MEETING EPA CONSENT DECREE COMPLIANCE WITH DYNAWAVE SCRUBBING

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Introduction

Many refineries worldwide are now required to limit SO_2 and particulate emissions from FCC off gases due to increasingly strict regulations imposed by various governments around the world.

One of the accepted methods of treating FCC off gases is wet gas scrubbing. Wet gas scrubbers contact the FCC off gas with a circulating liquid and essentially remove or 'scrub' the pollutants from the gas stream. SO_2, SO_3, and particulate can all be removed by scrubbing; however, different removal mechanisms are required for each of these pollutants. This paper will detail these mechanisms, as well as the parameters that are required for efficient and reliable wet gas scrubbing.

There are many different types of wet scrubbers. In addition to the above mentioned topics, this paper will present one such scrubber, the DynaWave® Froth Scrubber, by Monsanto Enviro-Chem. At the heart of the DynaWave is an open vertical duct or "inlet barrel". Liquid is injected into the "inlet barrel" countercurrent to the gas through a non-restrictive "injector", or Reverse Jet. Liquid, injected by the Reverse Jet, collides with the down coming gas to create a Froth Zone, which is a region of extreme turbulence, with a high rate of surface renewal. Quenching, as well as removal of SO_2, SO_3, and particulate all occur across the Froth Zone. This "elegantly simple" design minimizes capital and operating cost, as well as equipment footprint. In addition, the Reverse Jet is essentially a large bore, open-orifice, nozzle, with no restrictions or small openings. Due to these unique nozzles, the DynaWave can handle major catalyst dumps of over several tons in a few minutes without affecting the performance of the scrubber.

SO_2 Removal

As stated above, the primary acid gas in FCC off gases is SO_2. SO_2 is present as a vapor and remains a vapor even after the gas has been cooled, at least down to the dew point of the gas stream. SO_2 in FCC off gases is typically in the range of 500 ppmv to 2500 ppmv. At this time, most consent decrees are mandating SO_2 levels to be reduced to 25 ppmvd @ 0% O_2.

The amount of SO2 that can be removed from the FCC is primarily a function of:

- Process parameters of the mass transfer device (i.e. scrubber)

- Kinetics of the reagent

Mass Transfer

Wet gas scrubbers use circulating liquid to contact the FCC off-gas and absorb SO_2 into the liquid stream. The amount of circulating liquid is a key process parameter for wet scrubbers. Generally referred to in terms of L/G (liquid to gas ratio; gpm/1000 acfm), the amount of circulating liquid must be enough to fully quench the gas and absorb the appropriate amount of SO_2 from the gas stream. Scrubbing devices such as spray towers have several contacting stages with lower L/G per stage. The DynaWave uses only one or two contacting stages (i.e. Froth Zones) with higher L/G per stage. When comparing devices, it is important to consider the total L/G of the scrubber, as this will have a direct impact on operating power.

Reagent Kinetics

Simple kinetics of chemical reactions can affect the amount of SO_2 absorbed in a scrubbing device as well. Once the SO_2 vapor is absorbed into the liquid, sulfuric acid is formed, decreasing the pH of the circulating liquid. Lower pH inhibits SO_2 absorption. Therefore, reagents are added to the circulating liquid to react with the SO_2 in solution, maintaining an acceptable pH range for further SO_2 absorption. Figure 1 indicates the affects of reagent and L/G selection on SO_2 removal efficiency

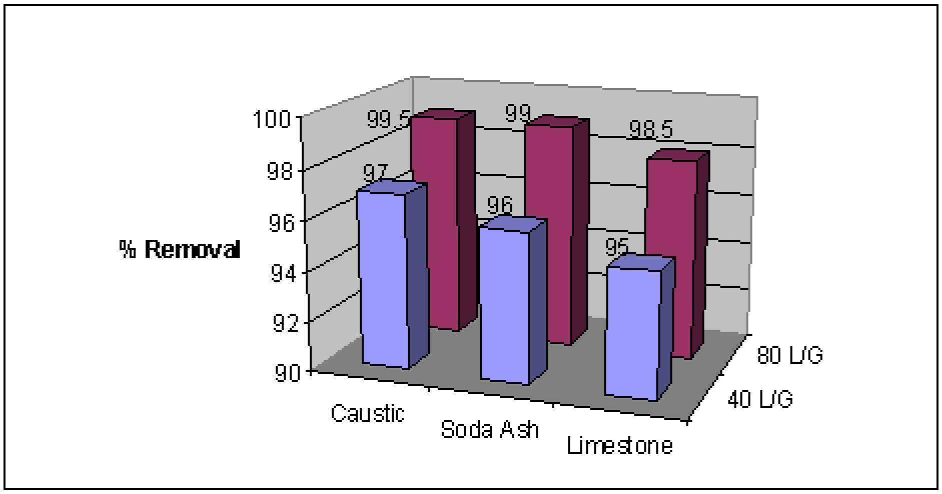

Figure 1. Typical SO_2 Removal Efficiencies of a DynaWave Scrubber

As shown, very high SO_2 removal efficiencies are possible with a DynaWave scrubber and proper liquid circulation rates.

There are several reagents available for use in SO_2 scrubbers, the most common are listed below in the order of most reactive to least reactive:

- Caustic, NaOH
- Soda Ash, Na_2CO_3
- Magnesium hydroxide, $Mg(OH)_2$
- Lime, $Ca(OH)_2$
- Limestone, $CaCO_3$

The following table lists the advantages and disadvantages of each:

Table 1. Advantages and Disadvantages of various reagents

Reagent	Advantages	Disadvantages
Caustic	Most reactive Lowest capital cost Refinery familiarity Reactants -soluble salt Readily available	Highest reagent cost Most difficult/dangerous to handle
Soda Ash	Very reactive Low capital cost Moderate reagent cost Safe to handle Reactants - soluble salt	Requires a mixing system Limited availability
Magnesium Hydroxide	Very reactive Safe to handle Reactants – soluble salt	Requires a mixing system Insoluble Moderate reagent cost Limited availability
Lime	Low reagent cost Readily available Highest capital cost Reactants – insoluble solid	Requires a mixing system Scrubber liquid is a slurry
Limestone	Lowest reagent cost Readily available Highest capital cost Reactants – insoluble solid	Requires a mixing system Scrubber liquid is a slurry Least reactive reagent

One of the most important criteria to consider in selecting a reagent is cost. Total reagent cost is a function of both the cost per pound of reagent as well as the amount of reagent used. For example, only 1.25 pounds of caustic (NaOH) are required to treat 1 pound of SO_2 (compared to 1.56 pounds of limestone ($CaCO_3$) required to treat 1 pound of SO_2). However, the cost per pound of reagent makes the final treatment cost using $CaCO_3$ significantly cheaper than using NaOH. Table 2 summarizes the treatment costs for various reagents.

Table 2. Reagent Treatment Costs

Reagent	Required Reagent, lb/lb of SO_2	Relative Reagent Cost NaOH =1	Treatment Cost/lb of SO_2
NaOH	1.25	1.0	1.25
Na_2CO_3	1.65	0.26	0.43
$Mg(OH)_2$	0.91	0.16	0.146
$Ca(OH)_2$	1.16	0.125	0.145
$CaCO_3$	1.56	0.025	0.04

It should be noted the reagent costs shown above do not include the disposal costs of the reaction products. The refinery should consider all costs involved before deciding upon a reagent to be used.

Of course, the scrubber design must be able to handle the specific reagent. For example, scrubbing with lime or limestone involves circulating and handling slurries, typically as concentrated as 20 wt%. This requires a specific knowledge of designing systems for slurry service to avoid pluggages and excessive erosion. In addition, the gas-liquid contact zone must be able to handle slurries without plugging while at the same time provide an efficient gas-liquid mass transfer contact zone.

The vast majority of FCC wet scrubbers use caustic. Caustic is typically on site, is familiar to refinery operating personal and requires the lowest scrubber capital cost. However, there may be specific circumstances where alternate reagents are more attractive. Each refinery should evaluate and analyze the relative costs, advantages and disadvantages for their particular situation.

Full Scale SO_2 Removal

The DynaWave has been successfully used to remove acid gases in over three hundred installations, including several in the refining industry. In 2003, a DynaWave Scrubber was installed at Navajo, using caustic as the reagent. Before construction of the full scale scrubber, pilot plant testing was conducted with two absorption stages at an L/G of 40, and a pH of 7.0. Table 3 lists the results, performed by an environmental testing agency.

Table 3. Pilot Plant SO2 Removal Results

	Run 1	Run 2	Run 3	Average
SO_2 Inlet (lb/h)	1.87	1.80	1.90	1.86
SO_2 Outlet (lb/h)	0.02	0.01	0.02	0.017
Outlet ppmvd 0% O_2	***5.11***	***3.87***	***5.57***	***4.85***
SO_2 % Removal	***98.9***	***99.4***	***98.9***	***99.1***

Since start-up of the full scale system in fall of 2003, the outlet SO_2 emissions have consistently registered < 1 ppmvd 0% O_2 corrected in the CEM. The system is designed for an L/G of 43, and operating at a pH between 6.5 and 7.0.

Particulate Removal

Unlike acid gases that are absorbed into the scrubbing liquid by mass transfer, particulates must be captured by physical energy in the form of gas side pressure drop. The higher the pressure drop, the greater the solid removal. Particulate removal is also controlled by the size of the particulate. The smaller the particulate, the more difficult it is to remove. This is especially true of sub-micron particulates or those solids that are less then one micron in size. The size of particulates or catalysts fines in the FCC off gas is measured in terms of a particle size distribution or PSD. A typical catalyst fines PSD for an FCC is shown below:

Table 4. Typical Refinery Particle Size Distribution (PSD)

Particle Size	Wt %
< 0.1 microns	0.1
< 0.3 microns	4
< 1.0 microns	35
< 1.5 microns	54
< 3.0 microns	75
< 20 microns	94
> 20 microns	6

The gas side pressure drop required by an FCC scrubber is dependent upon the desired percent removal and the particle size distribution. Figure 2 illustrates the relationship of gas pressure drop versus the percent removal for the above PSD example.

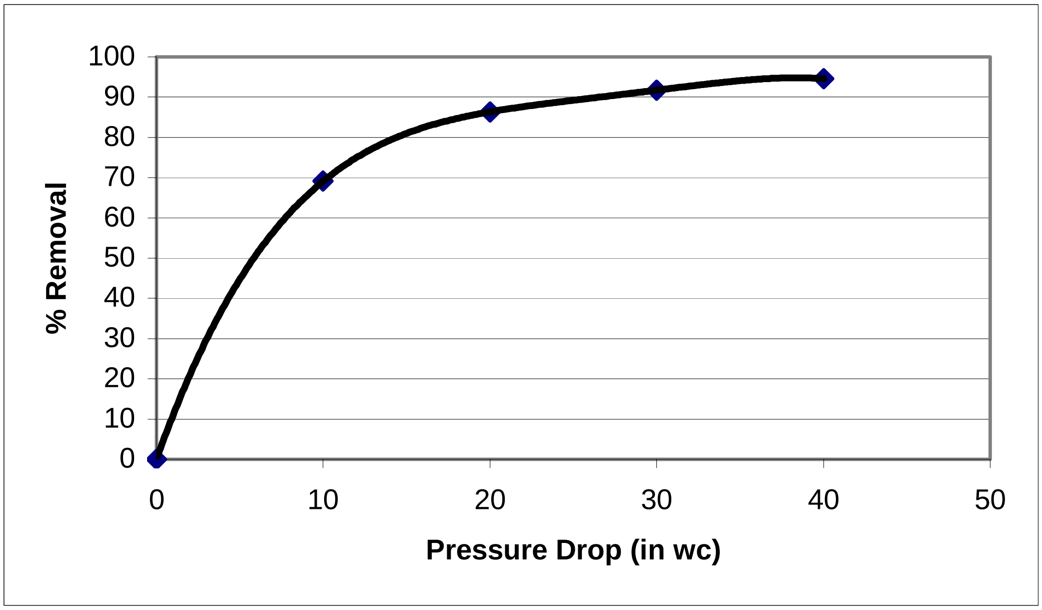

Figure 2. Typical Particulate Removal Efficiency for FCC Catalyst Fines

As shown, in order to achieve 90% removal of the catalyst fines in the FCC off gas, approximately 25" wc is required. However, each situation is unique. In many cases particulate size and loading are such that 90% removal of particulate is not required in order to meet typical consent decree particulate emission requirements of 0.5 pounds of particulate per 1000 pounds of coke burned. In those cases, the scrubber can be designed to operate at pressure drops as low as 8" wc.

Full Scale Results

One of the advantages of DynaWave technology is that particulate removal occurs at the same time SO_2 removal occurs. Therefore, extra equipment is not required to remove particulate from the gas stream. It is for this reason that the DynaWave is often used in situations where both particulate and acid gases are present.

Pilot plant testing at Navajo was conducted with 2 scrubbing stages. Table 5 lists the results, performed by an environmental testing agency.

Table 5. Pilot Plant PM Removal Results

	Run 1	Run 2	Run 3	Average
PM Inlet (lb/h)	1.15	2.39	0.78	1.44
PM Outlet (lb/h)	0.01	0.01	0.01	0.01
PM % Removal	***99.1***	***99.6***	***98.7***	***99.1***

Since start-up of the full scale system in the fall of 2003, the outlet particulate emissions have been reduced by 93% (compared to 1998 test data), well within the requirements of the consent decree.

SO_3/H_2SO_4 Acid Mist Removal

A certain percentage of the total sulfur in the FCC off gas will be in the form of SO_3 acid mist. Unlike SO_2, which can be easily absorbed by adequate gas-liquid contact, SO_3 actually becomes a submicron particulate (H_2SO_4) once it is exposed to the scrubber liquid. The SO_3 condenses and forms an H_2SO_4 submicron mist. It cannot be removed or captured by simple gas-liquid contact but requires physical energy just as particulates. In the case of SO_3 mist however, all of the SO_3 is submicron and requires a substantially higher level of gas pressure drop for the same capture efficiency, compared to typical catalyst fines. Figure 3 shows the required gas pressure drop to remove SO_3 mist.

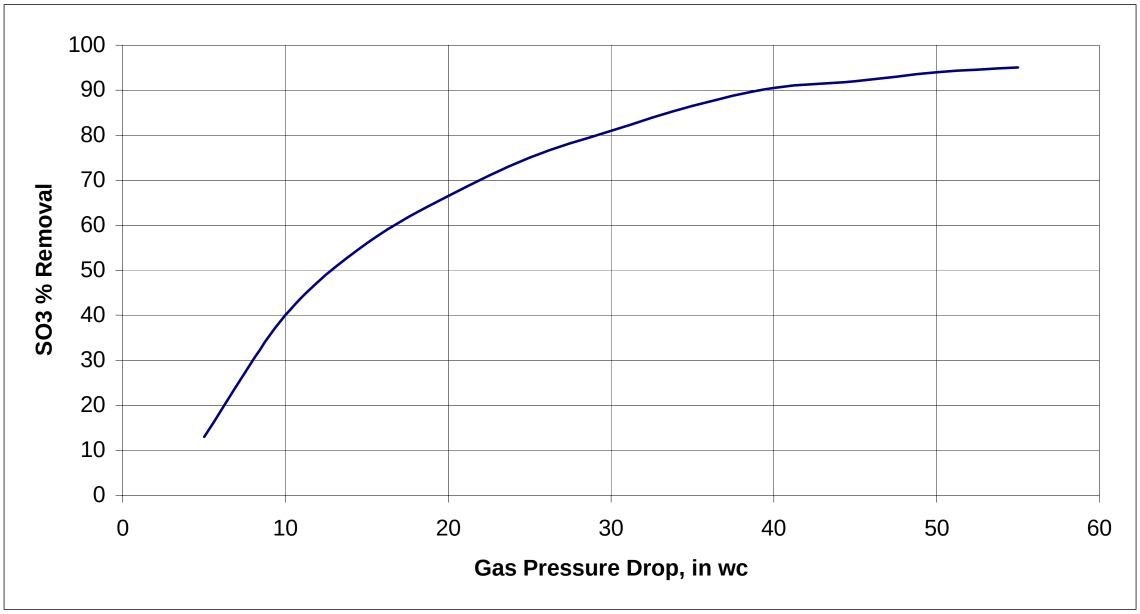

Figure 3. Required Gas Pressure Drop for SO3 Mist Removal

As shown in Figure 3, approximately 30" wc is required just to remove 80% of the SO_3 mist. Fortunately, the level of SO_3 in most FCC off gases is small compared to other contaminates. The SO_3 level in FCC off gases can range from 2% to 10% of the total SOx present. However, the SO_3 level in most FCC gas streams, is between 3% and 5%.

Since SO_3 is only a small percentage of the total SOx, many refineries are not required to remove the SO_3. However, SO_3 can create an opacity problem. Opacity is caused by particulates and mists in the size range of 0.3 to 0.6 micron. As little as 10 ppm of SO_3 mist can create a visible opacity. For this reason, some refineries desire the scrubber system to remove SO_3 as well as SO_2 and particulate.

Gas pressure drop is not the only means for removing SO_3. It can also be removed by a wet electrostatic precipitator or WESP. This device uses an electrical charge to attract the SO_3

particle and remove it from the gas stream. Gas pressure drops for WESPs can be as low as 4" wc, but are relatively expensive compared to other gas treatment methods.

It should be noted that SO_3/H_2SO_4 removal was not tested during the Navjo pilot plant operation, or during full scale operations. The full scale system design was dictated by overall particulate removal, not opacity. However, the plant has not seen evidence of opacity, caused by SO_3/H_2SO_4 mist, during full scale operations.

Effluent Treatment

The extent to which a refinery must treat their effluent is very specific to each site. Effluent treatment can range from no required treatment to total treatment and discharge of potable water. In most cases, the refinery must at least provide an effluent that has been oxidized and contains no sulfite salts. This can be accomplished by the injection of air directly into the scrubber liquid. This is knows as "in-situ" oxidation. The oxygen in the air reacts with the sulfite, SO_3 to produce sulfate, SO_4. The oxidation reaction rate is dependent upon several factors including, the amount of excess oxygen present, the time the oxygen is in contact with the liquid and the total retention time.

The level of oxidation in the scrubber discharge is sometimes measured as a COD or chemical oxygen demand. COD is measured as ppm or grams of oxygen required to oxidize any chemical compound per cubic meter of liquid. Typical COD level requirements can range from 50 to 200 g/m^3. For example, a COD of 200 for a 20% solution of sodium sulfite requires a sulfite oxidation of 99%. A COD of 50 represents a 99.8% sulfite oxidation.

The DynaWave scrubber employs a unique oxidation system. Air is injected directly into the sump of the DynaWave scrubber vessel. This greatly reduces the need for downstream treatment and reduces capital costs. A sparger-piping array in the bottom of the scrubber vessel distributes the air throughout the sump liquid and creates fine bubbles. The vessel sump is then sized to maximize contact time with the air and oxygen as the bubble migrates to the surface of the liquid. The sump is also sized to provide adequate retention time of the liquid in the sump allowing ample time for the oxidation reaction to occur.

DynaWave® Scrubber

Over 300 DynaWave scrubbers have been installed throughout the world since 1985 in many different industries including many installations in refineries. The DynaWave scrubber is a unique scrubbing device because it can quench a hot gas, absorb acid gases and remove particulate all in one vessel.

DynaWave® Scrubber Froth Zone

The DynaWave® FCC Scrubber is a gas cleaning device that creates a zone of intense gas-liquid mixing called the 'froth zone' within the inlet duct to the scrubber. The froth zone is depicted in Figure 4 and is formed with the proper liquid to gas ratio, gas velocity, and nozzle pressure. It is bounded by other gas-liquid regions between atomized, stratified, and bubble regimes.

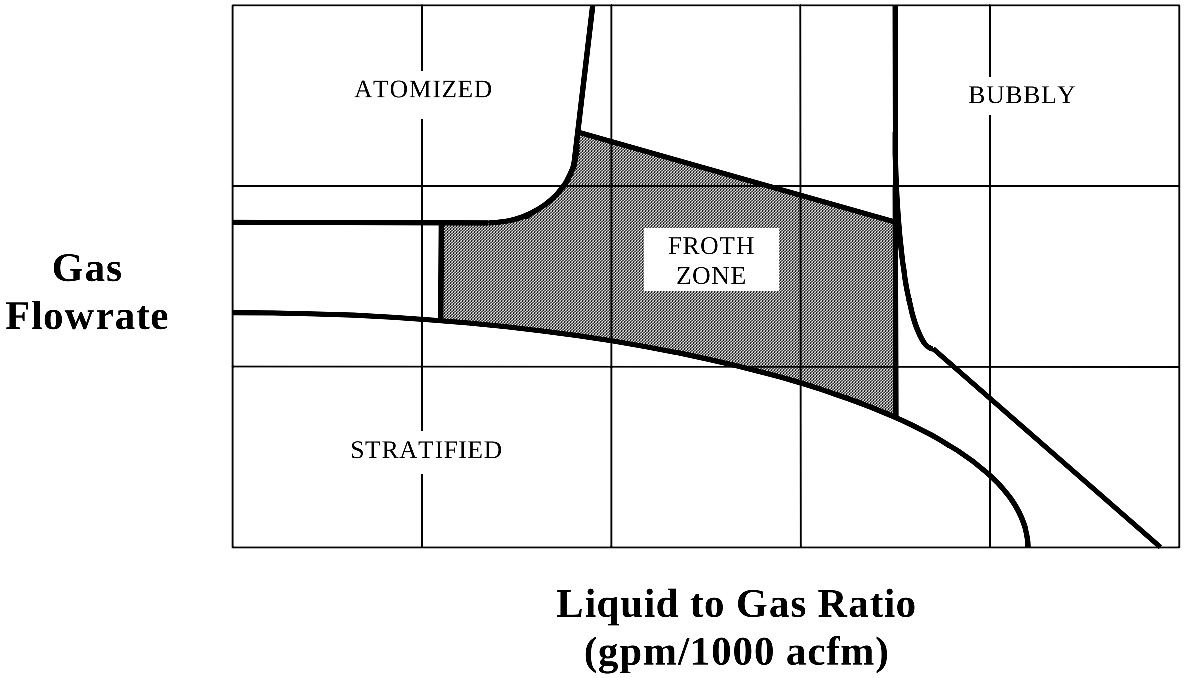

Figure 4. Froth Zone Formation

The DynaWave scrubber is a very efficient contacting device. As shown in Figure 5, the gas enters the inlet duct at the top of the scrubber. The scrubber circulating liquid is injected upward into the gas stream. The injection nozzle also referred to as a 'Reverse Jet', is a non-atomizing high capacity liquid injector. Depending upon the gas flow rate, typically only one to three Reverse Jet nozzles are required in a DynaWave FCC Scrubber compared to multiple levels of nozzles required for other scrubber designs.

A froth zone is established as the liquid contacts the gas in a counter current flow pattern. In the froth zone, the gas is immediately quenched, acid gases are absorbed, and particulates are captured.

Figure 5. DynaWave Scrubber Schematic

The cleaned gas and liquid then exit the inlet duct and enter the scrubber disengagement vessel. The scrubber liquid falls to the sump of the vessel where it is pumped back to the Reverse Jet nozzle for further capture of acid gases and particulate. The treated gas flows through a gas-liquid chevron separation device and exits the top of the scrubber.

The DynaWave Reverse Jet injector or nozzle, shown in Figure 6, is a proprietary design, incorporating a full open throat design that is virtually impossible to plug. For an FCC application the diameter of nozzle throat can range from 8 to 14 inches. The Reverse Jet Spray Nozzles are fabricated of abrasion resistant silicon carbide.

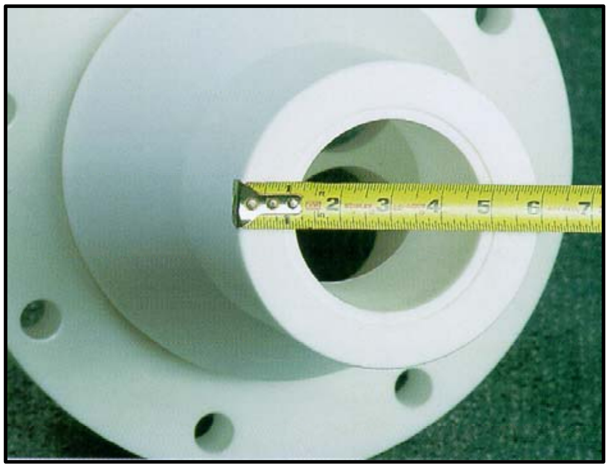

Figure 6. DynaWave Reverse Jet Nozzle

DynaWave Advantages

The DynaWave scrubber has specific advantages over other types of scrubbers. These advantages can be summarized below:

- The DynaWave scrubber can quench hot gases, absorb acid gases, and remove particulates all in one vessel.
- The DynaWave scrubber design incorporates in-situ oxidation of the sulfites, reducing the need for oxidation down stream in a separate vessel or in the water treatment plant.
- The DynaWave reaction zone is confined to the inlet ducting into the vessel, allowing this smaller section of the system to be fabricated of a high corrosion-resistant alloy while the separator vessel can be fabricated of a less expensive alloy.
- The DynaWave system is designed as a slurry scrubber, virtually guaranteeing that pluggages due to solids or FCC reversals will never occur. The large bore non-atomizing liquid injectors are fabricated of abrasion resistant silicon carbide.

Other Refinery Applications

The DynaWave has also been applied in other refinery applications, including gas streams with extremely high levels of SO_2, such as SRU tail gas. SO_2 levels in these gas streams can be as high as 50,000 ppm, especially during SRU bypass modes. Very high L/G ratios (liquid to gas ratios) are required in order to reduce SO_2 from these levels to those levels required by MACT II. Typically, it is not practical to operate conventional scrubbers at these elevated L/G ratios, as the higher L/G ratios can require a series of multiple spray towers or packed columns. However, as the DynaWave technology contains two scrubbing stages in the "inlet barrel", final scrubbing can occur in the gas/liquid disengagement vessel, drastically reducing required equipment sizes and cost. Therefore, the DynaWave can be applied as a cost effective alternative to a SCOT, especially when the SCOT unit's load on the SRU is taken into consideration.

Conclusion

When considering wet scrubbers for the treatment of emissions from FCC off gases, the refinery must consider a wide range of parameters including type of reagent, required particulate removal, SO_3 acid mist removal, materials of construction, and discharge effluent requirements. The DynaWave scrubber offers distinct advantages in several areas and should be considered for FCC scrubber applications. In addition, DynaWave technology can be readily applied to other acid gas removal applications within the refinery, such as SRU tail gas scrubbing.