WET SCRUBBING SYSTEM CONTROL TECHNOLOGY FOR REFINERIES-
AN EVALUATION OF REGENERATIVE AND NON-REGENERATIVE SYSTEMS

By

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Abstract

The use of both regenerative and non-regenerative wet scrubbing systems to control the emission of particulate and SO₂ is well proven and established. Systems in operation have proven to operate continuously and reliably while maintaining emission levels comfortably below 50 mg/Nm³ for particulate and the U.S. Environmental Protection Agency (EPA) target level of 25 ppm for SO₂. However, the selection of the most appropriate system for any location requires a detailed evaluation of the technical aspects, capital cost and operating cost of each technology. In addition to the air emission requirements, the liquid effluent discharge from the wet scrubbing system is an issue that must be closely examined in some locations.

An operating system in a refinery that use regenerative and non-regenerative wet scrubbing systems is examined in detail. The design criteria for each installation is discussed, along with the operating performance of each of the installations. The technology for each system is also examined. The major components of each system are discussed along with the function for each of these components. Finally, the reason for the selection of regenerative or non-regenerative wet scrubbing at each installation is examined.

In order to illustrate the different scenarios that a refiner might face in technology selection several possible situations are discussed. The scenarios that are examined include situations of high uncontrolled SO₂ emissions, low uncontrolled SO₂ emissions, a location where effluent discharge is not an issue, a location where effluent discharge is an issue and the impact of particulate control needs. For each situation the use of regenerative and non-regenerative wet scrubbing is discussed with respect to the technology required, capital cost, operating cost and any other factors that might be pertinent.

Finally, a summary is provided to help refineries identify and quantify the key issues that are important to them as they search for the solution that best fits their needs.

A Caustic Based Non-Regenerative Wet Scrubbing System

For many years, refiners worldwide have decided to use wet scrubbing for control of particulate and SO₂ emissions from FCCUs and other air emission sources within the refinery. For most of these sources, both particulate and sulfur emissions in the flue gas are simultaneously controlled. This scrubbing technology is well proven in providing flexibility to handle added capacity that comes with FCCU expansions and in providing uninterrupted operation/performance exceeding that of FCCUs. Each refiner's specific reasons for choosing wet scrubbing differ, but these have generally been related to environmental compliance as well as relative costs, reliability and flexibility of wet scrubbing compared to other emission control options.
The EDV® Wet Scrubbing is a state-of-the-art wet scrubbing system for controlling particulate and SO₂ emissions from FCCUs and other process units. One arrangement of this system is shown in Figure 1.

The system treats hot flue gas containing particulate and SO₂ from an FCCU or other process unit and discharges cleaned gas to the atmosphere through an integral stack. At the scrubber inlet, flue gas is quenched and saturated by means of multiple water sprays in the Spray Tower's horizontal quench section. Normally, the flue gas enters the wet scrubber after passing through a heat recovery device. However, the system is designed so that it can accept flue gas directly from the FCCU regenerator or other process unit at the temperature at which it exits the FCCU regenerator or process unit.

The proprietary LAB-G spray nozzles produce high-density water curtains through which the gas must pass. Each nozzle sprays water droplets that move in a cross-flow pattern relative to the flue gas. These cover the entire gas stream and uniformly flush the vessel's surfaces clean. The spray nozzles are non-clogging and able to handle highly concentrated slurries.
SO₂ absorption and particulate removal takes place immediately after quenching as the flue gas rises up through the main Spray Tower where gas is again contacted with high-density water curtains produced by additional spray nozzles. The Spray Tower itself is an open tower with multiple levels of LAB-G spray nozzles. Since it is an open tower, there is nothing to clog or plug in the event of a process upset. In fact, this design has handled numerous process upsets where over 150 tons of catalyst has been sent to the wet scrubber in a very short period of time.

The scrubbing liquid is controlled to a neutral pH with reagent addition to drive SO₂ absorption. Caustic soda (NaOH) is typically used as the alkaline reagent. However, other alkali, such as soda ash and magnesium hydroxide, has also been utilized with excellent results in terms of performance and reliability. Multiple levels of spray nozzles provide sufficient stages of gas/liquid contact to remove both particulate and SO₂. An illustration of the Spray Tower and the spray nozzles is provided in Figure 2.

![Spray Tower and LAB-G Spray Nozzles](image)

**Figure 2 - Spray Tower and LAB-G Spray Nozzles**

Makeup water is added to the system, replacing water lost to evaporation in the quench zone as well as water purged from the system. Captured pollutants, including suspended particulate and dissolved sulfites/sulfates (NaHSO₃, Na₂SO₃, and Na₂SO₄) from SO₂ removal are purged from the Spray Tower recycle loop. The treatment of this purge stream is addressed later.

In order to remove very fine particulate, flue gas leaving the Spray Tower is distributed to a bank of parallel Filtering Modules. Within each module, the flue gas first accelerates (compresses) and then decelerates (expands). This action causes water to condense
from the flue gas. The water uniformly washes the module’s walls. More importantly, water condenses on the fine particulate and acid mist (H$_2$SO$_4$) present in the flue gas, increasing both their size and mass. Some agglomeration also takes place.

A LAB-F nozzle, located at the exit of the filtering module and spraying counter-current to gas flow, provides the mechanism for the collection of the fine particulate and mist, which has been enlarged and agglomerated. This device has the unique advantage of being able to remove fine particulate and acid mist with an extremely low pressure drop and no internal components which can wear and be the cause of unscheduled shutdowns. It is also relatively insensitive to fluctuations in gas flow. This device is illustrated in Figure 3.

Prior to being discharged to the atmosphere through a stack, the flue gas enters a bank of parallel droplet separators. Each treats a portion of gas flow and separates/collects free water droplets. The gas entering each separator passes through a fixed spin vane where centrifugal acceleration causes free water droplets to impinge on the separator's walls. Collected water droplets flush the walls uniformly clean and drain to the bottom. Collected water is recycled for flue gas cleaning in the Filtering Modules or Spray Tower. This device is also illustrated in Figure 3.

This liquid that is purged from the scrubber is typically processed in a Purge Treatment Unit (PTU). Here, a clarifier removes suspended solids and generates concentrated slurry that is de-watered in settling bins. Water, now free of suspended solids, overflows from the clarifier and is oxidized in a series of vessels using air and agitation. Oxidation converts sulfites in the purge to sodium sulfate, reducing any chemical oxygen demand.
(COD), so the water can be safely discharged. A typical arrangement of a PTU is provided in Figure 4.

![Diagram of a PTU](image)

**Figure 4 - Typical Purge Treatment Unit**

**Typical Non-Regenerative Wet Scrubbing System Performance**

In order to illustrate the typical performance of this system, the EDV® system installed at a U.S. refinery is utilized. At this refinery, an EDV® wet scrubbing system was installed in order to comply with New Source Performance Standards (NSPS) for particulate and \( \text{SO}_2 \) emissions.

Emissions testing was performed to verify the emissions performance of the system. Testing was performed at both the inlet to the wet scrubbing system and at the stack. The results of these tests were exceptional.

First, the testing at the inlet to the EDV® wet scrubbing system demonstrated that the system was operating at higher than design values for gas flow and \( \text{SO}_2 \) loading while having a lower than design loading for particulate. The flue gas flow rate was approximately 20% over design on a mass basis. \( \text{SO}_2 \) was approximately 3.1 times the design value on a mass basis. However, the particulate was approximately 50% of the design value on a mass basis. A summary of the average inlet test values, compared to the system design values, is presented in Figure 5.
The performance of the system was excellent. SO$_2$ was only a small fraction of the design outlet value. The mass outlet SO$_2$ emissions were only 12% of the design values, while the tested removal efficiency was 99.92% vs. a design efficiency of 97.90%. Particulate emissions were also very low. The mass emission rate was approximately 24% of the design value, while the tested removal efficiency was 92.24% vs. the design removal efficiency of 83.70%. A summary and comparison of this data is provided in Figure 6.

The system has also been excellent from an operations and maintenance perspective. Over the first several months of operation, the RFCC® experienced multiple process upsets which resulted in as much as twenty to thirty percent of the catalyst inventory being carried out of the regenerator and into the wet scrubbing system. The wet scrubber readily handled all of these process upsets. The operation of the scrubber was not interrupted. The system continued to operate and the excessive solids were washed out of the system by overflowing the main scrubber re-circulation tank to a tank where the solids could be settled out. These upsets also did not cause premature wear of the nozzles.

From an operator’s perspective, the scrubbing system has required very little attention. Normally, the only attention required is a routine walk-by of the equipment to ensure that everything is in normal operation.

**Regenerative Wet Scrubbing Systems**

In today’s environment, the transfer of pollutants from one source (i.e. air) to another (i.e. water) is an increasingly important issue. In order to prevent this, technology is combined with the EDV® wet scrubbing system to prevent the discharge of soluble salts from the wet scrubbing system. The involves the use of a regenerative wet scrubbing...
technology known as LABSORB™. The regenerative system removes the SO$_2$ from the flue gas with a regenerable non-organic buffer. This buffer is sent to a regeneration plant where the buffer is regenerated and the SO$_2$ is extracted from the buffer as a concentrated stream of SO$_2$. The concentrated SO$_2$ stream can be sent to the sulfur recovery unit for recovery as elemental sulfur. This approach has a major side benefit in the reduction of operating costs since the buffer that removes the SO$_2$ is reused.

**Description of the LABSORB™ Process**

The LABSORB™ process is a regenerable process for the recovery of SO$_2$ from flue and tail gases at utility and industrial plants, and represents a significant improvement over other flue gas desulfurization (FGD) and SO$_2$ recovery processes currently in use.

Unlike caustic/lime/limestone systems, the LABSORB™ process produces concentrated SO$_2$ as a byproduct. This byproduct, through commercially available processes, is converted into valuable products such as liquid SO$_2$, sulfuric acid or elemental sulfur. These products are widely used in the fertilizer, chemical, and pulp and paper industries.

The process is highly flexible and can be used in connection with flue gases generated from any kind of process. It is economically favored when flue gases with high SO$_2$ content are to be processed, and especially suited to meet all emission regulations even at high fluctuating SO$_2$ loads in the flue gas. Gases containing from 1,000 ppm, to more than 3-5% (vol.) SO$_2$ may easily be treated to meet stringent environmental standards. The flow diagram shown in Figure 7 below outlines the process design and chemical basis for the LABSORB™ process.

![Figure 7- Basic LABSORB™ Process](image-url)
The LABSORB™ process utilizes a patented non-organic aqueous solution of sodium phosphate salts as buffer for the absorption of SO₂. The second dissociation step of phosphoric acid represents the active buffer. The main reactions are:

\[
\begin{align*}
\text{SO}_2(g) & \rightarrow \text{SO}_2(aq) \\
\text{SO}_2(aq) + 2\text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{HSO}_3^- \\
\text{HPO}_4^{2-} + \text{H}_3\text{O}^+ & \rightarrow \text{H}_2\text{PO}_4^- + \text{H}_2\text{O}
\end{align*}
\]

The process operates in the pH region of 5.0 - 6.5. The high buffer concentration and the high pH values throughout the process lead to high cyclic capacity and to high absorption efficiencies. Technical grade caustic and phosphoric acid are used for buffer production and makeup.

**Typical System Description**

A LABSORB™ system normally consists of a quencher/pre-scrubber/absorber section, a regeneration unit, and a sulfate removal/buffer makeup unit. A simplified flow diagram of the process is shown in Figure 7 above. In the process shown, the regeneration is accomplished by single-effect evaporation. For the purpose of energy saving, double-effect evaporation may be used in larger installations. Low-pressure steam can be produced by cooling the incoming gas before the quencher/pre-scrubber in a waste heat boiler. This steam may be used to reduce the operating cost of the regeneration unit.

Although the following process description describes regenerating the buffer from one scrubber, the buffer from several scrubbers can be combined and sent to a single regeneration plant within a facility. The regeneration unit and storage tanks may also be located at a different location than the absorber if space is limited in the area where the absorber is located.

1. **Flue Gas Quenching/Pre-Scrubbing**
   The incoming flue gas is cooled to adiabatic saturation (typically 40° to 75°C) in a quencher/pre-scrubber. The pre-scrubber also serves the purpose of washing out remaining particles carried over from the process as well as acid components present, such as HF, HCl and SO₃. Water used in the quencher and pre-scrubber is recycled to minimize water consumption and disposal. The water pH is maintained below 2.0 to minimize any absorption of SO₂. Makeup water is added to compensate for the system bleed and evaporation. A minimal bleed from the system is discharged to the facility’s wastewater treatment plant or treated in a small dedicated purge treatment unit.

2. **Absorption**
   The absorption of SO₂ is carried out counter-currently in the absorber. For gases rich in SO₂, the absorber may be equipped with a high-efficient structured packing. This approach gives the advantage of a single pass of the liquid through the absorber, eliminating the need for liquid re-circulation over sections of the packing. For gases with lower SO₂ concentrations, multi-stage packed beds of ordinary random packing,
or spray or plate towers with individual liquid re-circulation, are commonly used to ensure sufficient absorption efficiency. To avoid buffer losses to the stack, an efficient droplet separator is installed, and the recovered buffer will be feed to the regeneration system. In many cases, the absorber is combined with the quench/pre-scrubbing section in a single vessel.

3. Buffer Holding Tanks
A regenerated buffer (lean) buffer tank, a non-regenerated (rich) buffer tank, and a regenerated buffer-mixing tank ensure a steady supply of buffer for absorption and regeneration. Normally, the lean and rich buffer tanks provide twenty-four hours of storage while the regenerated buffer-mixing tank provides one to two hours of storage and mixing.

4. Buffer Preheat
To minimize steam consumption for the regeneration of the buffer, the SO$_2$ rich buffer from the absorber may be preheated prior to entering the evaporator by utilizing the heat in the steam condensate and regenerated (lean) buffer as heating sources.

5. Evaporation/Regeneration
The regeneration of the buffer is carried out in a forced circulation evaporator using a heat exchanger with steam as heating medium, followed by a gas/liquid separator. The buffer temperature, pressure and density in the evaporator loop serves as control parameter for the steam supply to the evaporator. A high re-circulation ratio of circulating buffer ensures stable operation of the evaporation process.

SO$_2$ and water vapor leaves the gas/liquid separator to a stripper and condenser. Concentrated SO$_2$, saturated with water leaves the condenser as product for further treatment. Water from the condenser is stripped of SO$_2$ in a regular steam stripper before going to the mixing tank where this effluent is used to control the water balance in the regenerated buffer-mixing tank.

Buffer concentrate is bled from the evaporation loop to a mixing tank. There, a controlled amount of condensate from the stripper is added to obtain the desired density of the regenerated buffer. Control of the regenerated buffer composition in the mixing tanks is by density and pH measurements. The buffer is then cooled to the absorption temperature before being sent to the absorber. This ensures full absorption capacity.

The recovered SO$_2$ from the condenser may be feed to a compressor to maintain required pressures in the evaporator system and to feed the SO$_2$ to further processing. In the case of CLAUS plants and sulfuric acid plants, the SO$_2$ may be returned to the main process, or converted into elemental sulfur, sulfuric acid or liquid SO$_2$ in a separate plant.

6. Sulfate removal
Very low sulfate formation has been observed during pilot test and demonstration of the LABSORBTM process. The minor amount of Na$_2$SO$_4$ formed by SO$_3$ from the flue gas and/or oxidation of SO$_2$ is removed by a proprietary method developed for this purpose. A small stream of buffer is bleed off from the evaporator together with some stripper effluent to a filtering system. Solid Na$_2$SO$_4$ particles are removed along with
co-precipitated phosphates, while the liquid is returned to the mixing tank. The small amount of chemical losses is balanced by buffer makeup.

7. Buffer Makeup
A set of NaOH and H₃PO₄ tanks are provided to supply makeup for buffer losses. Typically, the tanks provide approximately 30 days of chemical storage. The amount of buffer makeup is determined by pH and buffer analyzers.

A simplified process diagram showing a double effect regenerative system is shown in Figure 8.

Figure 8 – Simplified Double Effect Regenerative Process

Benefits of the LABSORBTM Process

The LABSORBTM process is characterised by the following features:

- Low total investment and operating cost compared to other FGD and SO₂
recovery processes.

- Absorption at adiabatic saturation temperature gives no external gas cooling in prescrubber, consequently low liquid purge.
- Very low sulfate formation, resulting in the low consumption of chemicals.
- Easily available buffer chemicals (caustic and phosphoric acid).
- No system discharges must be landfilled. The byproduct (Na₂SO₄) may be used in the fertilizer industry.
- Less than 1% waste as compared to limestone processes. Materials transported in and out of the plant are less than 10% when compared to limestone processes, recovered sulphur included.
- High SO₂ removal efficiency.
- Highly flexible regarding SO₂ concentration in the untreated gas.
- The buffer is non-volatile, non-odorous, non-toxic and otherwise harmless.
- SO₂ recovered is a valuable, high purity SO₂ (90 - 95% SO₂).

### Regenerative Scrubbing System Performance Data

A LABSORB™ regenerative wet scrubbing system is installed to control emissions from the FCC Unit at the Eni Sannazzaro refinery. This FCCU has an approximate capacity of 5,500 tons/day (approx. 38,000 bpsd) and uses HVGO & Sweet Residue as feed.

The system has been in operation since mid 2004. The actual performance of the system is illustrated in Figure 9. As can be seen from this Figure, the system performed very well, meeting all of the performance guarantees.

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<th>Scrubber Inlet Conditions:</th>
<th>Design</th>
<th>Actual as tested</th>
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<td>180,000 Nm³/h</td>
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<td>Gas pressure:</td>
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<td>SO₂ concentration:</td>
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<td>1,700 mg/Nm³</td>
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<td>Particulate fines:</td>
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<td>50 mg/Nm³</td>
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<td>208,000 Nm³/h</td>
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<td>Stack gas pressure:</td>
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<tr>
<td>SO₂ concentration:</td>
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<td>&lt; 250 mg/Nm³</td>
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<tr>
<td>Particulate fines:</td>
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<td>&lt; 50 mg/Nm³</td>
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<tr>
<td>SO₂ sent to Claus (95% wt SO₂+ 5% wt H₂O)</td>
<td>450 Kg/h</td>
<td>250 Kg/h</td>
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Figure 9 – Regenerative Wet Scrubbing System Performance

The outlet SO₂ emissions from the LABSORB™ system were recorded for a period of approximately two months. This data is shown in Figure 10. As can be seen from this
data, The system performance was excellent, with outlet SO$_2$ emissions ranging from a peak of 275 mg/Nm$^3$ to a low of approximately 25 mg/Nm$^3$, all well below the design outlet emission rate of 450 mg/Nm$^3$. The system continues to operate very well, with actual emissions well below the design levels.

Figure 10 – Actual SO$_2$ Emissions from LABSORBTM System

**System Costs**

The capital and operating costs of both regenerative and non-regenerative systems will be dependant on the specific site that is considering wet scrubbing and the design parameters for the system. However, over the course of several years general guidelines have been developed to help refiners make a very course evaluation of these technologies.

The capital cost for a regenerative scrubbing system will be higher than that of a non-regenerative (caustic based) scrubbing system. A good factor to apply to the capital cost of a regenerative scrubbing system is approximately 2.4 times the capital cost of a non-regenerative wet scrubbing system. This increased cost is primarily due to the additional complexity of the wet scrubber and the cost of the regeneration plant in the regenerative wet scrubbing process.
A regenerative wet scrubbing system has a significant operating cost advantage over a non-regenerative wet scrubbing system. Primarily this is due to the cost of the reagent in the non-regenerative process, although liquid effluent discharge can also be a significant factor depending on the specific requirements of the site. The regenerative system has a low operating cost, with reagent costs only a small fraction of that of non-regenerative systems. It also has the benefit of almost no liquid effluent discharge and has a by-product of SO₂ which can be processed into elemental sulfur in the sulfur recovery unit. With the regeneration plant properly designed, the system can also add scrubbers to other emission sources and process their buffer in the same regeneration facility. This is a great advantage if multiple scrubber systems are being considered or required. A representative factor is that a regenerative process will have an operating cost of approximately 35% of a non-regenerative process. An illustration of the relative capital and operating costs of the regenerative and non-regenerative process is provided in Figure 11.

![Figure 11 – Capital and Operating Costs](image)

It is interesting to see how the operating cost of a regenerative wet scrubbing system is distributed. Chemicals (caustic and phosphoric acid) represent a low percentage of the total operating cost, in total only about 20% of the total operating cost. Power and steam are some of the more significant operating cost. However, steam costs can be reduced by using low pressure steam that may limited uses in the process facility. Water costs and solid disposal costs are very low. Also note that since there is minimal water discharge the water discharge cost is essentially zero. O & M costs are higher due to the higher capital cost of the system, since O&M is normally calculated as a percentage of the system capital cost. Finally, cooling water is required, so there is a cost associated with the cooling water. A graphic representation of the regenerative system operating costs is provided in Figure 12.

It is important to remember that this Figure illustrates operating costs. It does not take into account the credit that will be gained by producing a by-product from the concentrated SO₂ stream. When developing an economic comparison the systems this credit certainly needs to be considered as part of the evaluation.
Summary

The control of pollutants from refineries is an increasingly important issue. Particulate, and SO₂ continue to be scrutinized by authorities that regulate these emissions. The technologies discussed here are well proven technologies to control these emissions. The most important task for refiners is to establish a program to select technologies that will address the present needs, while planning for the future so that equipment installed today will fit into that plan.

The basic wet scrubber design used in regenerative and non-regenerative wet scrubbing systems is still the same design that has provided proven reliability for many years. Development continue in order to add proven new and innovative technologies that address additional pollutants of concern, combining these with the established wet scrubbing systems to provide a complete solution to address environmental needs today and for the future.