from overhead.

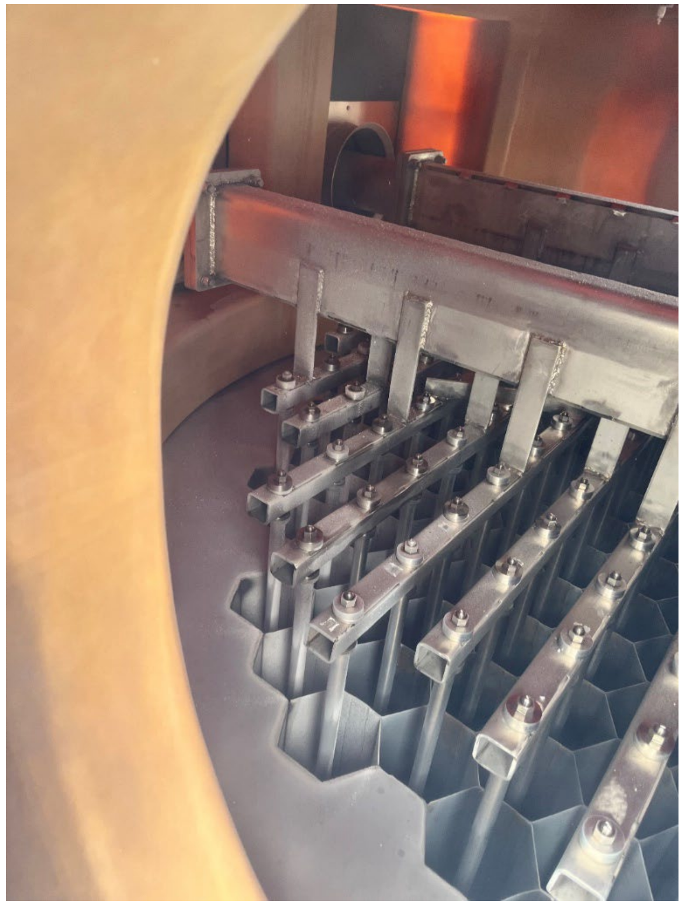
Candle filters make use of the principle of Brownian motion to capture aerosols. Brownian motion is caused by gas molecules randomly colliding with particles sufficiently to alter the particle's path. Brownian displacement, while random, increases with decreasing particle size, making it an excellent capture mechanism for ultrafine (<1-micron) particulate.[3]

Unlike traditional sieve or membrane filters, where particulate builds on a single barrier layer, candle filters allow particulate to penetrate the body of the filter. Candle filters are sized to produce laminar gas flow through the filter media. The dense bed of small-diameter fibers generates an enormous amount of surface area. The wobbles invoked by the Brownian motion cause the slow-moving aerosol to collide and become captured by the dense bed of fibers. The collected aerosols coalesce and the collected liquid drains by gravity. Candle filter efficiency is a product of the amount of surface area provided for capture.

Wet Electrostatic Precipitators

[3] Koch-Glitsch. (2025). *Mist Elimination and Phase Separations*. https://kochind.scene7.com/is/content/kochind/Mist-Elimination-and-phase-separation

A wet electrostatic precipitator consists of an array of high voltage and grounded electrodes. The precipitators are either tubular or plate-type. Tubular precipitators consist of an outside, grounded, collecting electrode and an inner, high voltage charging electrode. Plate type precipitators consist of a series of parallel, grounded collecting plates with wire electrodes in between the plates. Gas flow can either be up-flow or downflow with slight differences in design and minimal differences in performance. The photo to the right shows a tubular precipitator with a hexagonal collecting electrode and a rigid mast high voltage electrode.



Wet electrostatic precipitators employ the principle of electrostatic deposition to capture aerosols. The high voltage electrodes and grounded electrode generate a strong electrical field. Emitter discs ionize the gas, forming a corona discharge which charges the particles. The charged particles then migrate to the grounded electrode with assistance from the electrical field.

The term wet refers to the conditions of the gas entering the precipitator and the method of cleaning. Wet electrostatic precipitators operate best in a moist, fully-saturated environment. The moisture wicks the particulate from the surface of the collector. Additionally, the moist environment reduces issues associated with particulate resistivity. Water is commonly used to remove particulate. According to the EPA, “Wet ESPs are typically employed when gas streams contain sticky particles with low resistivity.”[4] Wet electrostatic precipitators are typically located downstream of wet scrubber devices like Venturi scrubbers or packed bed absorbers.

Technological Differences

The two technologies produce similar results through different mechanisms. Naturally, there are advantages and disadvantages to each approach.

For a candle filter:

- Removal efficiency is scalable and a function of filter surface area.
- Changes in efficiency are predominantly due to variance in gas flow.

[4] Monitoring by Control Technique - Electrostatic Precipitators. (2025). In EPA.gov. Retrieved August 1, 2025, from https://www.epa.gov/air-emissions-monitoring-knowledge-base/monitoring-control-technique-electrostatic-precipitators.

- Operational cost is dependent on gas flow and the resulting pressure drop and consumption of filters.
- Soluble and liquid aerosol trickle through fibers via gravity and atomized wash water sprays.
- Filter life governed by the amount of impurities in the gas (coke or iron contamination stemming from corrosion)

For a WESP:

- Removal efficiency is scalable and a function of collector area.
- Gas flow and composition can impact efficiency.
- Operational costs can vary significantly due to changes in the gas conditions and particulate loading, which can either improve or impair corona discharge and thus power consumption.
- Consumes relatively low pressure drop, minimizing upstream and downstream mechanical costs.
- Soluble and liquid aerosol drain from the collector's flat surface is augmented by directed wash water sprays.

In general, the upfront capital expenditure for candle filters is generally less than for a wet electrostatic precipitator for the following reasons:

- Candle filters use lower-cost materials.
- Candle filters consume less space for similar removal efficiencies.
- Wet electrostatic precipitators require costly high voltage components.
- Wet electrostatic precipitators demand more custom engineering and fabrication costs.

Due to its lower upfront capital cost, early adopters of sub-micron control equipment have shown a preference for candle filters.

Small Refinery Equipment Train

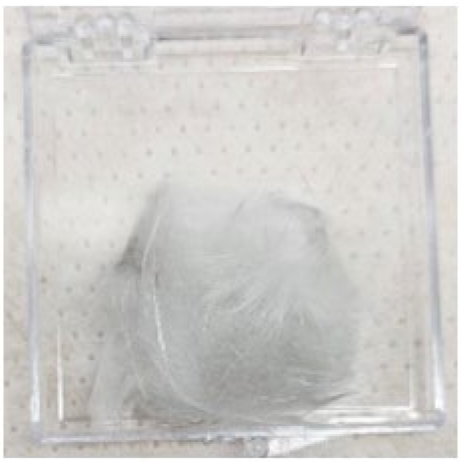
After the refinery was unable to meet new sulfur dioxide and sulfuric acid emission requirements with its existing thermal oxidizer, the refinery chose to use existing equipment to address hydrocarbon emissions and add-on equipment to mitigate sulfur dioxide and sulfuric acid emissions.

The refinery directs vents from process heaters, flux tanks, storage tanks, and vacuum distillation columns to an existing thermal oxidizer. The thermal oxidizer operates at a temperature of 1800°F (982 °C). Stack test reports showed very low carbon monoxide emissions. The refinery did not anticipate substantial particulate emissions, although later did concede that smoke was occasionally released from the stack.

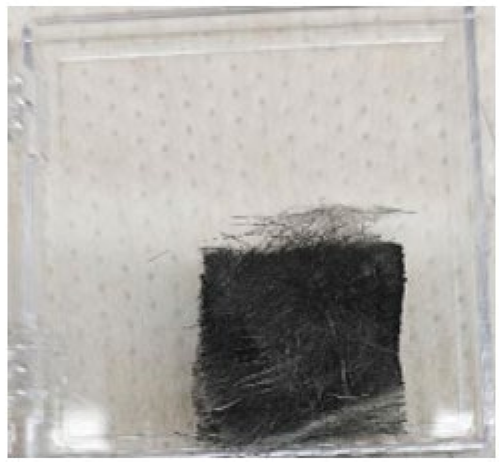
The refinery chose an equipment train consisting of a Venturi-quencher, packed bed absorber, and a candle filter to address sulfur dioxide and sulfuric acid emissions. The purpose of the Venturi-quencher is to cool the gas to its adiabatic saturation temperature using recirculated water. The Venturi-quencher operates with a pressure drop of 3- to 5-inches of water (7.5 to 12.4 millibar). This type of low energy scrubber effectively removes particulate 5-micron and larger in size. Downstream of the Venturi-quencher is a packed bed absorber. The packed bed absorber is a counter-current flow device where recirculated, neutralized liquid absorbs sulfur dioxide from upward flowing gas. Liquid from both the Venturi-quencher and packed bed absorber fall to the scrubber sump, which recirculates the liquid back to both pieces of equipment. Upon exiting the packed bed absorber, gas flows through a set of top hung, inside-out candle filter to remove sulfuric acid aerosol. A cleaning spray header sporadically adds water to the gas to wash accumulated liquids and soluble salts from the candle filter fibers.

Operational Performance

The lube oil refiner started operating the new scrubber equipment in 2020. Within a matter of days, the differential pressure began to increase across the candle filter, indicative of fouling. Within a month, the differential pressure across the candle filter exceeded the manufacturer's recommendations. Inspection of the filter showed black soot penetrating through the candle filter. See the photo below showing clean and dirty filter media, side by side.



Clean Filter



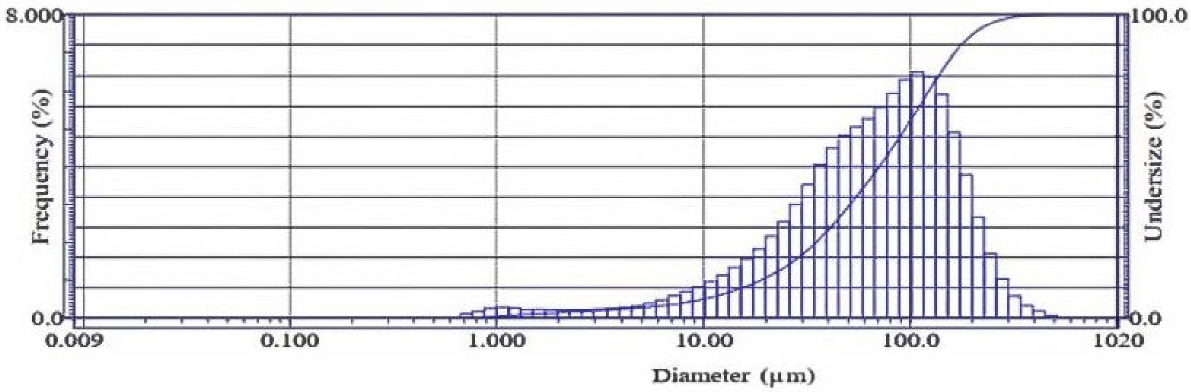
Dirty Filter

The refinery assessed the performance of the candle filter via a stack test despite the ongoing operational issues. The stack test found a 91% reduction in sulfuric acid aerosol as compared to initial tests performed in 2018 without air pollution control equipment. The reduction matched performance guarantees and met regulatory compliance requirements.

While the stack test was successful, the operations staff continued to struggle with the short lifetime of the candle filter. The operations first focused on improving combustion performance. The operator's engineers tuned the burners and optimized flame arrestors and knockout pots upstream of the thermal oxidizer. Despite the changes, soot continued to plague operation of the candle filter. Reported filter life ranged from one week to one month, compared to a normal expected lifetime of two to five years. The replacement cost of the filter is $12,500. The refinery spent an estimated $900,000 on replacement candle filters alone in the first year of operation, a much higher operational expense than anticipated. Candle filter replacement also generated 200 hours of downtime in the first year.

The refinery collected additional data to review its initial assumptions. In the design phase, refinery engineers did not expect to encounter significant particulate. Rather, they expected the thermal oxidizer to completely combust incoming hydrocarbons based on very low carbon monoxide levels found at the stack prior to the addition of air pollution control equipment. Later testing found this to be inaccurate.

The refinery sampled particulate in the thermal oxidizer outlet ductwork and found a range of particulate from 1 to 500 microns, as shown in the distribution below.



Thermal Oxidizer Particle Size Distribution

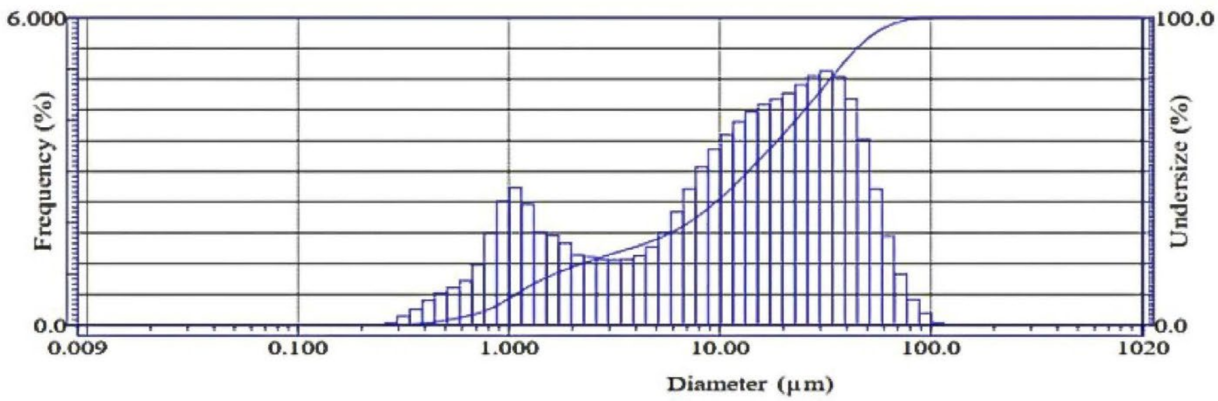
The refinery first attempted to address the soot by optimizing the thermal oxidizer and upstream equipment. The refinery cleaned and optimized its knockout pots to minimize liquid and solid carryover to the thermal oxidizer. They added insulation to the waste gas feeds into the thermal oxidizer to prevent condensation. Operators also tuned the fuel to air ratio and adjusted operating temperatures to try to reduce soot formation. Despite the changes, the candle filter lifetime continued to be an issue.

The refinery turned its attention to the new air pollution control equipment to assess its performance. The air pollution control equipment consists of a low pressure drop Venturi-quencher and a packed bed absorber prior to the candle filter. The Venturi-quencher quickly cools the gas to enable the use of a fiberglass vessel for the packed bed absorber. The Venturi-quencher operates with approximately 3 to 5 inches (7.5 to 12.4 millibar) of pressure drop, which should effectively remove particulate greater than 5-microns. The primary purpose of the packed bed absorber is to remove sulfur dioxide. The initial stack test confirmed it achieved its objective. Studies also show that a packed bed absorber removes most particulate greater than 10-microns, adding a secondary cut of particulate emissions.

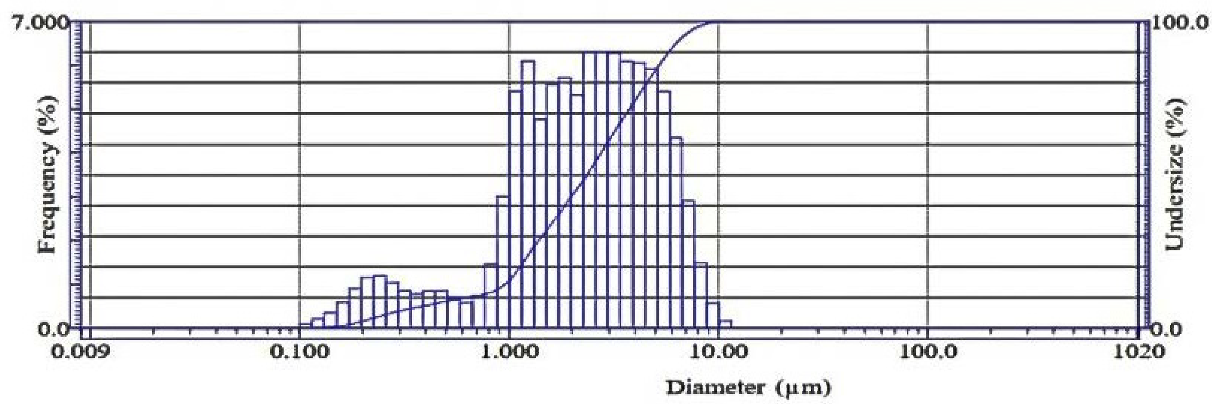
The refinery assessed the performance of the wet scrubbers by performing a mass balance around particulate and assessing removal in the scrubber and candle filter sump, as well as the stack. Recirculated water for the Venturi-quencher and packed bed absorber both collect in the scrubber sump. Wash water for the candle filter collected in a separate sump. The refinery also sampled the scrubber and candle filter sumps to generate particle size distributions of the particulate captured. Also, the refinery collected a sample of the candle filter and performed an element analysis of the particulate recovered.

The mass balance of particulate yielded interesting, though predictable, results. The test showed the Venturi-quencher and packed bed absorber removed 75% to 85% of the incoming particulate. Candle filter sump particulate inflows (via the wash cycle) showed particulate rates of 0.0020 lb/hr (900-mg/h), with occasional spikes to nearly 0.022 lb/hr (10,000-mg/h). Estimated particulate emissions from the incinerator were 0.6-grains per 1000-dry standard cubic feet (2.5 mg per Nm^3); very low, but over time, sufficient to plug the candle filter.

The particle size distributions in each sump are consistent with the size range each device captures effectively. Compared to the sample collected from the thermal oxidizer walls, the sample collected in the packed bed absorber is smaller, though with a similar wide distribution. Most of the particulate capture is greater than 5-microns, as anticipated. A second maxima around 1-micron might reveal the capture of particulate via diffusional processes with coagulation in the sump. Compared to the scrubber sump particle size distribution, the candle filter sample shows a narrower distribution and a much smaller average size, confirming the scrubber targets larger particulate. Like the scrubber, the candle filter shows two maxima, one centered around 5-micron reflecting the particulate passed by the scrubber and a second distribution of submicron particulate formed by metallic condensation. The distributions for each sump are shown below.



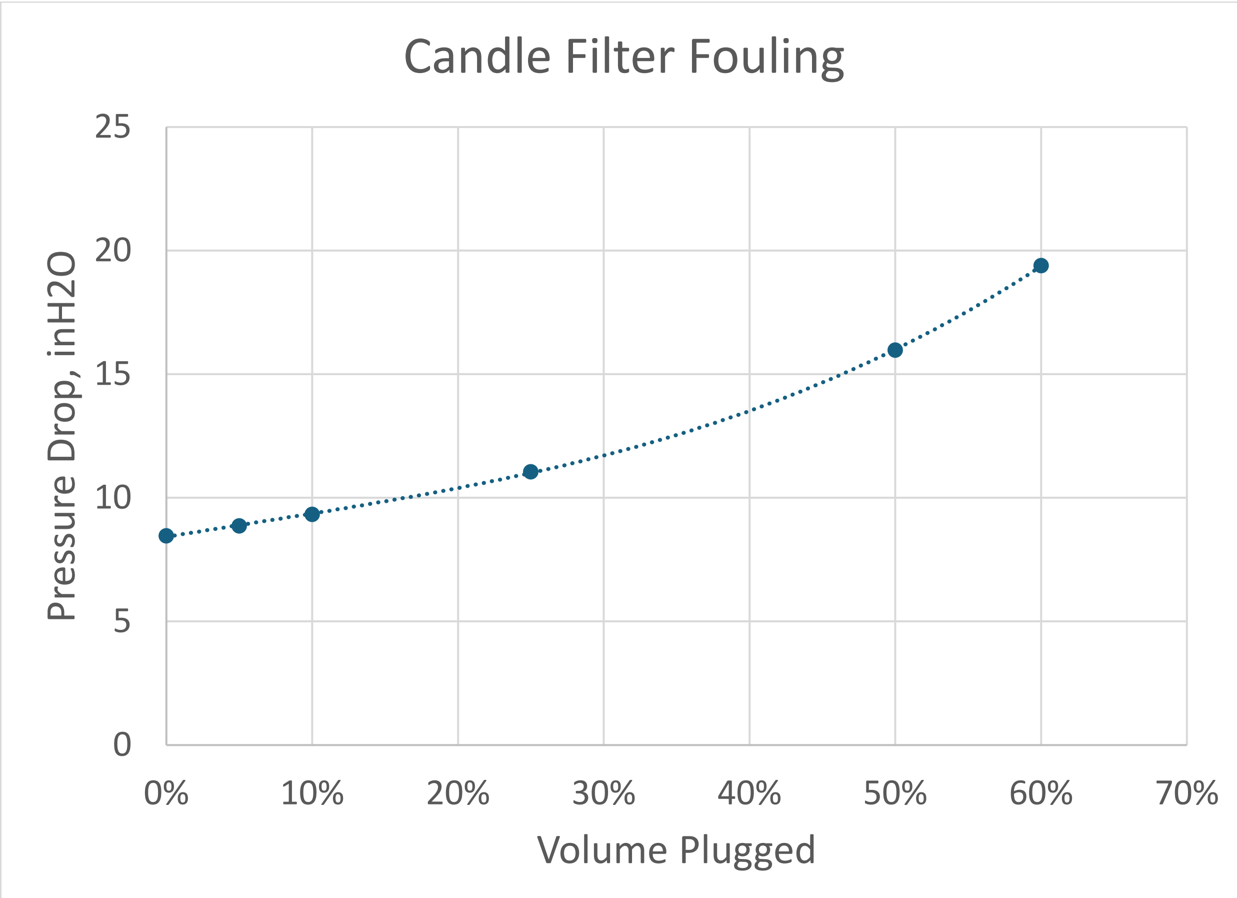
Packed Bed Sump Particle Size Distribution



Candle Filter Sump Particulate Size Distribution

The refinery also performed an elemental analysis of the candle filter element after sonication (ultrasonic waves to breakdown particles). As expected, the primary cation was sulfur, indicating the candle filter were effectively removing sulfuric acid aerosol. However, twenty other ions were found, including significant concentrations of boron, calcium, silicon, and sodium. Silicon composed nearly 10% of the cation mass, and calcium over 3%. Silicon likely took the form of silicon dioxide, an insoluble particulate that forms submicron aerosol when combusted. Calcium may have been introduced in various unsoftened water sources within the system. Reaction of calcium with sulfuric acid forms calcium sulfate, or gypsum, an insoluble particulate. Silicon and calcium likely contribute to the fouling. The candle filter manufacturer provided additional data to quantitatively assess the degree of fouling.

The graph below shows the anticipated pressure drop through the candle filter based on volume plugged. When it reaches the end of life (~20-inches of water (50 millibar)) over 60% of the candle filter has been plugged.



Alternative Technology: Wet Electrostatic Precipitators

Wet electrostatic precipitators have been the workhorse for aerosol mitigation in applications with insoluble or sticky particulate. The collectors are often flat plates or round tubes easily accessible to installed cleaning sprays and possess a simple shape for sloughing off captured particulate. If buildup occurs, collector surfaces are accessible to online sprays for cleaning. Operators can remove long-term buildup during scheduled outages using a pressure washer.

There are numerous applications with impressive performance. WESPs are used in the offgas of mineral processing plants which see a wide variety of contaminants. At a North American gold roaster, WESPs located downstream of a Venturi scrubber collect sulfuric acid mist and residual particulate consistently requiring only yearly maintenance shutdowns. A North American battery recycler employs WESPs at its facilities. The WESPs, downstream of baghouses, capture residual lead fume and sulfuric acid aerosol produced from electric arc and reverberatory furnaces. Maintenance occurs only during furnace rebuilds on a 6 to 9 month cycle.

WESPs are prominent in sulfuric acid production with similar operational uptime. WESPs remove sulfuric acid mist and metal contaminants to protect the catalyst beds and also serve to remove SO_3

downstream of liquid contactors for air pollution control. Operators report stable performance and significant uptime.

In this particular application, a wet electrostatic precipitator could have been integrated into a packed bed absorber, reducing the equipment footprint. In an integrated packed bed/WESP, gas flows upward first through a bed of packing to remove sulfur dioxide. The packing has the co-benefit of straightening the gas in advance of the WESP. Water sprays above the packing remove the sulfur dioxide. Some of the spray entrains into the gas, increasing the liquid water load to the precipitator, improving online cleaning. The photo is of an integrated packed bed absorber/wet electrostatic precipitator.

In hindsight, a wet electrostatic precipitator would have been a more appropriate selection for this application. Wet electrostatic precipitators have a broad installation base treating gas containing solid particulates. It's prominent use in controlling sulfuric acid emissions in acid plants mitigates any performance risk. Integrating a packed bed into the precipitator would improve its performance, reduce total cost, and maximize performance. While the upfront capital cost would exceed the cost of a candle filter, it would have offered a quick payback if the frequency of filter plugging was known in advance.

Conclusion

The refinery initially chose a candle filter to mitigate its sulfuric acid aerosol regulatory issue. The refinery based its decision on:

- Sulfuric acid forms sub-micron aerosol through the reaction of sulfur trioxide with water.
- Candle filter effectively remove sub-micron mist through the principle of Brownian motion.
- Low carbon monoxide emissions were thought to correlate to low particulate emissions.
- Technology offers a lower capital cost compared to competing technologies.

The candle filter met the emission target but fouled much more frequently than anticipated. Fouling occurred more than anticipated for the following reasons:

- Carbon monoxide emissions did not correlate to particulate emissions.

- The existing single-stage thermal oxidizer was not designed with the residence time sufficient to fully combust solid and liquid hydrocarbons.
- The designers did not account for the salt in the used oil which contributed to fouling.

The rate of fouling dramatically increased the expected operating costs of the candle filter.

- The refinery anticipated one turnaround per year and a yearly filter replacement cost of $12,500.
- Fouling varied from once a month to once per week, increasing the yearly filter replacement cost to $900,000.
- Fouling led to 20 hours of lost production per month.

The refinery is revisiting the candle filter technology for a wet electrostatic precipitator. A wet electrostatic precipitator offers the following advantages in this application:

- Precipitator cleaning sprays more directly clean and remove particulate from the collection surface.
- Precipitators drain particulate along a smooth collector wall.
- Precipitator geometry allows offline cleaning with minimal downtime.
- Collector and high voltage electrode surface can be cleaned and reused.
- Anticipated WESP power consumption is expected to be less than the fan power consumption by the candle filter.