Sulfur Plants: Simplify Tail Gas Clean Up, Lower Costs

Tougher regulations for emissions reductions require refiners to achieve ever higher sulfur recovery efficiency in their Sulfur Recovery Units. A classic solution is to use an amine-based tail gas clean up unit (TGCU) behind a Claus plant. A U.S. refiner, working on a major capacity increase, evaluated and selected an alternate technology. They selected the SUPERCLAUS® Tail Gas Clean Up Process, followed by a DynaWave™ Wet Gas Scrubber. This system both meets stringent emission limits and provides advantages such as lower capital cost (TIC), smaller footprint and simple operation.

This paper presents the sulfur recovery efficiency achieved by the SUPERCLAUS® followed by DynaWave™, a comparison of the complexity and footprint for an amine-based TCCU versus SUPERCLAUS®/DynaWave™, along with the features and benefits of the process that convinced the refiner to choose SUPERCLAUS®/DynaWave™ over a traditional amine-based TGCU.

SUPERCLAUS®

The SUPERCLAUS® process was commercially demonstrated in 1988, and today more than 150 units are now under license and over 130 in operation. The SUPERCLAUS® process was developed to catalytically recover elemental sulfur from H₂S containing gases originating from refinery and natural gas treating plants such as alkanolamine units or physical solvent plants. SUPERCLAUS® is compatible with an ammonia burning SRU Design, with no ammonia salt deposition risk.

The SUPERCLAUS® process consists of a thermal stage followed by three or four catalytic reaction stages with sulfur removed between stages by condensers (see figure 1). The first two or three reactors are filled with standard Claus catalyst while the last reactor is filled with the selective oxidation catalyst. In the thermal stage, the acid gas is burned with a substoichiometric amount of controlled combustion air so that the tail gas leaving the last Claus reactor typically contains 0.5 to 0.9 vol.% of H₂S.

Figure 1: Claus – SUPERCLAUS® - DynaWave™
Two main principles are applied in operating the SUPERCLAUS® process:

- Operating the Claus plant with excess H$_2$S to suppress the SO$_2$ content in the Claus tail gas
- Selective oxidation of the remaining H$_2$S by the SUPERCLAUS® catalyst selectively converts the H$_2$S in the presence of water vapor and excess oxygen to elemental sulfur only.

The combined SUPERCLAUS®/DynaWave™ process offers the refinery over 99.9% removal efficiency. Stack emissions below 50 ppm of SO$_2$ can be easily achieved.

**DynaWave™ Process**

Following SUPERCLAUS® and the incinerator, is the DynaWave™ Wet Gas Scrubber, a unique open bore, reverse jet scrubber that utilizes “Froth Zone” technology to perform desulphurization in a wet gas environment. Since its introduction in the 1970s, over 300 DynaWaves have been installed. Sulfur Recovery Tail Gas Clean Up is a typical DynaWave™ refinery application.

In the DynaWave™, scrubbing liquid is injected, through a non-restrictive jet nozzle, counter current to the inlet incinerator flue gas (see figure 2). Liquid, containing caustic reagent, collides with the down-coming gas to create the “Froth Zone”, a region of extreme turbulence with a high rate of mass transfer. Quench, SO$_2$ removal, and particulate removal occur in the Froth Zone. The clean, saturated gas and charged liquid continue through a separation vessel.

![Figure 2: DynaWave™ Reverse Jet Scrubber](image-url)
The saturated gas continues through the vessel to mist removal devices. The liquid descends into the vessel sump for recycle back to the reverse jet nozzle. In the vessel sump, oxidation air is used to convert sodium sulfite to sodium sulfate. The vessel sump is concentrated up and blow down occurs using a density control sequence.

The above-mentioned U.S. refinery used the DynaWave™ process in other sulfur recovery applications, and recently chose a DynaWave™ for emissions reductions on an FCC application. Their very positive experience with the DynaWave™ in Tail Gas Clean Up led them to consider combining DynaWave™ with a sulfur recovery process. After investigating amine-based TGCU, the SUPERCLAUS® process was chosen for its many advantages.

**Positive Experience with DynaWave™**

The refinery noted that the DynaWave™ technology was less complex than other wet gas scrubbers, had a smaller footprint, and was very forgiving during process swings.

**Quench and SO₂ Removal**

The DynaWave™ combines multiple functions in one vessel, providing quench, SO₂ removal, particulate removal and oxidation. Quench occurs during the contact between the incoming gas and the liquid/reagent stream. As such, a separate quench zone is not required. At the same time, reaction between the reagent and the SO₂ takes place, also during contact and intense mixing in the Froth Zone. Because of the level of SO₂ in the incinerator gas stream, two stages of contact were designed. The two stages translate into two froth zones and therefore two levels of open bore nozzles, one nozzle at each stage.

**Materials of Construction**

Quench occurs at the first level froth zone. This area requires a material of construction which can handle the high incinerator gas temperature. A performance stainless steel was chosen, and was specified only from the bottom of the first nozzle to the top of the inlet barrel. The rest of the inlet barrel, where the temperature was lower, was specified as Duplex 2205. This offered cost savings.

Particulate removal was not required in the Tail Gas Clean Up application, but occurs according to the pressure drop created across the scrubber. Sub-micron particulate removal, such as SO₃, can be accomplished in the DynaWave™.

**In-Situ Oxidation**

In-situ oxidation of the scrubbing effluent to a benign Na₂SO₄ solution is achieved by air spargers in the bottom of the separation vessel. This represents a cost savings compared to other scrubbers which require separate oxidation tanks. Sulfites are oxidized to sulfates which can be sent to waste water treatment without increasing COD load. Because of the highly efficient SUPERCLAUS® process upstream, the effluent volume
discharged from a SUPERCLAUS®/DynaWave™ SRU is very small compared to other processes in the refinery.

**Keeps on ticking**

The forgiving nature of the DynaWave™ has been demonstrated in situations involving higher than anticipated flow rates, temperatures and SO₂ loading. The installed DynaWaves have not faltered or shut down under these conditions. Variable flow rates are designed into the system through a self-compensation feature. As the gas flow increases, the froth zone is pushed down the inlet barrel. As the gas flow decreases, the froth zone moves up the inlet barrel. Quench and SO₂ removal are not affected.

**Process Flexibility and Redundancy**

For the Tail Gas Clean Up Process, flexibility is key. The SUPERCLAUS® can be temporarily bypassed and the DynaWave™ scrubber can handle the full Claus tail gas SO₂ load and still maintain the required SO₂ stack limit, allowing the refiner to meet EPA regulations at all operating conditions.

**SUPERCLAUS® Advantages**

During evaluation, the refinery recognized a number of advantages of the SUPERCLAUS® process:

- Oxidation of H₂S to sulfur is complete
- No sensitivity to water vapor
- Long catalyst lifetime
- Simple, continuous operation
- Handles NH₃ destruction without plugging risk
- High turndown
- High reliability, typically less than 1% unscheduled shutdown time.

**Less Complex**

It is very straightforward to compare the complexity of a traditional amine-based TGCU process with the smaller and equally efficient SUPERCLAUS®/DynaWave™. The typical amine-based process train requires 24 different pieces of equipment, versus only 16 pieces of equipment in the SUPERCLAUS®/DynaWave™ process. The smaller equipment count indicates less complexity, lower capital cost and lower maintenance cost.

The simplicity of SUPERCLAUS®/DynaWave™ is evidenced by the several functions that are not required compared to an amine-based TGCU process, including:

- No Reducing Gas Generator step, which can be difficult to operate and maintain
- No Hydrogenation Reactor (with expensive Co-Mo catalyst), which is subject to fouling (soot) and degradation (O₂ breakthrough).
- No Quench tower, subject to severe corrosion and fouling during upset conditions
- No Amine system, subject to many operational and maintenance problems, especially during upset conditions

**Smaller Footprint**

An SRU using the amine-based TGCU process, for a representative 135 tons per day of sulfur production, requires a space approximately the size of half a football field. SUPERCLAUS®/DynaWave™ for the same capacity requires only about one-quarter of a football field, saving plot space in refineries which tend to have inadequate space available.

A typical footprint for the DynaWave™ stage alone is only about 20 feet by 20 feet, which includes the vessel, two circulation pumps, one as a spare, and other hardware.

**Lower Capital Cost**

Less equipment also translates to lower capital cost as well as lower operating and maintenance costs. SUPERCLAUS® DynaWave™ systems tend to cost **25-40% less** than amine-based TGCU processes while providing the same removal efficiency.

Additional savings are realized in operating costs:

- No recycle of H₂S to the front of the SRU. This translates into capacity gain of up to 5% for the SRU.
- Less energy (reduced CO₂ emissions are a side benefit)
- Simpler to operate and maintain

**Accommodating Tighter Regulations**

As tighter regulations force refineries to review their emissions control equipment in the future, SUPERCLAUS® DynaWave™ provides the flexibility to further reduce SO₂ stack emissions. When preceded by SUPERCLAUS®, the DynaWave™ process can be operated to SO₂ emission levels as low as 10 ppm without equipment changes.

In addition, reliability is part of the package. Achieved at a lower capital cost than amine-based TGCU processes, with lower operating costs and less complexity, the SUPERCLAUS®/DynaWave™ process offers refineries a superior alternative to the traditional choice.