Advances

in

Sulfuric Acid Plant

Equipment and Processes

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Sulfuric acid production, being one of the oldest chemical processes in the world, has seen remarkable technology improvements over the course of its history. Sulfuric acid plants have progressed from a low efficiency, smokestack industry, to a highly efficient, environmentally responsible industry.

From its birth into commercial production, using the chamber process, sulfuric acid quickly moved into adolescence, with the adoption of the markedly improved contact process. In the early 1970's, sulfuric acid became of age, with the introduction of environmentally friendly and energy efficient double catalysis process. And in the last decade, sulfuric acid technology has moved into its prime, becoming more refined and proving the adage that the industry is not getting older, but is getting better.

In recent times, environmental regulations and market forces have shown a need for lower emissions, higher energy recovery and increased reliability. These needs have been addressed by technology suppliers with subtle refinements of equipment and products, not by broad changes to the process. Because of this, the improvements are not outwardly apparent, even to the trained eye. This paper will be to call attention to those somewhat "hidden" changes, which continue to improve the sulfuric acid industry.

Some of the more significant improvements evident in the industry are summarized below and will be discussed in more detail in this paper:

- As environmental awareness has increased, catalyst technology has improved, leading to lower emissions.
- Mist eliminator capture efficiencies have improved, providing owners with options for very low mist emission requirements.
- Candle mist eliminators in dry towers can provide increased protection for downstream equipment, without excessive fouling.
- Analysis of tower hydraulics has lead to more efficient distributors, without sacrificing absorption or paying significantly higher prices.
- Acid cooler anodic protection systems have moved forward with digital controllers and Graphic User Interface (GUI).
- Plate gas/gas heat exchangers provide greater material and capacity flexibility for sulfuric acid plants.

ADVANCES IN SO_2 ABATEMENT TECHNOLOGY:

Over the last several years, the reduction of SO_2 emissions from sulfuric acid plants has become an increasingly important topic, both from a legislative and environmental consciousness viewpoint. It has been demonstrated in numerous cases that an SO_2 emission level of 100 ppm can be achieved using low feed gas strengths, large catalyst volumes, and four or more catalyst beds.

Recently developments in low ignition temperature, cesium promoted sulfuric acid catalysts, have revolutionized the concept of reducing SO_2 emissions in a cost and energy effective manner. Using cesium-promoted catalysts (Cs-120 and Cs-110), Monsanto Enviro-Chem has demonstrated significant emissions reductions, compared to standard potassium promoted vanadium-based catalysts. The following examples will demonstrate this cost effective application of catalyst technology for enhanced production and reduced emissions within the sulfuric acid industry.

CASE # 1:

A sulfur burning customer wished to increase their production while maintain their total SO_2 emissions limit. The plant is single absorption with air dilution to beds # 3 and # 4 and a feed gas composition of 9.50 % SO_2 and 11.45 % O_2. The converter contained conventional catalyst in beds # 1, # 2, and # 3 with cesium-promoted Cs-110 ring catalyst added to bed # 4.

The use of the cesium promoted catalyst allowed pass #4 to be operated at **770°F** (410°C), which resulted in a more favorable equilibrium conversion level and lower emissions. The result was an ***18 %*** increase in production, with **no increase** in daily so_2 emissions. This can be compared to standard catalyst, which would have resulted in emissions which were 13 % higher than the allowed limit.

CASE # 2:

A metallurgical customer, needing to control smelter-wide sulfur emissions, found it necessary to minimize sulfuric acid plant emissions. The plant is a conventional double absorption plant with HRS. The design feed gas composition is 14.0 % SO_2 and 14.0 % O_2. The converter contained conventional catalyst in beds # 2, and # 3 with a 50% cap of cesium-promoted Cs-120 in pass #1 and Cs-110 ring catalyst in bed # 4.

The cesium promoted catalyst in pass #1 was used to control the highly exothermic reaction in the first pass. By operating the first pass inlet at **734°F** (390°C) the outlet temperature could be controlled to **1,175°F** (635°C). The use of cesium promoted catalyst in pass #4 allowed it to be operated at **734°F** (390°C), which resulted in a more favorable equilibrium limits and lower emissions. The overall result was a stack emission ***< 75 ppm***. This can be compared to standard catalyst, which would have had a theoretical limit of 110 ppm, with considerably higher catalyst loading.

CASE # 3:

A sulfur burning customer was regulated by governing authorities to a maximum of 100 ppm, adjusted to an 8% O_2 basis. To do so, required the sulfuric acid plant emissions to be 99.9%. The plant was a 3 X 2 interpass plant with dilution cooling between passes 4 and 5. The a feed gas composition is 11.50 % SO_2 and 9.45 % O_2. The converter contained conventional LP-120/LP-110 catalyst in beds # 1, # 2, # 3 and #4, with cesium-promoted Cs-110 ring catalyst added to bed # 5.

The use of the cesium promoted catalyst allowed pass #5 to be operated at **734°F** (390°C), which resulted in a more favorable equilibrium and lower emissions. The result was a stack emission level ***< 100 ppm***.

There are also many examples in which the cesium-promoted catalyst has been used to circumvent a plant-related problem which was causing high SO_2 emissions: fouled heat exchangers leading to low bed inlet temperatures, high start-up emissions, difficulties in heating certain catalyst beds during plant startup, etc. Furthermore, the cesium-promoted catalyst can be utilized to redirect heat from one heat-extracting unit to another in order to optimize steam production. All of these applications are uniquely designed for each client. Use of this catalyst may not be economically appropriate for all sulfuric acid producers. Each situation must be studied to determine the applicability of cesium catalyst.

Reducing Acid Mist Emissions:

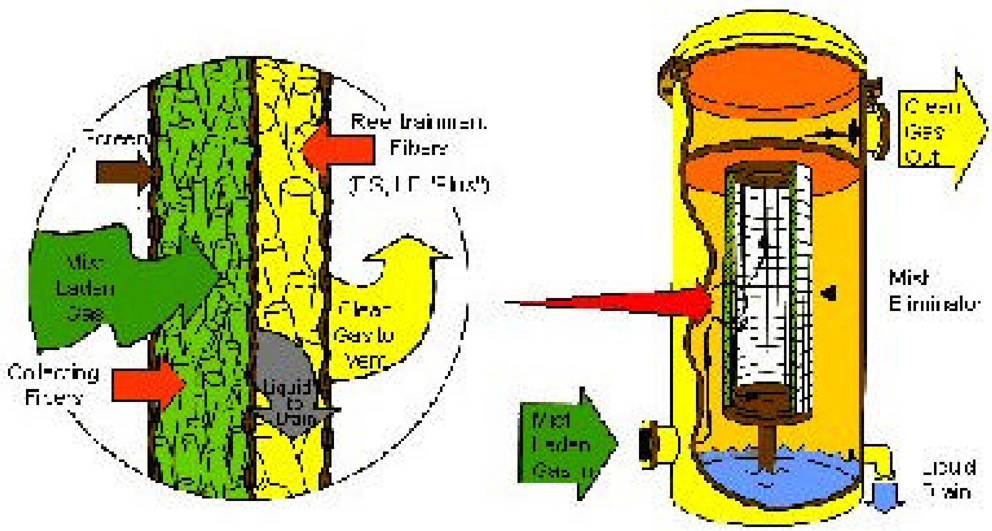
An equally important emission issue centers around sulfuric acid mist. And, control technology has progressed here, equally as well. Acid mist emissions can be reduced below the EPA limit of 0.15 lbs/ST and is being more frequently required by sulfuric acid clients to suite local regulations and permitting.

There are many design parameters to consider when low level acid stack emissions are required. Acid mist formation in absorbing towers is very complicated. Resultant mist particle size distribution is typically bi-modal since submicron particles are formed by reaction/condensation while larger particles are formed by mechanical means.

Mist eliminator design is based on the amount of mist that is generated, mist particle size distribution and maximum allowable emissions. Effective performance can be achieved by proper selection of mist eliminator type, style (orientation), and design velocities, along with careful installation and maintenance.

For low exit mist emissions, the bi-component ES mist eliminator as shown in Figure 1 or the HE "Plus" are good choices since they have high collection efficiency on small particles which improves with plant turndown. The inclusion of a drainage layer significantly reduces acid mist re-entrainment.

Figure 1: ES and HE-Plus elements



A good example of the capability of these mist eliminator elements is the recent startup of a sulfur burning IPA sulfuric acid plant, with a design rate of 700 STPD. The stack acid emission requirement was < 0.075 pounds mist per short ton of acid produced as measured by Method 8. This is half the EPA standard acid mist limit.

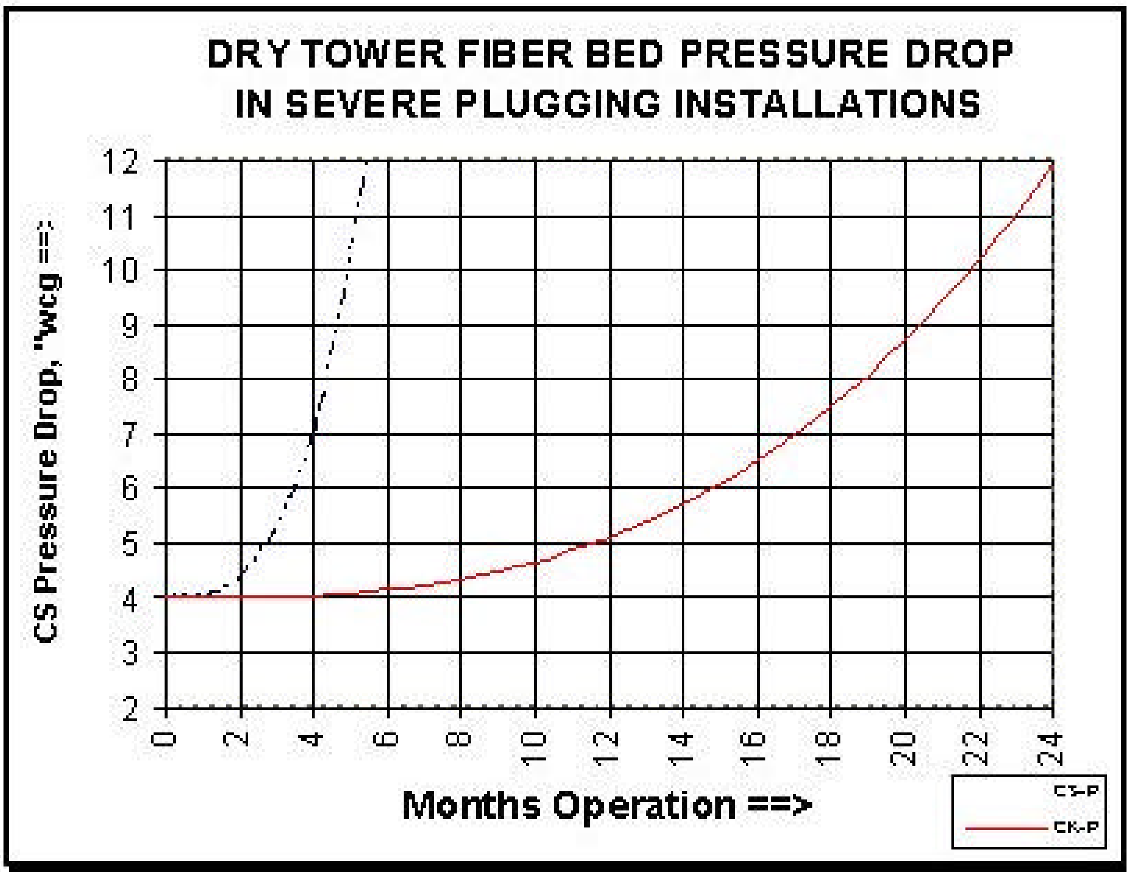
Utilizing 16 ES elements in the final absorbing tower, the actual measured acid mist emission was less than 0.012 pounds mist per short ton of acid produced at design plant rate. This is equivalent to a mist loading of about 0.08 mg/ACF. Thus for this new Monsanto sulfuric acid plant, maximum measured acid emission at start-up was about eight percent of the standard EPA limit.

<u>Impaction Candles for Dry Towers</u>

Because fiber bed impaction devices have higher removal efficiency on smaller particles, compared to mesh pads, they provide more protection for downstream equipment such as a compressor wheel, first pass catalyst, expansion joints and ductwork. The candle arrangement has horizontal gas flow, which improves liquid drainage, since collected acid mist is not held up in the media by the gas. Candle elements also operate at lower velocity compared to mesh pads and are more tolerable to volumetric flow variation.

In addition to improved performance, consideration should also be given to the cost of the operation. Candle elements in dry tower service are usually repacked after several years due to the corrosion of the wire mesh re-entrainment control layer and loss of interwoven glass fibers. In some cases, portions of the drainage layer can be reused. Removing and installing candle elements is safer and quicker than mesh pads, thus saving plant downtime.

Figure 2: CS-1P and CK-1P Field Performance



The standard in this service has been the CS-IP impaction fiber bed. It is designed for improved dry tower performance in sulfuric acid plants. The bed is a cylindrical bi-component packing design using a fiber glass mat for collecting small particles plus an alloy mesh re-entrainment control or “drainage” layer. In sulfur burning drying tower service, CS elements usually need to be washed every 6 to 18 months depending on tower design, and the level and nature of plugging agents.

A new impaction fiber bed for dry towers, the CK, is now available to operate longer between washings and extend time between maintenance shut downs. For sulfur burning plants, service life is typically two years or longer. Although CK elements look the same as CS elements from the outside, the internal Co-knit collection layer is significantly different than standard CS collecting glass media. CK beds are identical in size and capacity to standard CS beds operating at the same gas volume and clean pressure drop. Like the CS design, CK elements also include an alloy mesh re-entrainment control layer.

CK elements use a metal mesh for the collecting layer but this metal mesh structure has small diameter acid resistant glass fibers knitted together into the metal wires to increase the collection targets and thus small particle collection efficiency. The Co-knit metal mesh collecting layer is considerably thicker and has a higher void fraction than the glass collecting layer used in standard CS elements. Because of this open structure, in severe plugging situations, CK elements operate much longer between cleanings than regular CS elements.

Figure 2 illustrates actual field performance of standard CS-IP elements compared to new CK-IP elements in severe plugging installations where towers were highly sulfated and no upstream air filters were used. The new CK elements ran significantly longer in dry tower service before needing to be washed or repacked.

CS or CK beds can be washed outside the tower very easily by dunking in a sump or using low pressure hose water flushing. Washing this way normally restores beds to their original pressure drop.

Alloy Distributors at Cast Iron Prices

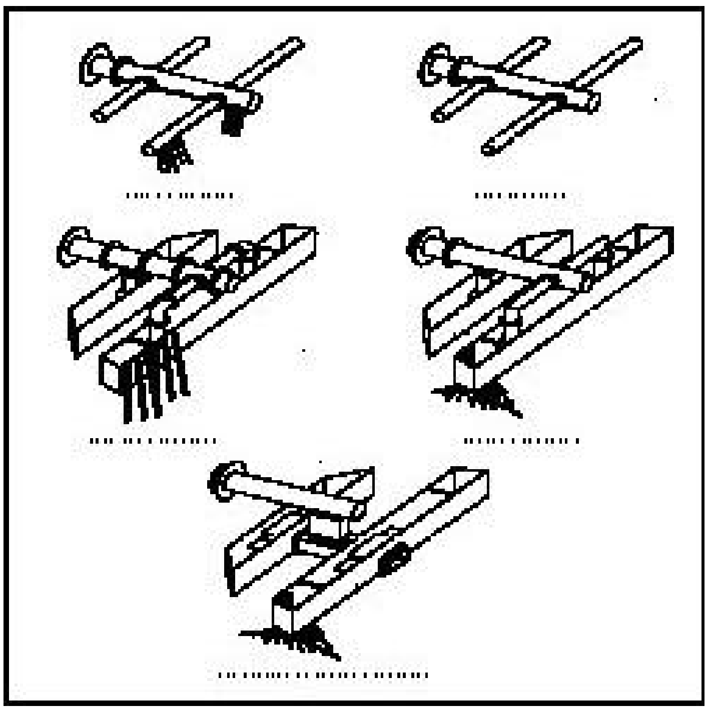
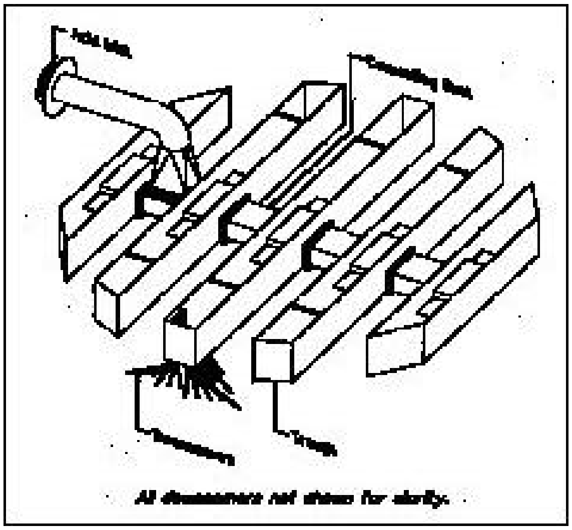


Figure 3: Types of Sulfuric Acid Distributors

Acid distribution systems are the key component to good SO_3 absorption in sulfuric acid plants. Over the years, acid distributors have evolved into designs using alloy materials and better acid coverage across a tower cross section. Since there are many approaches to any given problem, one must be careful in choosing an acid distributor that is best suited for the given situation.

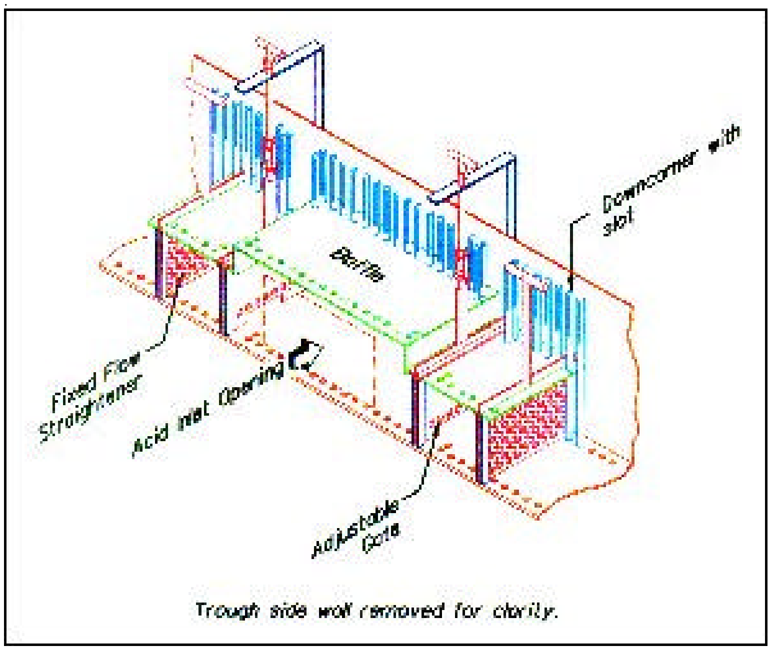
Acid distributors are designed to uniformly distribute acid over a bed of packing. A gas stream flowing counter-currently to this acid flow is contacted by the acid to absorb SO_3. Good SO_3 absorption is crucial to tower performance and is a function of the uniformity of the acid distribution. Non-uniform distribution can cause problems such as mist generation and SO_3 slippage. This can result in exceeding emission standards and excessive corrosion in downstream equipment. As shown above, there are three main styles of acid distributors used in the sulfuric acid industry today.

<u>**New Generation Alloy Trough Distributors**</u>



Taking trough style distributor design one step further, the New Generation Alloy Trough Distributor (patent pending) by Monsanto Enviro-Chem Systems is the state-of-the-art distributor on the market today. This distributor maintains the alloy trough and downcomer design, but eliminates the required overhead pipe system. Instead the trough sections are connected together by a series of ducts. A set of gate valves in each trough then regulates the flow to each segment of the trough.

The New Generation distributor can accommodate varying flow rates by just raising or lowering the adjustable gates in each trough. This makes the system easy to retrofit for higher capacity. A computer program models each individual system to calculate the correct gate heights required to ensure uniform distribution. Wider and deeper troughs result in very low acid velocities inside the troughs. These low velocities translate into very smooth acid flow and equal distribution to all areas of the tower. Optional flow straight-eners downstream of the adjustable gates can make trough acid velocities even lower. Concerns that solids, such as packing chips, will stay suspended in alloy style troughs causing pluggage of the downcomers are further reduced with the larger, less turbulent, pool of acid. Without the need for header piping in a trough there is now more room for downcomers in a single troughThis reduces the number of troughs required to correctly cover a tower diameter. Systems where 6 and 7 troughs were needed before now, require only 4 or 5 troughs. This keeps gas velocities low and mist generation to a minimum.



Trough side wall removed for clarity.

New Generation distributors can be made from a choice of alloy materials which suit a customers specific design needs. Lighter materials and fewer troughs has made this system even easier to install. This distributor also requires very little maintenance.

Other benefits of alloy trough distributors are:

- Complete coverage of the perimeter of the tower. Downcomers can be designed to cover all portions of the tower, even the perimeter. This means no channeling of gas through the packing as seen with the pipe, cast iron and hybrid distributors.

- More coverage means less packing is required. (Increasing the distribution pts/ft^2 to 4 can reduce packing height to 8 ft.). This in turn reduces pressure drop across the tower and can increase capacity, in some cases.

- The design occupies a much smaller cross sectional area of the tower thus reducing gas velocity. Lower velocity results in less mist generation.

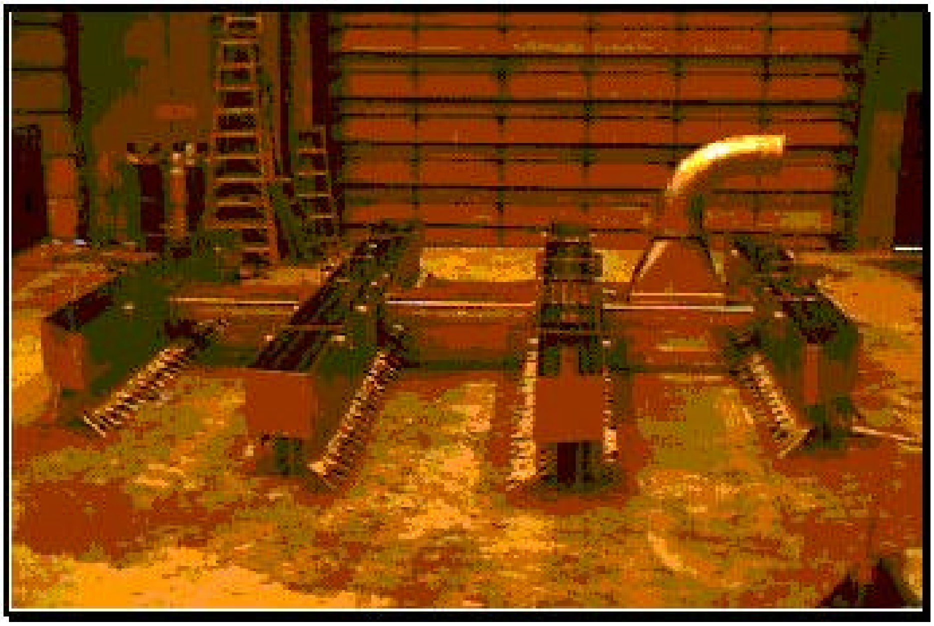
- Can be used in new and retrofit applications.

By removing header piping from the design, New Generation style distributors are more cost efficient. A couple of cost comparisons are shown below for towers approximately 20 feet in diameter.

	Comparison 1	Comparison 2
Acid Concentration	98.6%	96%
Acid Distribution Points	1.4 pts./ft2	2 pts./ft2
Base Cast Iron Acid Distribution System	\$260/ft^2	
310M New Generation Distribution System	\$275/ft^2	
Hybrid Distributor System (Estimated)		\$450/ft^2
SX New Generation Distribution System		\$450/ft^2

As it can be seen, the New Generation Trough Style Distributor in 310M is very cost competitive with basic cast iron distributors. Interestingly, premium materials, such as SX, can even be purchased for the same price as a hybrid style distributor.

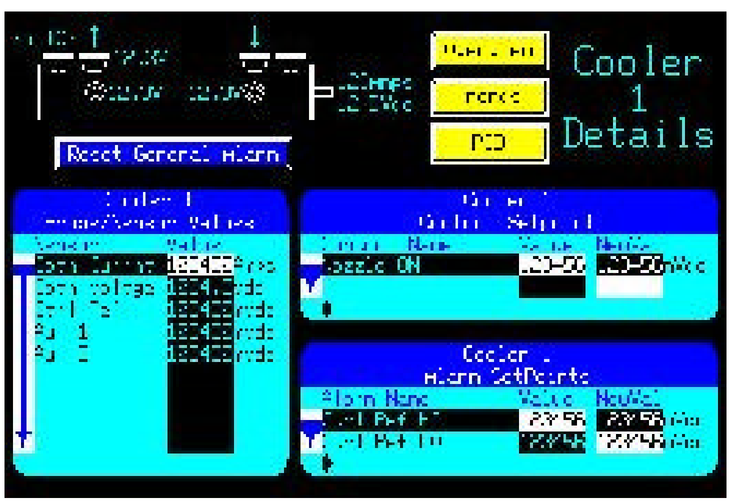
Figure 4: New Generation Distributor for a 21.75 ft. ID Tower



Digital Anodic Protections Systems with GUI

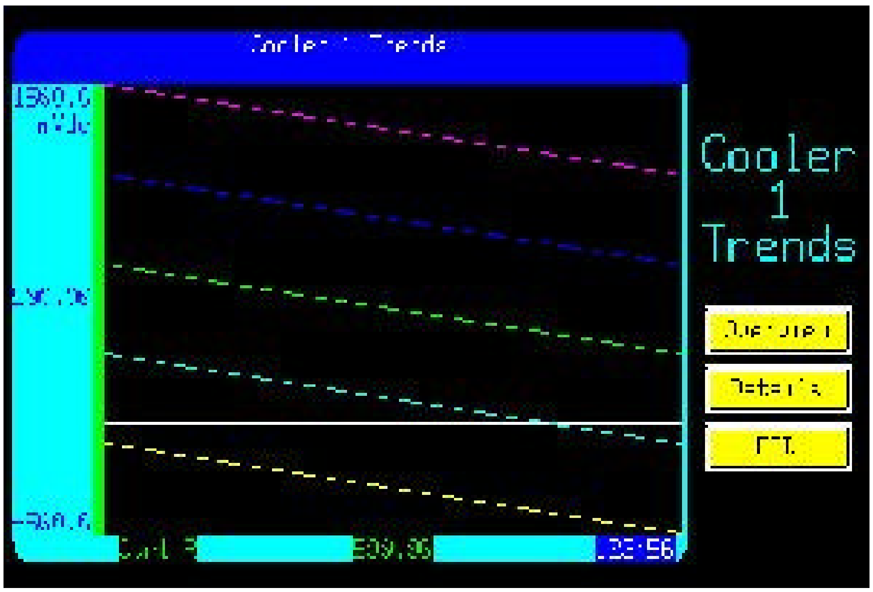
In a continuing effort to improve our products, Monsanto Enviro-Chem has introduced a new generation of Anodic Protection - Filmgard 4™ for acid coolers. The unit Filmgard 4™ offers a touch screen graphical user interface (GUI) for the input and monitoring of data, an integrated control system using state of the art equipment, increased Power Pac output and the ability to remotely troubleshoot cooler problems.

The operator interface on the Filmgard 4™ system features color graphics, which can concurrently present all electrode readings and control parameters for a cooler. The monitoring of values for cathodes and reference electrodes and the announcement and control of alarms are all functions controlled directly through the GUI. Setpoint input is through an integrated electronic number pad.



The input of critical information, such as control or alarm setpoints, are password protected to avoid any unauthorized tampering. Up to three individual coolers can be controlled from one operator interface. This feature allows for a reduction in costs, and centralization of control.

Another significant advantage to the new operator interface is that data received from a cooler's cathodes or reference electrodes will be trended and displayed for the previous 48 hours. The resulting trending will give plant operators and engineers a valuable tool in troubleshooting plant operational problems, and reviewing operating history. The following illustration shows the format in which the trended data will be displayed:



The Filmgard 4™ controller utilizes a proprietary integrated digital controller, which replaces the custom circuit boards. This controller contains a proprietary program, which graphically represents input and output signals and also controls the application of current from the Power Pac to the cooler cathodes. This controller is a less expensive, more reliable alternative to circuit boards, and has resulted in an approximately 10% reduction in the controller cost for Filmgard 4™.

Another advantage of the integrated controller is the ability to remotely troubleshoot problems. All Filmgard 4™ controllers come equipped with an external phone jack. Through this, Monsanto will be able to monitor the cooler remotely and diagnose the problem much quicker. This standard feature can reduce the necessity for field calls.

As with the last generation controller, certain pieces of the Power Pac have become outdated. The SCR firing circuit and the Triac from the Filmgard 3™ are no longer off the shelf items, and must be custom manufactured. These items have been replaced with a new, readily available firing circuit module for Filmgard 4™. Also, the output of the Filmgard 4™ Power Pac has been increased, to allow for most coolers to be passivated with only one Power Pac. With Filmgard 3™, if a cooler was larger than 5000ft^2, two Power Pacs were required for passivation. This benefit results in a lower price for customers with larger coolers, as it reduces the waste of multiple Power Pacs.

The Filmgard 4™ system is compatible with most DCS systems. Should the client wish to incorporate the Filmgard 4™ system into a new or existing DCS system, MEC can provide the necessary equipment and logic diagrams to make this possible. This option provides a significant cost savings, as it eliminates the controller portion of the stand alone system.

Plate Gas/Gas Heat Exchangers

Gas to gas heat exchangers are key components in modern sulfuric acid plants. They provide the effective heat transfer needed to maintain catalyst bed temperatures essential for good conversion efficiency. Most traditional designs utilize various arrangements of the shell and tube heat exchanger. Newer configurations, such as radial flow units, have improved on traditional designs, but these shell & tube units still lack flexibility, due to their unitized construction.

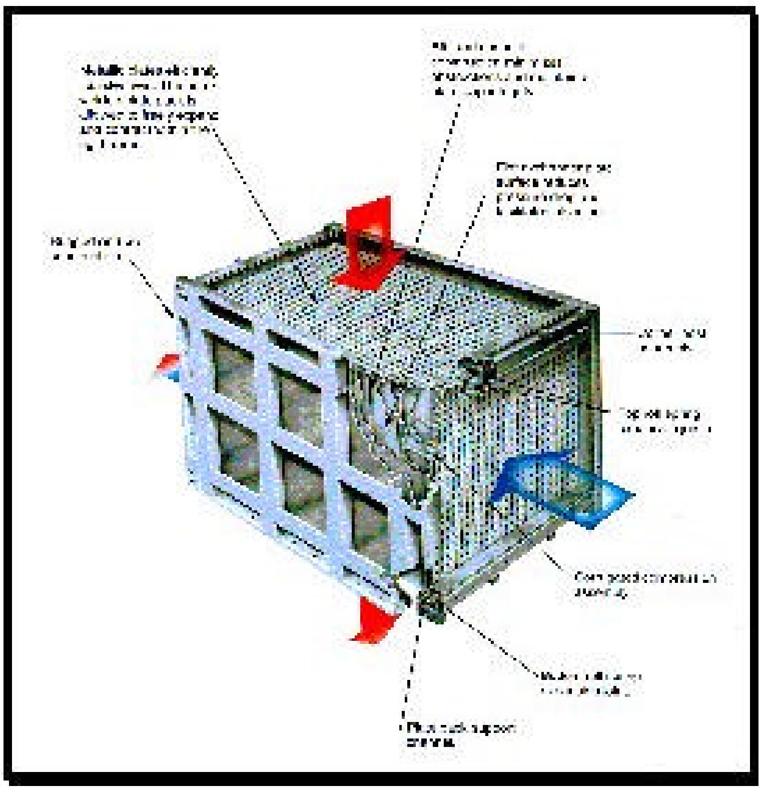


Figure 4: Assembled Modular Block

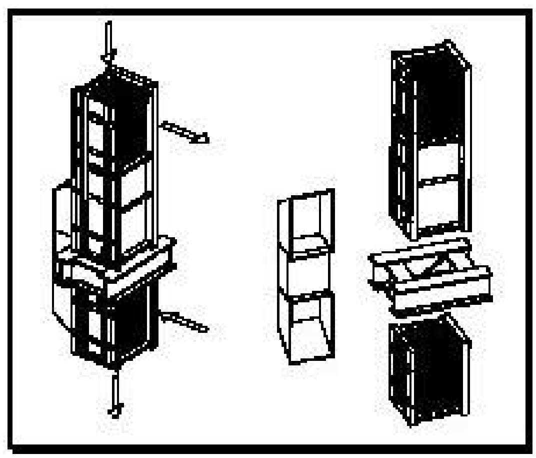
Enter Monplex™ gas-gas exchangers. These units are constructed using plate technology and are designed in modular blocks. These modular blocks are combined in various series and/or parallel configurations to meet the specific process need. The modular design of the Monplex™ gas-gas exchanger offers the benefits of flexible and efficient flow arrangements and freedom to select appropriate materials of construction for each heat transfer zone.

A single unit consists of one or more modular blocks of plate packs, configured in a crossflow, counterflow or other configuration. The blocks can be arranged in parallel or series, as the process requires. The gas flow passages are formed by directional ribs sandwiched between flat plates. These flat plates allow for efficient heat transfer, and reduce pressure drop over equivalent shell & tube units. Inter plate spacing is typically 7/16" to ¾" and has a typical rib spacing (pitch) of 4" to 8". The modular blocks are shop fabricated, and are designed to be easily transportable and assembled in the field into finished units, reducing costly field fabrication.

Monplex™ units have shown less than 0.5% leakage in shop testing. Once operational, the compressive forces of the rigid frame pack upon the expanded plate arising from
thermal expansion reduce leakage to a level generally too low to measure. Obviously, fabrication using stainless steel, instead of traditional carbon steel, offers better resistance to acid corrosion at the cold inlet of a shell & tube cold interpass heat exchanger and sulfidation in hot exchangers. The Monplex™ unit offers a unique opportunity for the heat exchanger designer to customize material selection for the service, by specifying the appropriate metallurgy for each block. For example the cold block with stainless steel plates, the intermediate block with carbon steel plates, and the hot block with stainless steel plates, or whatever the specific process may require. Also, if pressure and flow requirements change due to modification in the existing plant process, the Monplex™ exchanger can easily be modified by adding additional units in parallel to meet the new process needs.

Modular Block Breakdown

This modular design with different materials of construction also shows distinct advantages when a unit is due for replacement. A typical carbon steel shell & tube gas-gas exchanger will last anywhere from 5-15 years, depending on specific usage. Normally on a shell & tube exchanger, corrosion or excessive fouling is localized, and does not occur throughout the entire exchanger. Obviously, shell & tube designs do not easily allow for replacement of the damaged area alone. The Monplex™ design will allow for replacements of individual blocks, significantly reducing maintenance costs.



The Monplex™ exchanger design also allows for easier cleaning than a standard shell & tube unit. The relatively small length of the block in the cross flow direction coupled with the large width of the open unobstructed flow paths allows for inspection and water washing on both sides of the exchanger.

The first commercial installation of a Monplex™ Cold Interpass Exchanger started up last fall in the USA. The Monplex™ unit was designed with three passes on the cold side, and one pass on the hot side. A 3 series x 3 parallel configuration was used, with each unit with a crossflow configuration. The three cold pass blocks were constructed of 316 stainless steel, while the intermediate and hot passes were constructed of carbon steel. The exchanger was designed so that each pass could be removed independently of the other two, either for maintenance or replacement. The exchanger has been performing as expected. The design conditions of this unit are as follows:

Monplex™ reference unit design conditions

	SO_3 Gas	SO_2 gas
Flow Rate	440,511 lb/hr	334,377 lb/hr

Temp In	682 °F	180 °F
temp Out	456 °F	470 °F
ΔP	9.5 InWC	4 InWC

SUMMARY

In the last ten years, the changes in sulfuric acid technology have focused on refinement of equipment components that comprise the process. The changes have not been startling, but nonetheless significant.

In the environmental area, high performance Cs catalyst has made it possible to reduce SO_2 emissions by 50% or more, with a conventional 3 x 1 converter. It has been shown that more efficient mist eliminators can also significantly reduce acid mist emissions. However, one must also remember that these environmental advances do not come without a price and are generally not economically justified. Thus, that ever so delicate balance must be found between global competitiveness and environmental stewardship.

In other areas, improved mist eliminators offer better protection for downstream equipment, without the usual concern for loss of production due to pluggage. Age old distributor corrosion problems have been addressed by corrosion resistant steels designed specifically for sulfuric acid service. And in the latest leap forward, the premium costs of alloy trough distributors have been overcome by more efficient designs.

Acid cooler anodic protection systems have graduated from analog to digital with the introduction of Filmgard 4™, and in doing so, have greatly simplified the system. State-of-the-art components ensure very high reliability, ease of replacement, lower capital investment and remote troubleshooting.

And, not least in importance, the modular advantages of the Monplex™ gas/gas exchanger ideally fit today's sulfuric acid plant operations. The various combinations of construction materials and flow configurations, combined with the ease of maintenance and flexibility of replacement, make Monplex an exciting new alternative for gas-gas exchanger applications.

Like a fine wine, sulfuric acid production is improving with time. However, it is not necessary to wait for a special occasion to be able to enjoy these innovations. They are affordable and ready for immediate use, in a plant like yours!