"Highly Efficient SO_2 and SO_3 (sulfuric acid mist) Mitigation Using Sodium Sorbents in Refinery SRU Tail Gas Streams"

Zack Doran, SOLVAir®

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Abstract

Claus Sulfur Recovery Units (SRU) are the predominant technology to recover the majority of sulfur from crude oil refining. As regulation and public scrutiny increase, it is vital for refineries to further reduce emissions into the atmosphere and recover the remaining sulfur from crude oil and gas, following SRU treatment. SO_2 and SO_3 exiting the SRU incinerator can be mitigated at very high efficiencies with cutting-edge sodium dry sorbent injection (DSI) technology.

SOLVAir® DSI is a sodium-based sorbent technology alternative to traditional SRU tail gas treatment units (TGTUs). Sodium sorbents have demonstrated 99.9% removal of SO_2 and SO_3, in various industries, making sodium DSI the most versatile and economical choice for acid gas control for a wide variety of applications.

This paper presents a review of the SOLVAir® DSI processes, engineering principles, and sampling of refinery case studies to demonstrate the performance of SOLVAir® sodium sorbents.

Background

Before elemental sulfur can be recovered in the SRU process, the fuel gases (primarily methane and ethane) need to be separated from hydrogen sulfide (H2S). This is typically accomplished by dissolving the hydrogen sulfide in a chemical solvent (absorption) in the amine-treating units. The H_2S-rich stream is then sent to the SRU.

An SRU consists of a Claus process, followed by various TGTUs. SRUs represent around 10 – 25 % of the SO_2 emissions from refineries, even if the fuel gas volume from SRU represents only around 1.5 % of the total flue gas volume emitted by a refinery. On average, the sulfur recovered in the SRU represented 45 % of the sulfur entering the refinery with the crude oil. SO_2 emissions range from 50 to 52,000 mg/Nm^3. Emissions from these units typically contain some H_2S, SO_X, and NO_X.[1]

Although harmful SO_X emissions have reduced significantly since the Clean Air Act was imposed, the remaining emissions from refineries pose a significant challenge to public health and the

[1] EU BAT Refining of Mineral Oil and Gas (2015), Section 4.23.5

environment. Many jurisdictions in North America, as well as the rest of the world, are imposing ever-tightening acid gas emission regulations. Refinery SRU, fluid catalytic cracking unit (FCC), carbon black, sludge-incineration tail gas streams, as well as combustion devices, in general, are being considered for reduced sulfur oxide emission limits, which creates a technical challenge as these systems were typically designed decades ago with a different limit in mind. Moreover, their exhaust compositions can be highly variable. Examples of current rulemaking underway regarding SO_X emissions reduction include the Bay Area Air Quality Management District rule 11-18[2], as well as Ontario Regulation 88-22[3].

Dry Sorbent Injection (DSI) with sodium sorbents is usually the lowest capital cost and total cost of ownership option for SO_X treatment. Additionally, DSI can respond to highly variable stream and batch compositions and is an environmentally sustainable treatment option. Sodium sorbents can operate in variable flue gas conditions and a wide range of temperatures. Furthermore, DSI is a completely dry solution, requiring no water addition, and can be coupled with energy recovery equipment to maximize the operation efficiency of an SRU tail gas treatment system, thus improving the end user's bottom line.

Dry Sorbent Injection (DSI) system design

The SOLVAir® DSI system is placed downstream of a thermal oxidizer, incinerator, or boiler in a refinery to mitigate sulfur oxides and consists of three mandatory components and two additional optional components:

1. Sorbent and residue storage systems: The powdered sodium sorbents are typically stored in vertical silos. The resulting sodium sulfate residue is also stored in a silo and can be sold or sent to landfill.
2. Injection system: Responsible for injecting the dry sorbent into the flue gas duct, or reaction chamber (optional). This includes pipework, mill (optional), and lances for injection into the flue gas duct.
3. Separation unit: Typically, a baghouse filter separates sodium residues from cleaned flue gas. Other filtration units that are compatible include ESPs and ceramic filters. Wet scrubbers (caustic or water) are also an excellent option as the soluble SOLVAir® residues will dissolve in wet scrubbers and buffer against remaining acid gases.
4. Tail-end heat recovery (optional): As SOLVAir® works in a wide temperature range, 275-1,500ºF, a refiner may choose to recover excess heat in the flue gas stream with waste-heat recovery equipment.
5. Carbon capture unit (CCU) – (optional): A refiner may choose to mitigate CO_2 emissions. SOLVAir® technology can pre-treat CO_2 streams to remove acid gases ahead of an amine CCU to avoid amine degradation.

[2] https://www.baaqmd.gov/community-health/facility-risk-reduction-program/facility-risk-reduction-list
[3] https://www.ontario.ca/laws/regulation/r22088

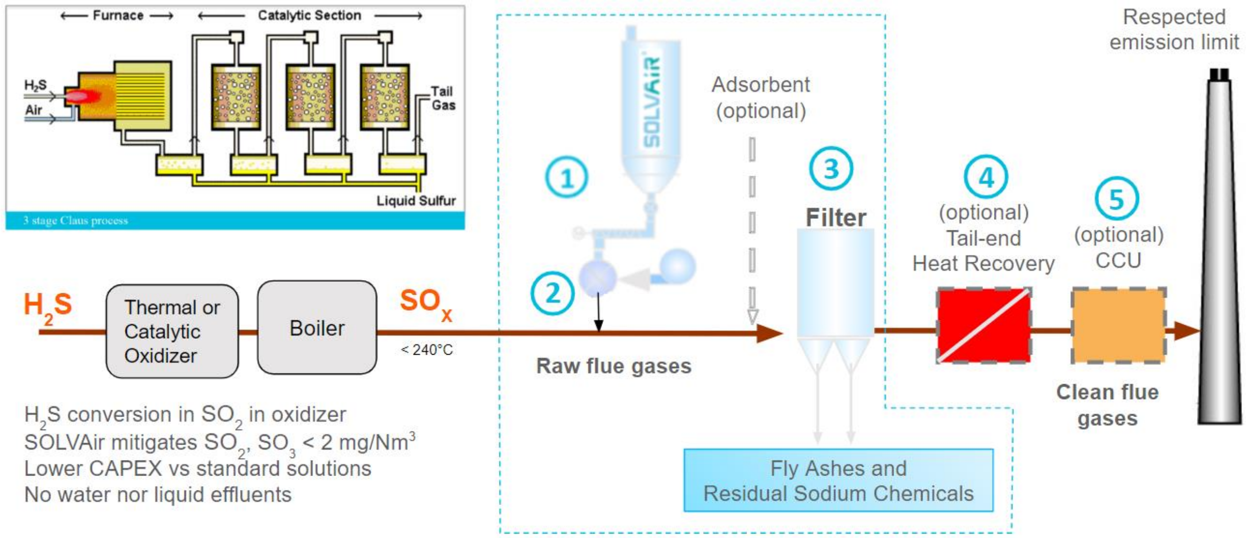
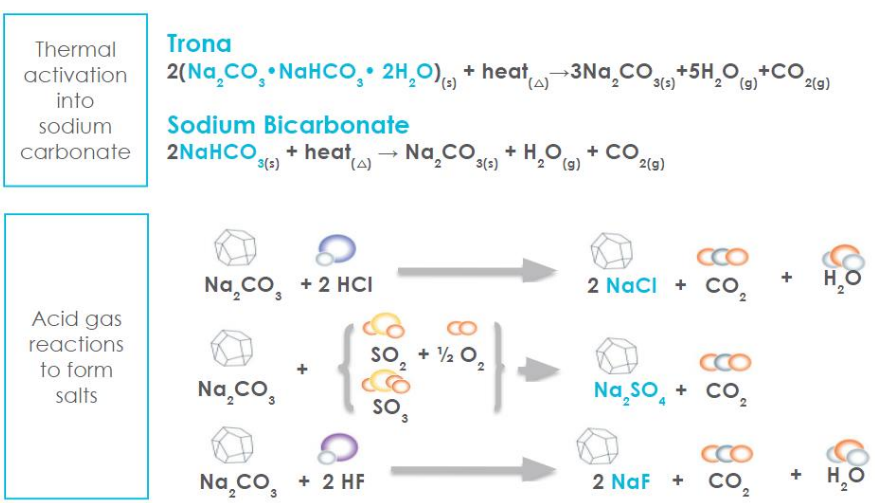


Figure 1 SOLVAir®® Solution: an alternative to TGTUs. Enhance S removal by treating tail gases from existing SRU units

Broadly speaking, the total installed cost of a medium size refinery DSI system (800 – 4,000 lb/h SO_X removal), is $5 MM +/- 30%. The total cost of ownership, which includes initial CAPEX, OPEX, and annual operating and maintenance costs is generally 10-30% lower using SOLVAir® DSI compared to standard alternative technology. With a small footprint, DSI systems can be retrofitted or incorporated into existing refineries.

SOLVAir® Chemistry and Working Principle

SOLVAir® sorbents were developed in the 1980s to mitigate acid gases from both coal-fired and waste-to-energy (WtE) power plants, and have since expanded to 20+ types of industries. These sorbents include sodium bicarbonate and trona (sodium sesquicarbonate) to mitigate acid gas pollutants, including SO_2, SO_3, HCl, and HF. SOLVAir® has achieved acid gas mitigation removal rates of >99.9% and emission reduction to <2 mg/Nm^3, at low stoichiometric ratios (1.01-1.20). The SOLVAir® reactions and stoichiometry are shown below in Figure 2.



Stoichiometric Mass Ratio		
Per 1 lb of pollutant	Trona	Bicarb.
HCl	2.09	2.30
SO_2	2.35	2.63
HF	3.77	4.20

Figure 2: Reaction chemistry of SOLVAir® sodium based sorbents

SOLVAir® employs the principle of adsorption and acid-base reactions to neutralize acidic components, resulting in stable and inert salt residues. The resulting sodium residues are separated from the clean flue gas before exiting the refinery stack. The reaction is completely dry and does not generate any liquid effluent.

The reactions are driven by mass transfer between the dirty flue gas and SOLVAir® sorbent particles. Four primary parameters control the effectiveness and efficiency of the SOLVAir® reactions. These parameters include flue gas temperature, solid-gas mixing time, sodium sorbent particle size, and back-end filtration device. The optimal operating window for each of these variables is shown below:

- Gas temperature at the inlet of the particulate removal device:

  275 – 1500°F

- Preferred solid-gas mixing time upstream of the filter:

  2 seconds

- Recommended ground sodium bicarbonate particle diameter:

  (D_{90}) 90 w% between 20 - 40 μm

- Particulate removal device effects: baghouse filter > ESP. Also, wet scrubbers are a great choice if present in the existing system.

Figure 3: Operating conditions for best performance

Generally, for maximum reaction efficiency, a hotter stream is recommended, up to 1,500ºF, longer residence time, and finer particle size.

Additional beneficial HSE features of SOLVAir® sodium sorbents include that they are non-corrosive, non-irritants, non-toxic, and non-flammable.

SOLVAir® Refining Examples

SOLVAir® has 500+ applications worldwide and increasing has found applications in various sectors of the refinery to reduce pollutant emissions, including SRU, FCC, sludge treatment, wax production units, and power generation facilities.

SRU tail gas treatment experiences

SOLVAir® has one existing SRU customer in North America, one project to start in Europe in late 2023, and three SRU tail gas treatment projects out for bid. The typical SO_2 stream properties (min/max) and removal requirements for an SRU application with DSI are shown below:

Stream Property	Minimum	Maximum
SRU tail gas flow (SCFM)	1,0000	10,000
Temperature (ºF)	300	1,000
SO_2 loading (lb/h)	100	1,000
Trona injection required (lb/h)	250	2,500
SO_2 %removal required (%)	70%	99%+

Generally, the refiner can choose to treat the entirety of the SO_2 exiting the thermal oxidizer, or selectively treat SO_3.

A small portion of SO_3, less than 5% of total SO_X, exists in a larger stream of SO_2 exiting the tail end of an SRU treatment system. Although small, the SO_3 portion of the stream is quite difficult to treat with traditional methods as it can create small, sub-micron, sulfuric acid mist (SAM) bubbles that slip through wet scrubbing systems. An existing refining customer has a Claus SRU followed by a thermal oxidizer and DSI system to selectively and completely treat SO_3 ahead of a caustic wet scrubber. This keeps the facility within its permit limits and avoids the infamous "blue" plume attributed to SAM.

Moreover, SOLVAir® has experience with SO_2 paraffin wax production units and refinery sludge waste treatment plants. Both applications are similar to post-SRU incinerator treatment having highly concentrated SO_x after an oxidizer.

An example of a European sludge incineration application where the operator was able to reduce post-combustion SO_2 by >98%. The operator needed to reduce sorbent costs, originally using hydrated lime. Thanks to the efficiency of SOLVAir® sodium sorbents, they were able to make the switch[4]:

In 2017 SOLVAir® performed industrial trials at the plant:

- Plant capacity: 6 - 7 t/h, 20% DM (dry matter)
- Sulfur content: 0,24 % - wet / (= dry: 1,25 %)
- Flue gas flow: 12.000 – 13.000 Nm³/h
- Emission limit SO2: 50 mg/Nm³
- SO2 in raw gas: 2400 - 3100 mg/Nm³
- Sorbent consumption: 106-123 kg/h → 15-20 kg/t wet sludge
- Total stoichio. ratio (SRT): 1,11 - 1,14
- Residues generated: 10 kg/t sludge

[4] https://www.SOLVAir®solutions.com/en/case-study-sludge

FCC tail gas treatment experiences

Due to tightened regulations, refineries in North America and Europe are adding DSI units to mitigate SO_2 at the tail end of FCC processes. The general layout of an FCC and sector of interest for SO_2 removal is shown below.

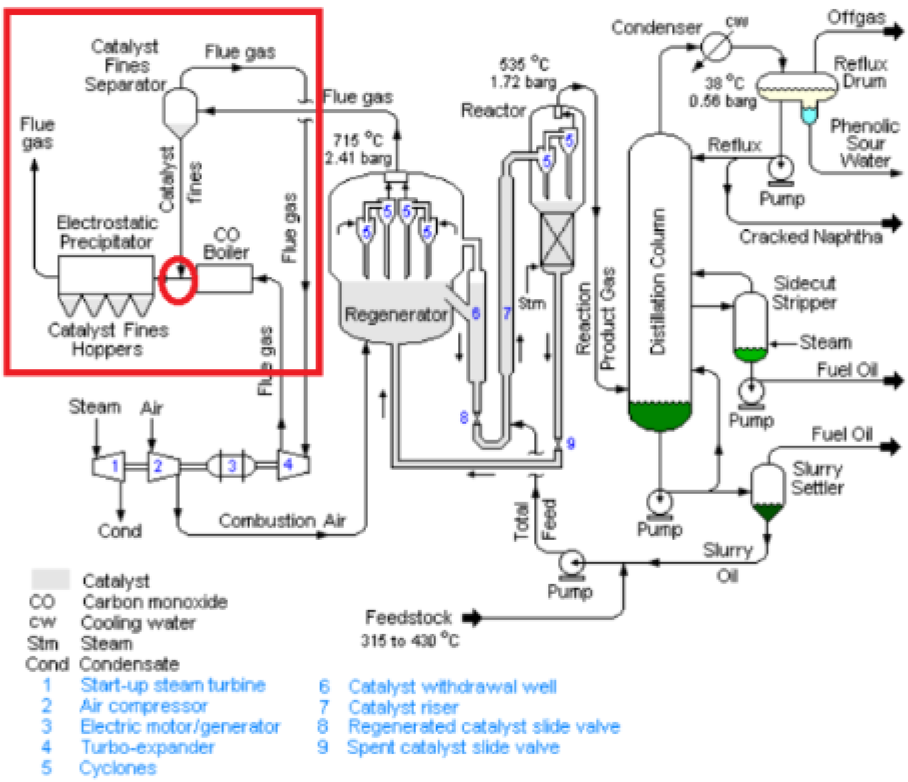


Figure 4: FCC layout. Source: https://en.wikipedia.org/wiki/Fluid_catalytic_cracking

As an example, a refinery in the EU, processing high-sulfur crude oil, required further SO_2 treatment after their FCC. In their FCC, coke is built up on a circulating fluidized catalyst, which is burned in the regenerator section. The EU refinery also has an SCNR with urea injection for NO_X control.

In partial combustion, the flue gas of the regenerator section contains about 6 % CO and is sent to a CO boiler. During the CO boiler step, SO_X is generated, ranging from 600 – 3,700 mg/Nm^3. Their required SO_2 limit for the FCC is 1,200 mg/Nm^3. Additionally, the refinery flue gas stream ranges from 60,000-95,000 Nm^3/h and operates at 200-300ºC (392-572ºF). The refinery also has an existing ESP for FCC regenerator dust control

The refinery tested and chose to retrofit to FCC CO boiler with a SOLVAir® DSI system using sodium bicarbonate at the exit of the CO boiler to mitigate SO_2. Using sodium bicarbonate, the refinery was able to remove SO_2 well below their regulatory target of 1,200 mg/Nm^3, reducing SO_2

as low as 400 mg/Nm^3. The SO_2 concentration and sodium bicarbonate injection rates, in hourly intervals, are shown below:

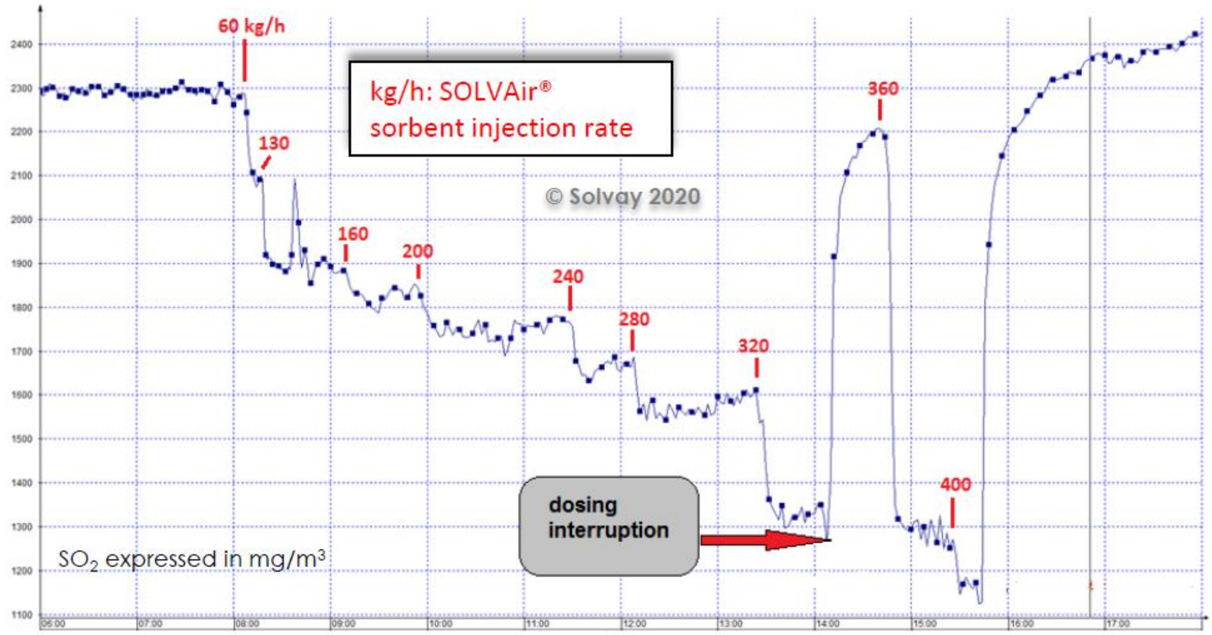


Figure 5: SO2 and sodium bicarbonate injection rates at EU refinery

One can see that using DSI with sodium bicarbonate effectively and rapidly can reduce sulfur dioxide concentrations in refinery flue gas streams.

Conclusion

A broad overview of SOLVAir® DSI technology and experience has been presented. The SOLVAir® technology is an advanced solution for mitigating hard-to-treat sulfur oxide streams from industrial flue gases.

Of SOLVAir®'s 500+ customers, there are about a dozen existing refinery experiences, worldwide. The refinery applications will grow with ever-tightening ambient air standards. DSI with sodium sorbents can remove 99%+ SO_X from industrial gases at typically the lowest cost of ownership for the operator. Additional benefits SOLVAir® offers include efficient peak mitigation for variable flue gas compositions, a large operating temperature window for sodium sorbents, ease to retrofit in existing refineries, and a completely dry sorbent, generating zero liquid effluent.