Department of Environmental Protection

Lawton Chiles
Governor

Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Virginia B. Wetherell
Secretary

September 17, 1997

CERTIFIED MAIL - RETURN RECEIPT REQUESTED

Mr. Ivan Nance
Corporate Environmental Manager
Mulberry Phosphates, Incorporated
Post Office Drawer 797
Mulberry, FL 33860

Re: Modification No. 1050048-002-AC (PSD-FL-238)
Mulberry Plant Sulfuric Acid Plant Increase in Annual Hours of Operation

Dear Mr. Nance:

We have reviewed your letter of August 14 to Howard Rhodes regarding the statement in the final BACT determination for the referenced project to increase hours of operation.

Among the sources available to us, which indicate that lower values are possible, are articles such as the one provided by you (July 6, 1990) on the rebuilt sulfuric acid plants incorporating the Monsanto Enviro-Chem Heat Recovery System at a facility in Korea. According to that article, the plants operated at 1430 and 1442 tons per day which was above their guaranteed and expected production rates of 1350 tons per day. They achieved conversion rates of 99.85 percent and 99.9 percent even though their guarantee was only 99.6 percent and the expectation was 99.7 percent. The performance equates to somewhere between 1.3 and 2 pounds per ton of sulfuric acid. Interestingly, the plants shut down for "scheduled maintenance" after 8 and 9 months of operation. It is probably not necessary to assume that emissions must reach 4 pounds per ton by the time of a planned turn-around.

Measures such as described by Monsanto in its 1992 article "SO_2 Emissions Reductions in Sulfuric Acid Plants," indicate that use of Monsanto Cesium Catalyst in conjunction with optimization of plant operations by the Monsanto Portable Gas Analysis System (PeGASyS), can result in emissions reductions. The article states that "pollution reduction commitments by many major corporations as well as government regulatory requirements are responsible for the continuing trend to develop new and cost-effective technologies to further reduce the SO_2 emission levels from sulfuric acid plants." We assume these reductions would be below the NSPS established in 1971.

If you still do not agree with the statements or the final BACT determination rationale, write back and we will consider your comments and revise the final BACT determination. We assume that you do not disagree with the BACT determination made in this case requiring control equal to the NSPS for sulfuric acid plants.

If you have any questions regarding this matter, please call Al Linero at 850/488-1344.

Sincerely,

C. H. Fancy, P.E., Chief,
Bureau of Air Regulation

CHF/aal

Enclosures

"Protect, Conserve and Manage Florida's Environment and Natural Resources"

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Mulberry Phosphates
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Mulberry, Fl
33860

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PS Form **3811**, December 1994

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PS Form **3800**, April 1995

MULBERRY PHOSPHATES, INC.

CERTIFIED/RETURN RECEIPT
NO. P 576 123 991

RECEIVED
OCT 06 1997
BUREAU OF
AIR REGULATION

2 October 1997

Mr. C.H. Fancy, P.E. Chief
Bureau of Air Regulation
Fla. Dept. of Environmental Protection
2600 Blair Stone Road
Tallahassee, FL 32399-2400

Re: Your letter of 17 September 97

Dear Sir:

On 23 September 1997, I received your letter response to my comment letter of 14 August 1997 to Howard Rhodes. I have read with great interest the three (3) attached articles. However, I find contradiction between the articles; but, also notice that a good explanation of the cause of needed "turnarounds" in the article by Leonard Friedman of *Acid Engineering and Consulting, Inc.*

Mr. Friedman's article at page 4 seems to indicate that improvements of catalyst geometry has led to longer periods between turnarounds--"Ring catalyst allowed an increase in operating time between turnarounds from 12 months to 18-24 months." The paragraph then goes on to discuss an even newer ribbed design with yet even lower pressure drops, inferring to this reader that even longer times between turnarounds are forthcoming. As this article implies, turnarounds in sulfuric acid plants are primarily a function of pressure drop across the catalyst; not a function of catalyst activity.

That paper at page 7 also discusses "cesium" catalyst and notes "cesium catalyst is rarely used in sulfur burning plants, but has found some advantages in spent acid regeneration and metallurgical plants."

Both of Monsanto's articles are of interest also, but they seem to lack specific information as to how the conversion rates were achieved. The article about the Korean plant indicates that prior to modification, the plant's performance in terms of production, had already been improved from

1,050 TPD to 1,350 TPD. The final design included "A final separate one-pass stainless steel converter for the after interpass absorption conversion of SO_2 to SO_3" Somehow, then maintaining or exceeding 1,350 TPD production capacity is not surprising, as greater conversion capacity was added. It is of interest, however, that Monsanto only guaranteed 99.6% conversion efficiency even with the added converter and the second absorber (heating recover system); this suggests that some room for error must be provided for in "design" criteria and emission estimates.

It is also interesting to note that the SO_2 strength of the Korean plant was improved to 8.3% (12.6% oxygen); compared with an SO_2 strength of 11.5-11.75% typical in Florida plants (9.4-9.15% oxygen). The effect of increased oxygen (12.6% in the Korean plant compared with 9.15-9.4% in Florida plants) on SO_2 to SO_3 conversion is addressed in Frideman's article. For MPI to operate at a SO_2 strength of 8.3%, we would have to operate our 2,000 TPD plant at a rate of about 1,420 TPD.

Monsanto's article "SO_2 Emissions Reductions in Sulfuric Acid Plants" is interesting, but seems to be more directly applicable to cesium catalysts installed in single-absorption, sulfur-burning plants, or double-absorption spent acid plants. The only direct reference to sulfur-burning, double-absorption plants is found in figure 5, which on page 7 is referenced as ".... a typical Converter Performance Summary for a sulfur burning double absorption plant."

Figure 5 indicates conversion after the fourth pass outlet as 99.744% and SO_2 emissions at 3.35 lbs. SO_2/ton. Without further knowledge of the plant's design or operating philosophy, i.e., maximum heat generation for cogeneration or maximum acid production, it is hard to imagine that this represents anything other than typical. As a "typical," then one would expect that there are plants with higher and lower conversion rates and SO_2 emissions.

In contrast to the assumption stated in your letter, none of the case histories cited are plants that are sulfur-burning, double-absorption. The single absorption, sulfur-burning plants are not achieving NSPS levels as their post-improvement emissions are 19 lbs. SO_2/STPD, 21 lbs. SO_2/STPD, and 12 lbs. SO_2/STPD, as compared to the NSPS limit of 4.0 lbs. SO_2/STPD. The other two case histories (double-absorption spent acid plants) do not mention specific emission levels for pre- and post-information.

Coincidentally, MPI has utilized Monsanto's portable gas analysis system at the Mulberry, Florida, plant to diagnose emission increases. The use of the device revealed SO_2 slippage due to leaks in heat exchangers. The system is valuable for optimizing operating conditions.

In closing, the three articles seem to contain contradictions as to the usefulness of cesium catalysts in sulfur-burning, double-absorption plants, indicating that the PEGASYS can be useful when properly utilized, and provide information that time periods between turnaround are increasing due to catalysts designs. With these concepts in mind, and without specific knowledge of the cited plant's design or operating philosophy, it does not seem that these articles are related to or support the Department's statement that more frequent catalyst screening or replacement will result in lower emissions. MPI has and will continue to utilize emerging technology to improve plant performance with respect to emissions.

Should further information or response be required, please contact our offices.

Very truly yours,

Ivan Nance
Corporate Environmental Manager

/rmm

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AUG 22 1997

DIVISION OF AIR
RESOURCES MANAGEMENT

MULBERRY PHOSPHATES, INC.

Clair - pls handle

CERTIFIED/RETURN RECEIPT
NO. Z 313136 250

14 August 1997

Mr. Howard L. Rhodes, Director
Division of Air Resources Management
Department of Environmental Protection
2600 Blair Stone Road
Tallahassee, FL 32399-2400

Re: Mulberry Phosphates, Inc.; Permit No. 1050048-002-AC

Dear Sir:

On 8 August 1997, Mulberry Phosphates, Inc. received from the Florida Department of Environmental Protection (the "Department") permit no. 1050048-002-AC. This permit allows for an increase in the hours of operation of the existing sulfuric acid plant allocated at MPI's Mulberry, Florida facility. No proposals to modify the actual plant were made.

After receipt and review of the permit and appendices, MPI has noted that the Department had added language or statements in Appendix BD; Best Available Control Technology, that had not previously been included in the permit package. Specifically, the Department added a second paragraph in its BACT Determination Rationale that reads, *"It is possible to achieve lower values by more frequent catalyst screening and replacement. Although such changes are probably feasible for new, refurbished or reconstructed plants, the Department considers such a requirement to be of marginal benefit for a slightly greater than four percent increase in hours of operation at an existing plant."*

MPI believes that the Department has acted inappropriately in modifying the draft document without first allowing the company to review the additions. MPI is confused what purpose the addition serves or the Department's basis for making the added statements. If the Department has pertinent technical information to support the additional language, MPI requests the information be provided to the Company for proper evaluation.

MPI does not believe the Department's statement is correct, and requests that the statement is removed from the permit.

Please consider the foregoing comments and respond accordingly. Should further information or response be required, please contact our offices.

Very truly,

Ivan Nance

Ivan Nance
Corporate Environmental Manager

/rmm

P.O. Drawer 797, Mulberry, FL 33860 · *Phone* 941-425-1176 · *Fax* 941-425-5446

Monsanto Enviro-Chem

SULFURIC ACID HEAT RECOVERY SYSTEM (HRS) OPERATIONS AT NAMHAE CHEMICAL CORPORATION, KOREA

R. M. Smith, J. Sheputis

Monsanto Enviro-Chem Systems, Inc.
P. O. Box 14547, St. Louis, Missouri 63178 USA

U. B. Kim, Y. B. Chin

Namhae Chemical Corporation
CPO Box 3259, Seoul, Korea

Presented at "Sulphur 88" - Vienna, Austria
November, 1988

ABSTRACT

Monsanto Enviro-Chem's (MEC) patented new Heat Recovery System (HRS) recovers most of the heat from sulfuric acid plant absorbers at up to 10 bars pressure. HRS was proven in pilot plant operation from 1983 to 1985. The first commercial unit was started up very successfully on Namhae Chemical Corporation's (NCC) 1350 t/d plant in November, 1987. With almost a year of operating experience, HRS has proven easy to operate, met all design criteria and has operated with a high on-stream time. HRS has been sold to several other customers and many others are evaluating the economics in their plants.

The following comment was made by K.P. Chae, Managing Director of Engineering and Projects and former Plant Manager of Namhae's Yeosu site:

> "Without challenging spirit, you can't get much. We are proud of being the first case of commercial application of Monsanto Enviro-Chem's HRS technology.
>
> After many sleepless nights during the initial start-up and then following eight months' uninterrupted operation, now I can comfortably say that Namhae has made the right decision to go ahead with HRS, which has been tremendously profitable for Namhae Chemical Corporation by killing 'three birds with one stone': Energy saving, production increase and lowering emission."

TECHNICAL BACKGROUND

The production of sulfuric acid in sulfur burning acid plants generates large quantities of heat from the combustion of sulfur to sulfur dioxide; the catalytic oxidation of sulfur dioxide to sulfur trioxide; and the heat of formation of acid as SO_3 is absorbed in sulfuric acid.

The heat of sulfur combustion and oxidation of sulfur dioxide have been utilized for years to generate steam. Until the mid-1970's, energy recovery from acid plants was about 55%. Then, as fuel prices increased, acid plants were optimized to generate more steam. Low gas-temperature economizers, low pressure drop catalyst, suction drying towers, increased SO_2 gas concentration and preheating boiler feedwater with acid became commonplace and energy recovery from acid plants increased to 70%. However, 30% of the heat was still lost. This heat loss was primarily in the acid formation and cooling process.

Monsanto Enviro-Chem initiated a major research effort in the late 1970's to recover more of this lost energy. The research progressed through studies and laboratory tests until 1983 when a pilot tower was installed in a 550 t/d acid plant to demonstrate the now patented Heat Recovery System (HRS).

The basis of the HRS is that sulfuric acid in the 99% range has low corrosivity toward certain commercially available alloys at temperatures up to 220°C and higher. The high acid temperature provides the driving force to economically generate steam while the acid still readily absorbs SO_3 gas.

The HRS becomes commercially viable when it is located before existing absorption towers or is used as the interpass absorption tower in a new plant. Figure 1 is a process diagram showing the major equipment items. The sulfur trioxide ladened gas flows to the Heat Recovery Tower (HRT) where the sulfur trioxide is absorbed in sulfuric acid. The absorption of the sulfur trioxide increases the temperature and concentration of the sulfuric acid. Concentrated, hot sulfuric acid leaves the tower at Point B. The acid is cooled by generating steam in a boiler and leaves the boiler at Point C. After the product is removed, the remaining acid is diluted with water and recirculated to the tower at Point A.

The process is shown on the HRS operating cycle diagram in Figure 2. The curves on the left are isocorrosion lines for 310 stainless steel. The right hand line defines the limiting conditions for the absorption of sulfur trioxide. The points on the triangle correspond to the process conditions identified in the Figure 1 process diagram. Acid near 100% concentration leaves the tower at 200°C (Point B). The acid is cooled in the boiler to approximately 160°C (Point C). The acid is diluted to 99% with a temperature rise due to heat of dilution (Point A). Finally, sulfur trioxide is absorbed in the tower, raising the acid concentration and temperature to complete the cycle.

This example is a 3.5 bar (50 psig) steam system but steam can be generated at up to 10 bar (150 psig). HRS can boost energy recovery to 90% to 95% of the total energy generated in a sulfur burning plant.

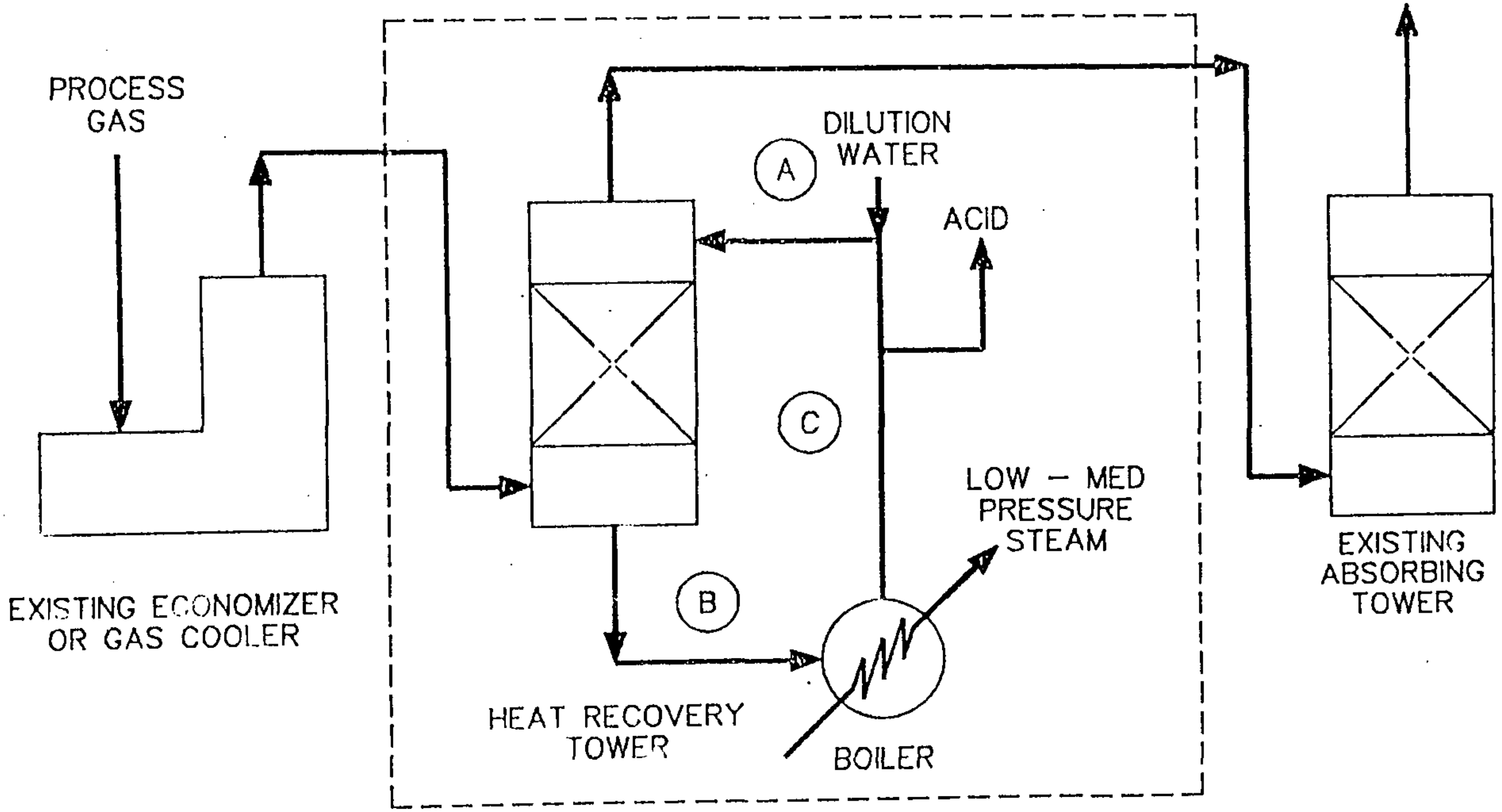

FIGURE 1 – HEAT RECOVERY SYSTEM

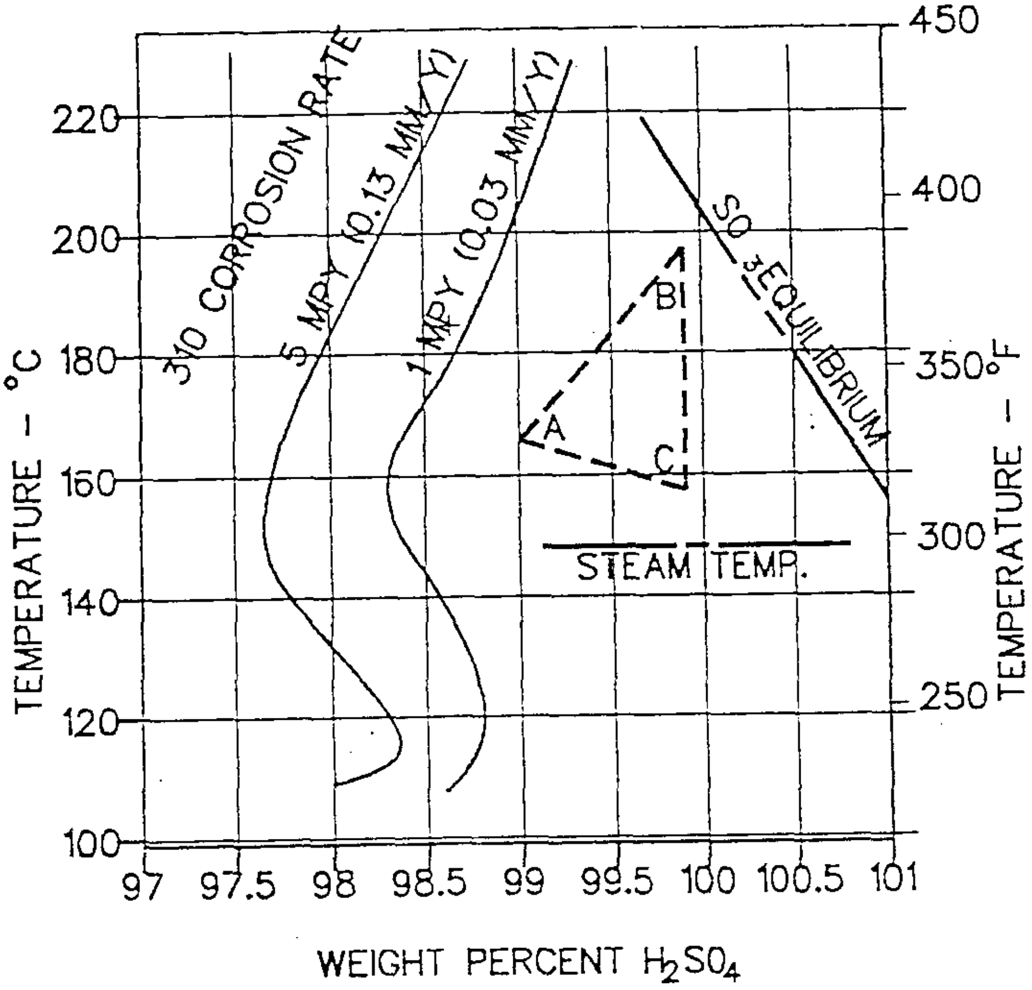

FIGURE 2 – HRS OPERATING CYCLE

NAMHAE HRS PROJECT

Namhae of Yeosu, South Korea is a billion dollar a year producer of fertilizer chemicals. Namhae is committed to supply competitively priced quality products to their worldwide clients through efficient operations and best available up-to-date plant technology.

In 1986, Namhae initiated a project to reduce the SO_2 emissions from their two existing, ten year old, single absorption sulfur burning sulfuric acid plants. Monsanto Enviro-Chem of St. Louis, Missouri, U.S.A., made several proposals for Namhae's consideration:

- Add tail gas ammonia scrubbing tower to the plants.
- Convert the plants to double absorption plants with an interpass tower and acid cooler addition.
- Convert the plants to double absorption using the new Heat Recovery System (HRS) as the interpass tower.

Although Monsanto Enviro-Chem had extensive pilot plant experience and data, there were no commercial Heat Recovery Systems in existence at that time. However, Namhae's commitment to cost effective operations and confidence in Monsanto Enviro-Chem's 55 years of reliable acid plant design experience convinced K. P. Chae, Namhae's Managing Director of Engineering and Projects, to select the new Heat Recovery System for Namhae's sulfuric acid plants.

In October, 1986, Namhae awarded Monsanto Enviro-Chem the contract to modify the plants. The project goals were to:

- Increase SO_2 to SO_3 conversion from 97.7% to 99.6%.
- Maintain each plant capacity at 1350 t/d. The original 1050 t/d plants were debottlenecked using Monsanto LP catalyst, increasing gas strength to 8.3% from 7.8% and adding low-temperature economics.
- Increase steam production by adding HRS and adding a new turbine generator dedicated to HRS steam.
- Maximize use of existing plant equipment.

The final design included:

- The Monsanto Enviro-Chem Heat Recovery System as the interpass absorption tower to remove SO_3 and a 150 psig heat recovery boiler to remove the heat of acid formation.
- A final separate one-pass stainless steel converter for the after interpass absorption conversion of SO_2 to SO_3. Monsanto Enviro-Chem LP catalyst was used here and in some passes in the existing converter to lower pressure drop and ensure required conversion was met.

- Cold interpass and hot interpass heat exchangers to heat gas going from the HRS interpass absorption tower to the final catalyst pass.
- Additional economizers and superheaters to recover more heat in the form of high pressure steam than in the form of low pressure steam.
- Much existing equipment was reused without modifications (blower, boiler, economizers and superheaters).

The gas flow diagram in Figure 3 shows the modifications.

In addition, a 9000 kWh turbogenerator was installed to convert the 130,000 lbs/hr of 150 psig steam from HRS to electricity.

Namhae's Project Manager, M. K. Oh, committed to a fast 14 month schedule. The first plant came on-line 13 months after the contract award and both plants and the turbogenerator were demonstrated in an excellent 14-1/2 months.

NAMHAE HEAT RECOVERY SYSTEM

The HRS operates very similar to a sulfuric acid plant absorbing tower. The main difference is higher acid temperatures; the acid is cooled in a boiler rather than an acid cooler; and the tower is stainless steel rather than bricklined steel. The flow diagram for HRS is shown in Figure 4.

The main equipment items in an HRS are:

1. Heat Recovery Tower

   This is a two stage 310 stainless steel tower with ceramic Intalox packing and Monsanto Enviro-Chem ES mist eliminators.

2. HRS Acid Circulation Pump

   This is a vertical submerged stainless steel pump manufactured by the Lewis Pump Co. The pump design is very similar to the proven design of the many vertical sulfuric acid pumps now in service.

3. HRS Boiler and Heaters

   This is a "kettle" type boiler with acid flow through stainless steel tubes. The water side of the boiler is operated and controlled similar to other firetube boilers.

   The HRS water heaters are similar to shell and tube acid coolers but without anodic protection. Their function is to cool product acid by heating the boiler feedwater coming to the HRS boiler.

4. The diluter is where hot dilution water is mixed and absorbed by the hot acid in a turbulent reaction.

5. Instrumention

   HRS includes flow, temperature and pressure measurement and control instruments that are normally used in acid plants, but there are also three special instruments that we want to tell you more about.

   A. Concentration Control

      The acid concentration to the tower must be controlled above 98.5% acid to minimize corrosion. Modern electrodeless torroidal conductivity analyzers were used to provide the reliable and accurate concentration measurement that is needed. These improved analyzers will rapidly become the standard of the industry in all drying and absorbing towers as well as in HRS.

   B. Corrosion Monitor

      The corrosion monitor measures the current generated by the corrosion reaction of the stainless steel probes in the acid circuit. The monitor, located in the control room, indicates the corrosion rate of the stainless steel and alarms if the rate exceeds set limits for any reason.

   C. Acoustic Leak Monitor (ALM)

      The acoustic leak monitor was especially developed several years ago by Monsanto and the manufacturer to detect boiler or heat exchanger leaks using acoustic (sound) emissions. The acoustic (sound) wave is transformed into an electric signal and is monitored in the control room.

      Boiler or heat exchanger leaks cause an increase in the acoustic emission which sounds the alarm so the plant can be shutdown safely for repairs. There have been no leaks at Namhae.

The other materials in an HRS such as pipe, valves, thermowells and etc. are made of stainless steels compatible with high temperature sulfuric acid.

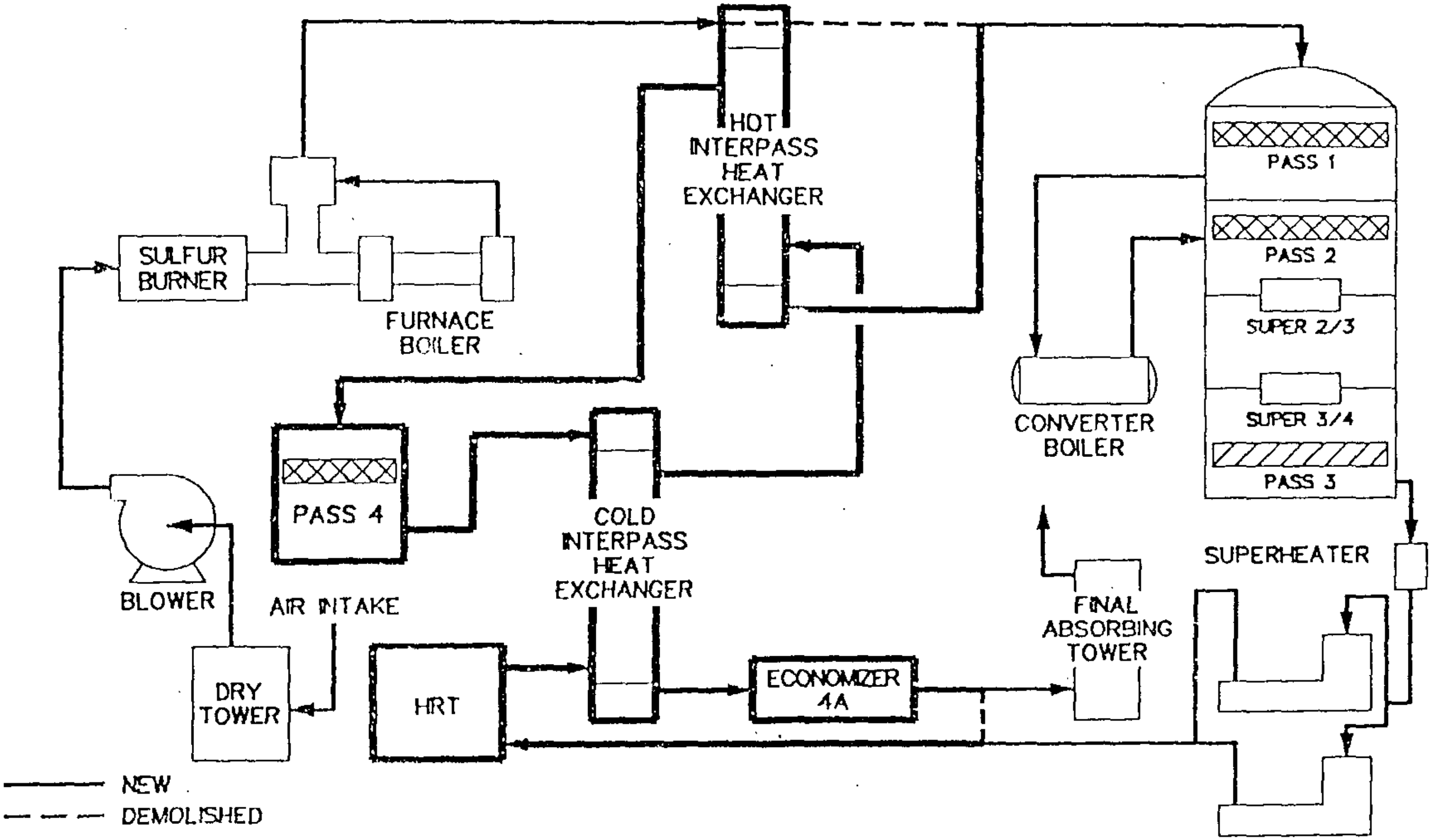

FIGURE 3 — GAS FLOW DIAGRAM

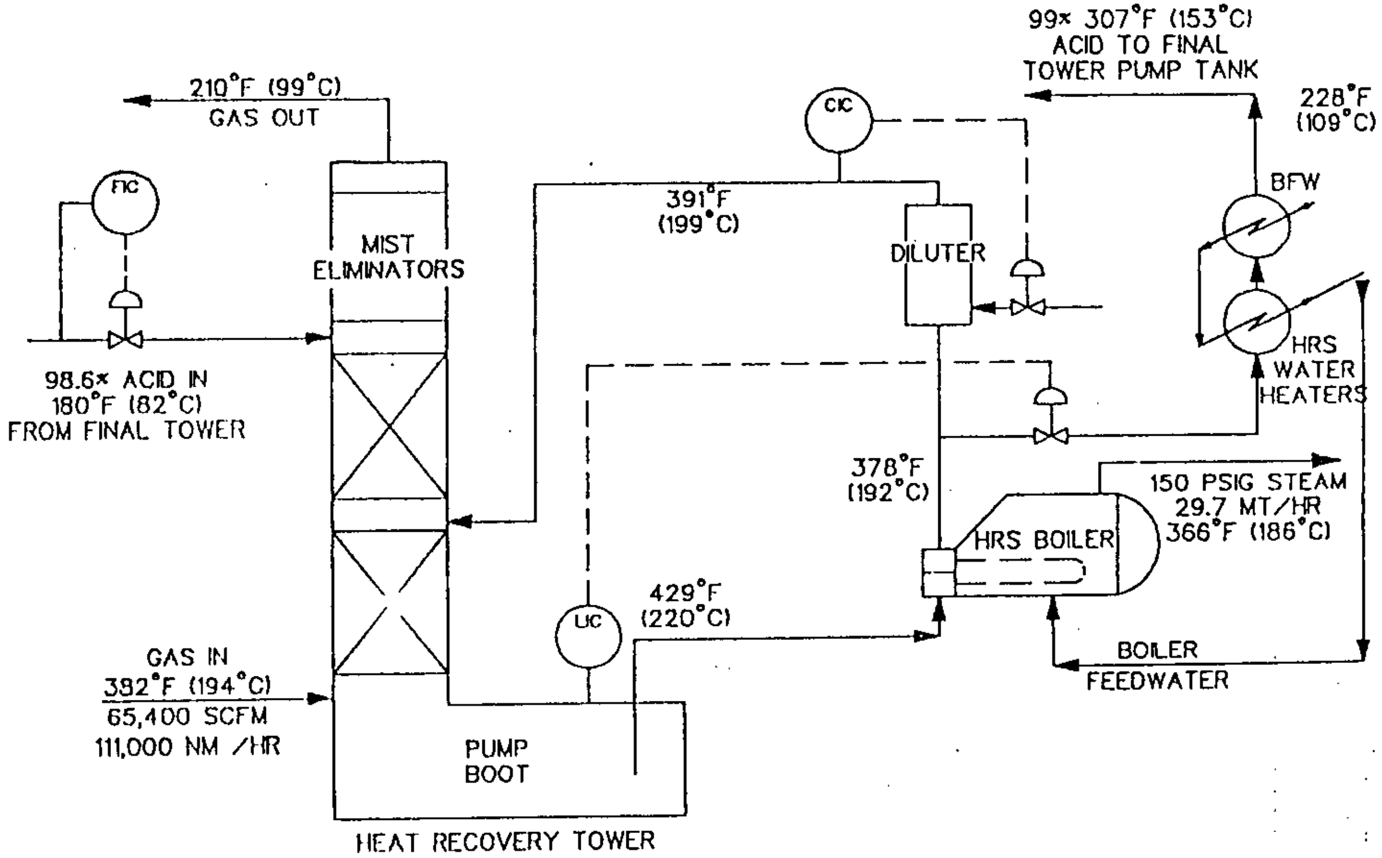

FIGURE 4 – HEAT RECOVERY SYSTEM

HRS START-UP (NOVEMBER AND DECEMBER, 1987)

The plant and HRS start-ups went extremely well. The first plant started up November 19, 1987, and all guarantees were demonstrated within 2-1/2 weeks. The second plant and the turbogenerator power guarantees were demonstrated 1 week after the Plant No. 2 start-up December 23, 1987.

All project guarantees and expectations were readily achieved. The conversion of SO_2 to SO_3 was much better than expected. In fact, the conversion analysis was double and triple checked before it was accepted.

HRS DEMONSTRATION RESULTS

	Guarantee	Expected	Plant #1	Plant #2
Production, t/d	1350	1350	1442	1430
SO_2 Emission, ppm	500	370	208	152
Steam Production, t/hr	27.9	29.7	33.2	30.6
Tons/Ton Acid	.50	.53	.55	.51
Conversion	99.6	99.7	99.85	99.9
T/G Electrical Power kWh	8760		8772 for both plants	

There were a few minor problems during the start-up. In fact, loss of control of acid strength, which is the major concern of many customers, occurred a few hours after start-up. When acid concentration was first put on automatic control, acid strength was rapidly dropped to 94% because the control action was reversed. It took a few hours to get the acid strenth into control and the plant was exposed to 200°C and 94% concentration. Inspection of the plant showed that the only damage was excessive corrosion on the acid pump impeller and wear parts where velocity is highest. However, the pump was still serviceable and was put back into operation. After examination of the pump, Lewis and Monsanto metallurgists concluded that damage was related completely to the low acid strength. However, Namhae had some concerns so some parts of alternate materials were installed for testing in one pump.

A second problem was excessive vibrations transmitted from the diluter to the platform walkway. The mixing of hot water and hot acid produces a turbulent reaction. The diluter requires a solid structural support to grade. The original diluter was supported from horizontal steel beams that support the walkway. The support was redesigned on heavier steel beams that extend down to grade. Excessive walkway vibrations were eliminated.

A third problem was collapse of some teflon lined pipe that was used between the diluter and the tower as a precaution against incomplete mixing which would cause higher than expected localized corrosion rates. Part of the pipe liner collapsed during the start-up period when the plant was shutdown and the acid was drained from the diluter causing a vacuum in the line. Some of the liner was removed as not being necessary and a vacuum breaker will be installed to further protect the remaining liner.

Typical start-up instrument adjustment difficulties were experienced on the Plant No. 1 start-up for the acoustic leak detector and the corrater. However, the Plant No. 2 instrument adjustment was minimal after Namhae's Instrument Section assumed responsibility from the construction contractor.

OPERATION - (JANUARY TO AUGUST, 1988)

Following the demonstration in December, both HRS units continued to operate according to the design and there were no significant operating or equipment problems.

In April, Namhae and Enviro-Chem showed the plant to 40 potential customers from all over the world. During the discussion a customer asked Namhae how many acid plant shutdowns had been caused by HRS equipment. After checking the record, Namhae stated there had only been one 4 hour shutdown to inspect the acid pump on the No. 1 plant. The pump was inspected in March and showed little additional corrosion since exposure to 94% acid during the initial start-up. The No. 2 acid plant continued to run well and was not even inspected until August.

Corrosion coupons that were installed in the acid system were checked occasionally. All showed the expected low corrosion rate except the one located directly after the diluter which showed 20 mils per year. This showed the need for improved mixing of the acid and water in the diluter. These modifications were delayed until the diluter supports were strengthened during the August turnaround because of the possibility that vibration would increase. It was not considered urgent because piping after the dilutor was teflon and no damage was being done.

During normal operation 0.5 to 1.0 liters per shift of drip acid was drained ahead of the cold interpass heat exchanger. This was considered to be condensation particularly on the dome of the tower which was not insulated and did not cause much concern. We have increased our attention to this matter since some duct leaks developed prior to the August turnaround. Improvements are being implemented which are expected to stop the drip acid.

The HRS performed well, consistently producing steam to generate over 9 MW of electrical power. HRS equipment performed as expected. Acid quality is significantly improved with the elimination of iron sulfates, cast iron slag, brick mortar particles and etc. as compared to bricklined acid towers.

The annual gross savings for both plants is 6600 tons of sulfur saved based on a 2.1% conversion improvement and a 350 day per year operating schedule at design rate. Also, 74,000 MWh of electrical power is generated under these conditions. The savings in U.S. dollars would be $0.9 million for sulfur, based on a $130/t delivered price, and $4.6 million for electrical power, based on $0.062/kWh costs, for a total yearly savings of $5.5 million. These cost figures are used for illustration only and are not necessarily those used by Namhae.

TURNAROUND INSPECTION - (AUGUST, 1988)

Plant No. 2 was shutdown for scheduled maintenance on August 20 after eight (8) months of operation. Plant No. 1 was shutdown on September 3 after nine (9) months of service. Both HRS units and sulfuric plants were inspected carefully to determine if any problems were developing.

Overall, both HRS units were in excellent condition. The corrosion rates were as expected.

The corrosion rates were determined by exact weight losses of metal coupons placed throughout the system and numerous metal thickness measurements of pipe and tower walls. Excluding the first start-up days, the corrosion rate of the tower and piping system was less than 2 mils per year (0.050 mm/yr) in all areas. The corrosion rate of the acid pipe from the tower to the boiler was about 1.5 mils per year (0.037 mm/yr) and less than 0.5 mil per year (0.012 mm/yr) after the boiler.

The corrosion rate of the coupons in the teflon lined pipe between the diluter and the tower was between 20 and 30 mils per year (.5 and .75 mm/yr). This higher than expected rate was attributed to inadequate mixing of the acid and water in the diluter. Inspection showed only normal corrosion on the tower as is discussed below. However, the diluter is being modified to improve acid and water mixing.

In addition to the corrosion coupons, the HRS units were checked by taking thickness readings with an ultrasonic thickness gauge ("D" meter) and micrometer. The ultrasonic thickness gauge uses sound waves to measure the thickness of equipment when it is impractical to reach both sides of a plate or pipe wall. The actual measured corrosion rates of HRS plate and pipe supported the data of the corrosion coupons.

The No. 2 plant HRS acid pump was pulled for the first time and inspected. The visual inspection of the pump showed it to be in good condition. Corrosion was no more than that experienced on other absorbing tower circulation pumps. The replaceable static wear rings were replaced to assure reliable service until the next turnaround and the pump was placed back in service. Although replaced, most of the wear rings were still within specification. We have concluded that the original materials of construction specification for the HRS pump was the proper choice for long-term life.

The HRS boiler was in excellent condition on both the acid and water side. The corrosion rate on the acid side was less than 2 mils per year.

All HRS equipment was inspected and found to be in good condition. The HRS tower shell, packing, packing supports and mist eliminators checked out in fine condition. Acid distributor header orifices showed some corrosion which could result from the poor mixing in the diluter or it could have occurred at the time the 94% acid corroded the acid pump.

The gas duct from the HRS tower to the cold interpass heat exchanger and the shell side inlet to the exchanger were inspected since drip acid had been routinely drained from the duct. There was significant iron sulfate in the bottom of the duct and on the exchanger tubesheet. There were a few leaking tubes which were repaired by driving a smaller tube inside. During the turnaround the top of the tower was insulated and the acid drain system ahead of the heat exchanger was modified to improve drainage and keep acid from getting into the exchanger. Drains will be monitored and gas sampling is planned to see that the problem has been solved.

The design, construction and successful demonstration of the first two commercial Heat Recovery Systems, complete with dedicated turbogenerator, is considered an outstanding success by Namhae Chemical Corporation and Monsanto Enviro-Chem Systems, Inc.

Many sulfuric acid plant operators from around the world have visited the Namhae acid plant. Visitors are quite impressed with the Namhae's HRS installation, clean and orderly facilities and Namhae's courage and dedication to install the first HRS.

SUMMARY

Namhae Chemical Corporation has proven that the HRS is a successful commercial process.

The initial concerns have been laid to rest and most of the minor problems have been solved. And, as a customer who visited the plant during the recent turnaround said, "The few remaining problems can be readily solved and I am not afraid of the Heat Recovery System".

Namhae and Monsanto Enviro-Chem will continue to review the HRS operations for good performance and maintenance. As with all new technology, improvements in design and HRS products are expected as experience is gained.

Three new HRS units are now being designed for clients who have visited the Namhae facilities. HRS projects are under consideration by other clients.

The attraction of using the HRS as an interpass absorption tower to reduce SO_2 emissions while producing an additional 0.5 t steam/t acid produced or 3.1 kWh of electrical power per t/d of H_2SO_4 will make the HRS a key component of future sulfuric acid plants.

FALCONBRIDGE, NORWAY

Several people have asked about the Falconbridge HRS start-up status. Falconbridge Nikkelverks of Kristiansand, Norway has a 240 t/d sulfuric acid plant and HRS for their smelter SO_2 offgas. Fenco Engineers of Toronto, Canada designed and constructed the acid plant as well as the SO_2 gas purification system. The acid plant is designed so that the HRS can operate as an interpass tower with normal interpass acid temperatures or as an HRS where steam is generated from cooling the acid.

The acid plant started up in October, 1987, in the conventional acid plant mode without steam generation. The HRS circuit has not operated much of the time because of operating problems in other parts of the acid plant and roasters. However, the HRS was successfully operated several weeks during mid-1988 and tests showed that it is operating in accordance with design. However, Falconbridge has commitments to produce liquid SO_2 which have required that the acid plant be shutdown until the last quarter of 1988.

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SO_2 EMISSIONS REDUCTIONS IN SULFURIC ACID PLANTS

by

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ABSTRACT

The current trend in the sulfuric acid industry is to reduce the emission of sulfur dioxide (SO_2) to the atmosphere while maintaining or increasing acid production. Utilizing Monsanto cesium-modified catalysts, a number of sulfuric acid producers have effectively reduced their SO_2 emissions in both single absorption and double absorption cases. This paper will present the realized possibilities for the reduction in emissions using Monsanto Cesium Catalyst and the optimization of plant operations utilizing the Monsanto Portable Gas Analysis System (PeGASyS). The portable gas analyzer has served as an invaluable tool to optimize plant operations and demonstrate the advantages of the cesium catalyst in reducing emissions. The utilization of both the Monsanto Cesium Catalyst and the Portable Gas Analysis System in many plant applications will set the new standard for sulfuric converter performance.

INTRODUCTION

The trends in sulfuric acid plant design have changed dramatically over the last several decades. The demand for operations with minimal SO_2 emissions has required the development of the double absorption contact process for SO_2 oxidation which is capable of generating greater than 99.7 % conversion of the sulfur dioxide fed to the plant. Pollution reduction commitments by many major corporations as well as government regulatory requirements are responsible for the continuing trend to develop new and cost effective technologies to further reduce the SO_2 emission levels from sulfuric acid plants.

There are still a large number of sulfuric acid plants in the world which operate in the single absorption mode with SO_2 conversion levels near 98 %. Although these plants are operating within authorized conversion limits, many companies are striving to reduce the SO_2 emissions as much as is technically and economically feasible. Until recently, the technologies to accomplish this goal were limited. Plant operations were "optimized" using crude chemical techniques and often inaccurate temperature measurements, resulting in less than ideal performance in the plants. Over the years, conventional sulfuric acid catalyst improvements have enhanced the plant performance significantly, but further advances were limited by thermodynamic and kinetic barriers.

This paper presents the results of implementing two new technologies in the sulfuric acid industry. Monsanto Enviro-Chem has developed a low temperature cesium-promoted catalyst which eases some of the aforementioned limitations and improves the overall conversion in both single and double absorption plants, resulting in significantly less SO_2 emissions to the stack. A discussion of some case histories of cesium (Cs) catalyst installations and the potential applications of the technology are presented. The second technology developed by Monsanto Enviro-Chem is the Portable Gas Analysis System (PeGASyS) which is used to measure and optimize sulfuric acid plant converter/heat exchanger performance. Using this state-of-the-art instrumentation, plant problems are quickly and easily identified and resolved. Catalyst performance can be quickly determined and optimum operation conditions can be determined based on the catalyst quality and desired conversion results. Examples of the applications of the PeGASyS technology are presented in this paper. When utilized together, the cesium catalyst technology and the PeGASyS system can generate the optimum performance from any sulfuric acid plant and lead to lower SO_2 emissions.

CATALYST DEVELOPMENT AND APPLICATIONS

In the contact sulfuric acid process, there is often an interest in lowering the inlet temperatures to the various adiabatic catalyst beds in order to provide more favorable equilibrium conditions. The addition of cesium (Cs) to the conventional alkali-vanadium sulfuric acid catalyst has long been known to enhance the low temperature properties of the catalyst (1). The cesium salt promoter stabilizes the vanadium +5 oxidation state at temperatures below 420°C (790°F) and keeps the vanadium species solubilized in the melt and available for reaction. In the conventional K-V catalyst, vanadium compounds precipitate out of the molten salt at lower temperatures, causing loss of catalyst activity (2,3). The stabilizing effects of the cesium appear at relatively low Cs concentrations. A qualitative display of this effect is shown in Figure 1. At high temperatures (> 430°C/806°F), the activity of the conventional catalyst and the cesium-promoted catalysts are fairly similar. However, near 410°C (770°F), the reaction rate of the conventional catalyst drops off dramatically due to the precipitation of vanadium compounds (curve breakpoint # 1). As the temperature is further lowered (moving to the right on the graph), the cesium-promoted catalyst maintains a higher reaction rate until the temperature drops well below 400°C (750°F) when its activity finally begins to decline due to vanadium salt precipitation (curve breakpoint # 2). Although the reaction rate of the cesium-promoted catalyst drops off at relatively low temperatures, it is still sufficiently high to generate good conversion at acceptable catalyst loadings. Over the last several years, Monsanto Enviro-Chem has utilized its strong base in cesium catalyst studies (4-7) to develop an optimized and affordable cesium promoted catalyst (Cs-120 and Cs-110). These products contain the optimum levels of alkali metal salts (potassium and cesium) to provide excellent ***low*** and ***high*** temperature performance in the converter. Following extensive lab development and field testing, the products were commercialized in 1989 and have been installed in over 20 sulfuric acid plants worldwide.

There are many applications for the cesium-promoted catalyst in sulfuric acid plants. The smaller 9.5 mm (3/8 in.) Cs-110 rings can be loaded into the lower beds and allow for lower bed inlet temperatures and higher overall conversion. Figure 2 shows a graphical display of the advantage of using the Cs-110 catalyst in the 4th pass of a single absorption plant. The lower inlet temperature with Cs-110 catalyst opens a larger thermodynamic "window" which permits greater overall conversion. This higher level of conversion is not possible with the conventional catalyst at the lower inlet temperature as the catalyst loadings would have to be extremely high, creating excessive pressure drop. A similar scenario can be devised for the lower beds of double absorption plants, resulting in lower stack emissions.

Another cesium-promoted catalyst application involves installing a 33-50 % cap of Cs-120 rings in the first pass of a sulfuric acid plant. This catalyst configuration will dramatically lower the required inlet temperature for good conversion in this bed. Figure 3 shows that the conversion versus bed depth profile for a capped Cs-120 bed with an inlet temperature of 380°C (715°F). A full bed of conventional catalyst will produce very little conversion with this low inlet temperature at any reasonable catalyst loading. A full first bed of Cs-120 rings is not required in this application as the outlet temperature from the cesium catalyst portion of the bed is high enough to ignite the remaining conventional catalyst layer. The lower first pass inlet temperature is advantageous for plants with very high inlet SO_2 strength. In this case, the lower inlet temperature will lead to a lower outlet temperature, therefore extending the life of the first pass exit posts and grids. Furthermore, the overall conversion in the first pass will also be increased over that possible with conventional catalyst. The use of the Cs-120 rings in Pass 1 will also reduce or eliminate the need for startup gas pre-heating in spent acid and metallurgical plants following short shutdowns.

The cesium-promoted catalyst can also be utilized in situations where heat exchanger deficiencies (undersized or plugged) limit the inlet temperatures to lower passes. The Cs-110 rings can effectively operate at the reduced temperatures and hence maintain the needed conversion in the lower beds. Also, the Cs-120 first pass caps and the full beds of Cs-110 in the lower passes can greatly reduce the time required to startup the sulfuric acid plant. The cesium catalyst beds will ignite at much lower temperatures than conventional catalyst beds and hence require less pre-heating. Also, due to the high activity at low temperatures, the cesium catalyst beds help to minimize the stack SO_2 emissions during plant startup operations. Examples of many of these cesium catalyst applications are presented in subsequent sections.

Cs-110/Cs-120 CATALYST APPLICATIONS

The applications of the Cs-110 and Cs-120 catalysts in reducing SO_2 emissions will be presented as a series of case histories. Although the applications vary from plant to plant, the common threads in each case are lower stack emissions and improved operating versatility. The following are five examples of Monsanto cesium promoted catalyst performance: (Note: STPD = Short Tons acid produced Per Day)

Case 1: *Single Absorption Spent Acid Plant*

Pre-Cs Data:

(1) Conventional catalyst in Pass 4.
(2) Pass 4 operating at 430°C (806°F) inlet temperature.
(3) Conversion at 98.0 % with 9 % SO_2 feed gas.
(4) Stack SO_2 emissions were over 25 lbs./STPD.

Post-Cs Information:

(1) Installed full bed of Cs-110 ring in Pass 4.
(2) Pass 4 inlet temperature optimized at 410°C (770°F).
(3) Conversion measured at 98.5 % with 9 % SO_2 fed.
(4) Stack SO_2 emissions at 19 lbs./STPD (24 % reduction).

Case 2: *Single Absorption Sulfur Burning Plant*

Pre-Cs Data:

(1) Aging, conventional catalyst in all beds.
(2) Pass 4 operating at 427°C (800°F) inlet temperature.
(3) Conversion at 97.5 % with 8 % SO_2 feed gas.
(4) Stack SO_2 emissions at 33 lbs./STPD.

Post-Cs Information:

(1) Screened all beds; full fourth pass of Cs-110.
(2) Pass 4 operating at 395-405°C (743-760°F).
(3) Conversion measured at 98.4 % with 8 % SO_2 fed.
(4) Stack SO_2 emissions at 21 lbs./STPD (36 % reduction).

Case 3: *Single Absorption Sulfur Burning Plant*

Pre-Cs Data:

(1) Used conventional catalyst in all five passes.
(2) Pass 5 operating near 430°C (806°F) inlet temp.
(3) Conversion at 98 % (air dilution plant).
(4) Stack SO_2 emissions at 26 lbs./STPD.

Post-Cs Information:

(1) Fresh catalyst in all beds; Cs-110 in Passes 4 and 5.
(2) Passes 4 and 5 operating at 410°C (770°F) inlet temp.
(3) Conversion reaches ***99.1 %*** with 8 % SO_2 fed.
(4) Stack SO_2 emissions at 12 lbs./STPD (***50 % reduction***).

Case 4: *Double Absorption Spent Acid Plant*

Pre-Cs Data:

(1) Standard catalyst in all beds; 12 % SO_2 gas strength.
(2) Pass 1 at 405°C (760°F); Pass 3 at 400°C (750°F).
(3) Heat exchanger pluggage limited Pass 3 inlet temp.
(4) Pre-heater required, especially after short shutdowns.
(5) Rate reduced to stay with SO_2 stack requirements.

Post-Cs Information:

(1) Cs-120 cap in Pass 1; full 3rd bed of Cs-110 rings.
(2) Pass 1 inlet at 360°C (680°F); outlet at 600°C (1110°F).
(3) Pass 3 operating well at 400°C (750°F).
(4) Need for pre-heater virtually eliminated.
(5) Rate dramatically increased with low SO_2 emissions.

Case 5: *Double Absorption Spent Acid Plant*

Pre-Cs Data:

(1) Used conventional catalyst in all beds; 7 % SO_2 fed.
(2) Pass 3 inlet at 410°C (770°F); heat exchange limits.
(3) Pass 4 inlet at 390°C (735°F) due to low 3rd pass temp.
(4) Emissions high (especially at startup);rate limited.

Post-Cs Information:

(1) Installed full bed of Cs-110 rings in Pass 3.
(2) Pass 3 operating very well at 410°C (770°F) inlet.
(3) Pass 4 operating very well at 425°C (800°F) inlet.
(4) Very low startup emissions; production rate increased; no gas pre-heating required after short shutdown.

Several other applications for the cesium promoted catalyst are under consideration. Scenarios have been developed for increasing the acid production rates for double absorption plants and yet maintaining the same permitted hourly SO_2 emissions. Using Cs-110 rings in the bottom pass of double absorption plants, it is possible to reduce the lbs. SO_2 per ton of acid and hence allowing for greater production at the same SO_2 ppm level in the stack.

In order to take advantage of the benefits of the cesium-promoted Cs-120 and Cs-110 catalysts, there are some considerations that need to be evaluated prior to installation. Firstly, the heat exchange capacity in the plant must be evaluated in order to insure the feasibility of reaching the lower inlet temperatures required for the cesium catalyst beds. Secondly, there may be a greater tendency for pressure drop buildup in first passes equipped with cesium catalyst caps if the incoming gas stream is very dust-laden or contains acid mist. The highly active cesium-promoted catalyst has a more mobile molten salt than that of the conventional catalyst, which has a slightly greater tendency for accumulating incoming converter dust. The larger Cs-120 rings (12.5 mm, 1/2 in.) were developed to minimize the potential pressure drop buildup and yet maintain the required performance. The low temperature benefits of the Cs-120 rings in the first pass must be weighed against the slight possibility of higher pressure drop. Cs-110 applications in all other passes have been in operation for over two years without any indication of pressure drop buildup and/or loss of activity.

Overall, the use of the cesium-promoted catalyst in sulfuric acid converters has contributed to the significant reduction in SO_2 emissions and improved operability of the acid plants.

PORTABLE GAS ANALYSIS SYSTEM (*PeGASyS*)

The Monsanto Enviro-Chem Portable Gas Analysis System was developed several years ago to provide sulfuric acid producers with the means to fully characterize their plant operations. The PeGASyS system consists of a highly specialized gas sampling system and the state-of-the-art gas analyzer. Figure 4 shows a photograph of a portion of the gas analyzer system, including the specially design gas syringe. The analyzer is generally set up near a control room or laboratory and occupies a desk-sized space. A gas sample is taken from a slip stream of gas at the converter, heat exchanger, or absorbing tower pressure tap (or any available sampling port). The gas sample is then injected into the analyzer (state-of-the-art gas chromatograph) which accurately determines the SO_2 and O_2 levels. The PeGASyS method for characterizing the sulfuric acid plant operations is much more reliable and accurate than the standard wet chemical Reich test method. A typical sulfur burning plant can be completely analyzed in only a few hours with the PeGASyS system.

The results obtained with the PeGASyS system consist of an analysis report of the SO_2 and O_2 levels in each sample and a conversion calculation for each specific converter sample based on the inlet gas to the first bed. Figure 5 shows a typical Converter Performance Summary for a sulfur burning double absorption plant. The custom PeGASyS software also calculates gas flow rates based on the given production rates. Utilizing the PeGASyS data, the converter performance can be effectively simulated using the Monsanto Enviro-Chem proprietary modeling software. This information can then be used to optimize the plant operations, adjusting bed inlet temperatures, upgrading catalyst charges to maximize conversion and minimize SO_2 emissions.

Another important application of the PeGASyS system is in gas-gas heat exchanger leak detection. The exchanger must have shell side and tube side gas streams which contain different SO_2 levelsin order for the analysis to be effective. Figure 6 shows the typical output for a heat exchanger analysis. Often, leaking heat exchangers contribute to high SO_2 emissions by bleeding high SO_2 gas directly to the stack or flooding lower pass catalyst beds with SO_2-rich gas. Once the leaking exchanger is identified, it can be repaired, leading to a direct reduction in the stack emissions.

The following are case histories of typical applications of the PeGASyS service to reducing stack emissions:

Case 1: ***Spent Acid Double Absorption Plant***

Issue: SO_2 emissions higher than expected.

Result: PeGASyS analysis indicated that the aging first pass was operating at a reduced efficiency. Replacement of the first pass resulted in significant reduction in stack emissions.

Case 2: ***Sulfur Burning Double Absorption Plant***

Issue: SO_2 emissions were approaching permitted limit.

Result: PeGASyS analysis indicated a severe leak in the cold heat exchanger. Following exchanger repair, SO_2 emissions decreased from 3.9 lbs./STPD to 2.0 lbs./STPD.

Case 3: ***Sulfur Burning Single Absorption Plant***

Issue: Emissions extremely high; poor conversion.

Result: PeGASyS analysis determined that Passes 2 and 3 were performing very poorly. It was determined that low bed inlet temperatures were responsible. Raising the temperatures led to a dramatic reduction in SO_2 emissions. The results also indicated that a 4th pass Cs-110 application was justified. With a full 4th pass of Cs-110 rings, this plant now has extremely low SO_2 emissions.

Case 4: *Spent Acid Double Absorption Plant*

Issue: SO_2 emissions approaching allowed limit.

Result: PeGASyS analysis of the cold heat exchanger identified a minute leak which was allowing some first pass feed gas to bypass directly to the final tower. This leak added over 200 ppm SO_2 to the stack. Repairs to this exchanger resolved the problem.

As can be seen from these examples, the Portable Gas Analysis System is an extremely effective tool for optimizing sulfuric plant operations and reducing stack SO_2 emissions. In a number of cases, the PeGASyS results have led to the installation of Monsanto cesium-promoted catalyst which resulted in the best overall conversion and the lowest level of sulfur dioxide escaping to the atmosphere.

CONCLUSIONS

The effectiveness of the Monsanto Enviro-Chem cesium-promoted catalysts (Cs-120 and Cs-110 rings) in improving sulfur dioxide conversion and reducing stack emissions has been demonstrated in a number of applications. The cesium catalyst can be applied in a variety of situations which can reduce emissions as well as enhance the versatility of the plant operations. In many situations, the catalyst can be used to reduce the impact of heat exchanger limitations. Cesium catalyst effectiveness in both single absorption and double absorption plants has been demonstrated and novel applications are still under development.

The Monsanto Enviro-Chem Portable Gas Analysis System (PeGASyS) has effectively been used in a variety of plants to optimize converter performance and identify problem areas. The results of the gas analyses are often used to identify the most effective applications of the Monsanto Cesium Catalyst in order to minimize SO_2 emissions and maximize converter performance. The use of these products and services allows for not only a positive impact on the environment but also improved performance and profitability for the sulfuric acid producer.

ACKNOWLEDGMENTS

The authors would like to acknowledge and thank David A. Berkel of Monsanto Enviro-Chem Systems, Inc. for developing the Portable Gas Analysis System and refining the unit into an extremely effective tool for our sulfuric acid customers.

The authors would like to acknowledge the St. Louis R&D Team and the Manufacturing Team in Martinez, CA for their work on the cesium-promoted catalyst development.

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Figure 1

SO_2 OXIDATION RATE VERSUS TEMPERATURE

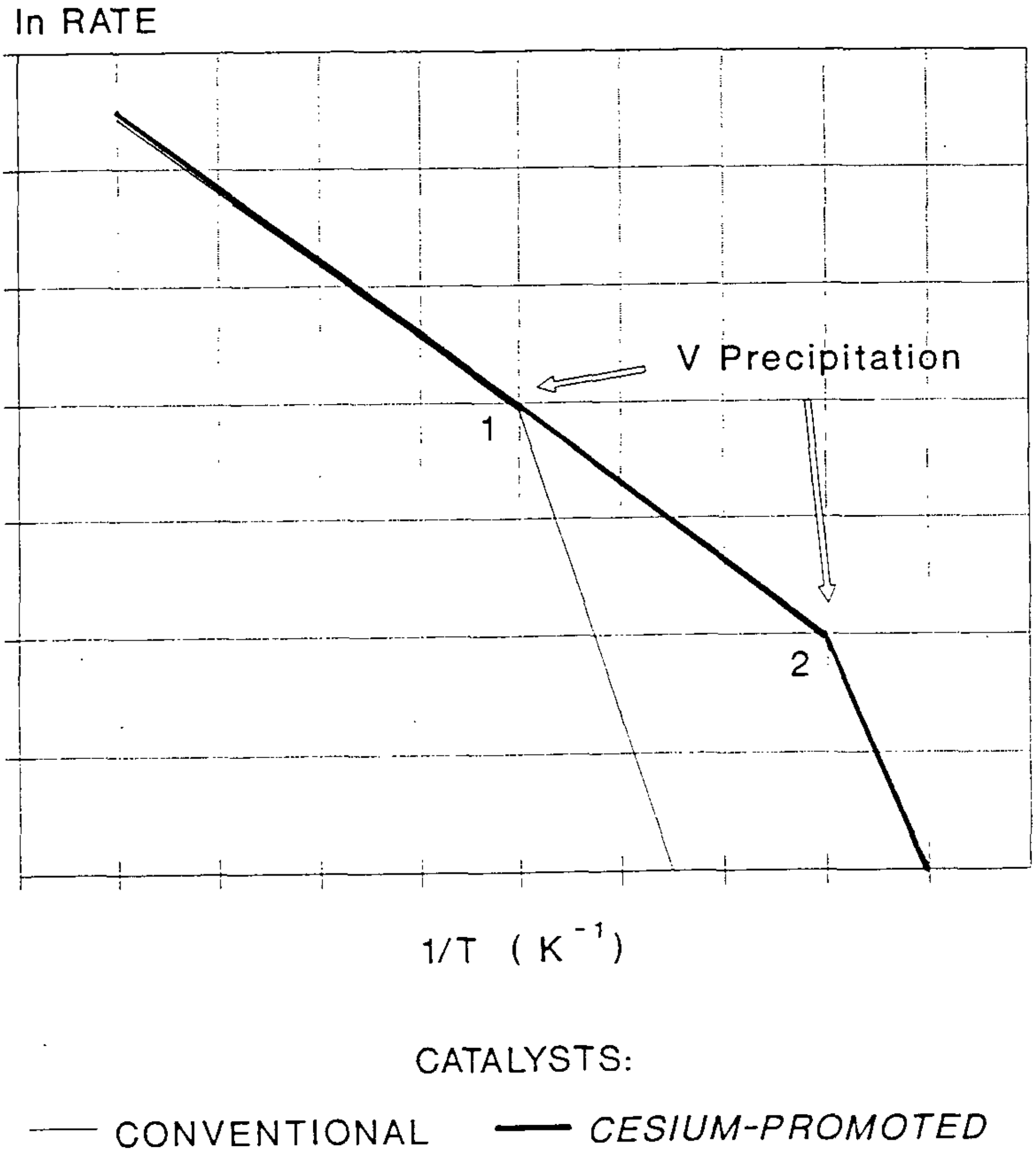
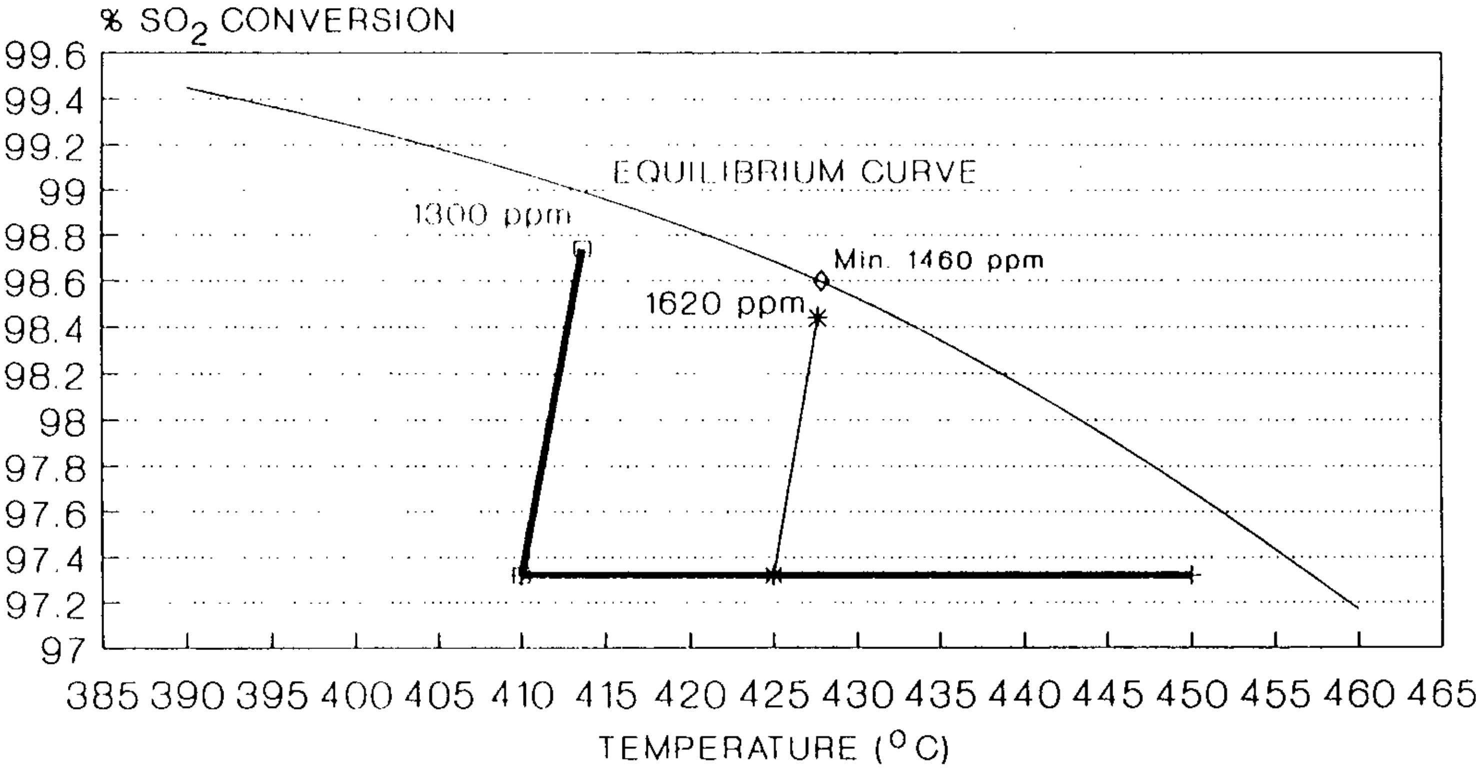


Figure 2

SINGLE ABSORPTION: Cs ADVANTAGE

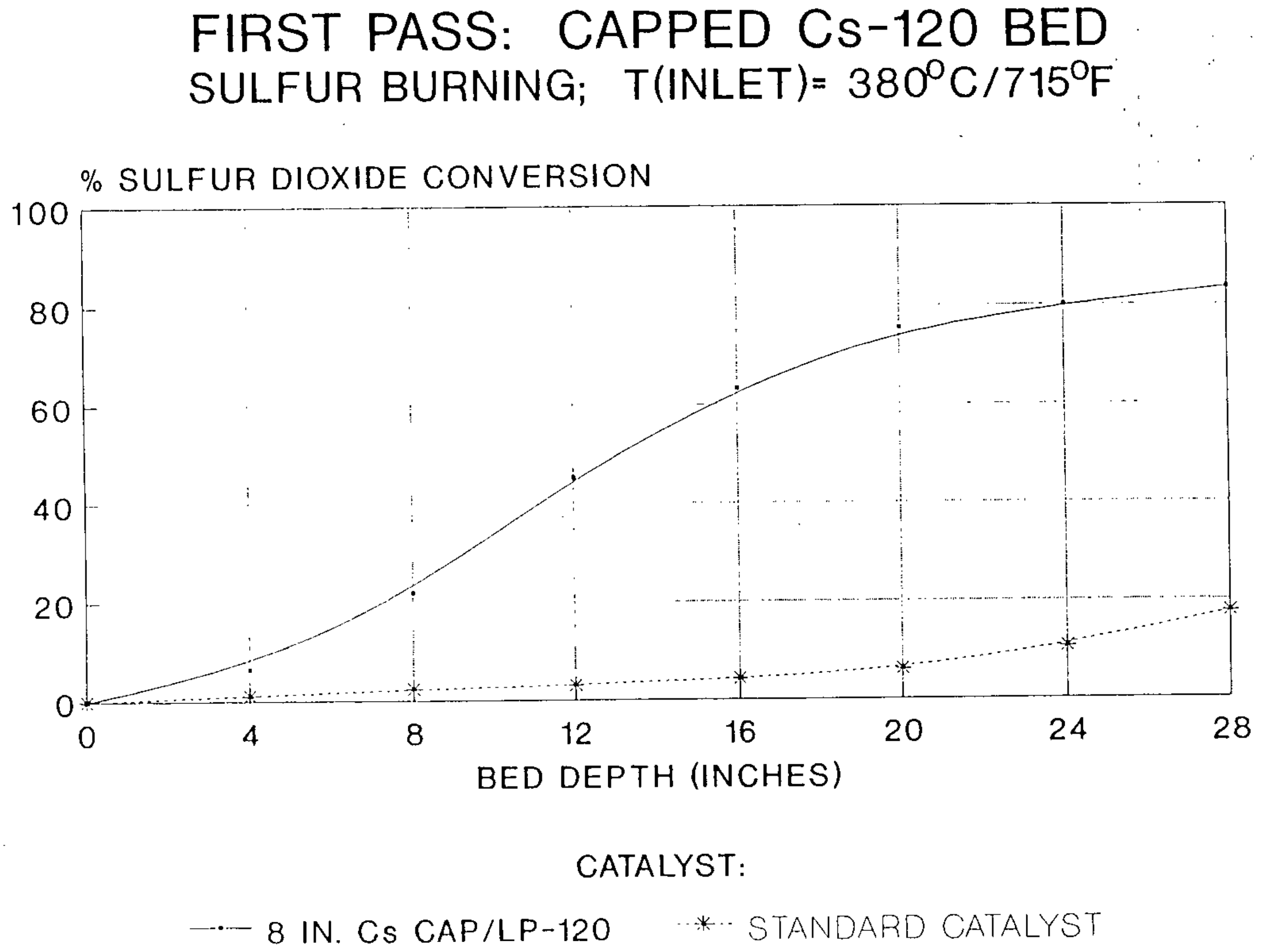


4th PASS CATALYST:

—✳— **LP-110** —⊟— **Cs-110**

FEED GAS = 9 % SO_2, 11.9 % O_2
410°C = 770°F; 425°C = 797°F

Figure 3

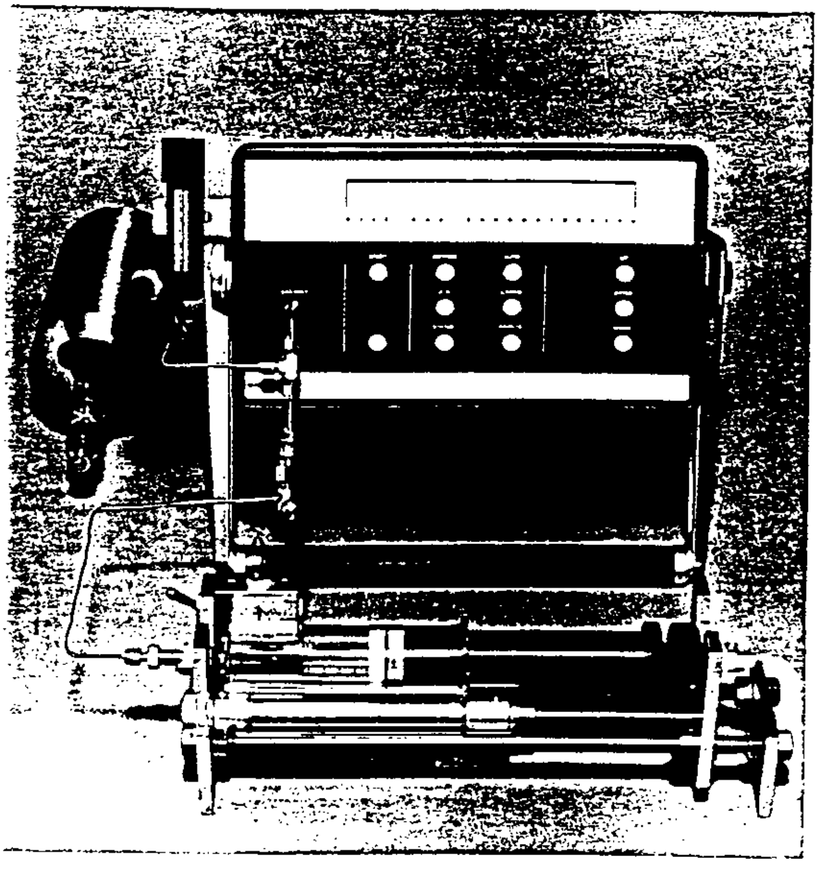


8 IN. Cs-120 CAP ON LP-120 RINGS

Figure 4

PeGASyS

Portable Gas Analysis System



Monsanto Enviro-Chem Systems, Inc.

Figure 5

MONSANTO ENVIRO-CHEM SYSTEMS, INC.

CONVERTER PERFORMANCE SUMMARY

CUSTOMER NAME: EXAMPLE 3 DATA FILE: XXX003.SAM

PLANT LOCATION: U. S. A.

PLANT NUMBER: 3

PLANT TYPE: SULFUR BURNER DOUBLE ABSORPTION

SAMPLE NO.	SAMPLE IDENTIFICATION	DATE / TIME OF SAMPLE		% SO_2	% O_2	% CONV.
5	SULFUR BURNER OUTLET	4-1-91	1600	11.209	9.506	1.563
4	FIRST PASS OUTLET	4-1-91	1600	5.135	6.998	59.394
3	SECOND PASS OUTLET	4-1-91	1600	2.088	5.638	84.269
2	THIRD PASS OUTLET	4-1-91	1600	0.911	5.144	93.257
1	FOURTH PASS OUTLET	4-1-91	1600	0.035	4.771	99.744
		SULFUR BURNER GAS		11.366	9.580	

SAMPLE NO.	SAMPLING POINT
1	OUTLET OF FINAL TOWER ABOVE MIST ELIM.
2	PASS 4 INLET AT CONVERTER TAP
3	PASS 3 INLET AT CONVERTER TAP
4	PASS 2 INLET AT CONVERTER TAP
5	PASS 1 INLET AT CONVERTER TAP

	KG/HR.	LBS./HR.
SULFUR FEED RATE	26054.80	57441.31
SO_2 EMISSIONS	133.04	293.30

LBS.SO_2/TON = 3.35 KG SO_2/TON = 1.67

	NM^3/HR	SCFM
AIR TO SULFUR BURNER	160139.22	94243.89
CONVERTER INLET GAS	160139.22	94243.89
CONVERTER OUTLET GAS	132907.50	78217.69
DILUTION AIR	0.00	0.00
TOTAL GAS TO PLANT	160139.22	94243.89

PRODUCTION RATE = 2100.00 SHORT TONS PER DAY

NOTE: ALL GAS VOLUMES ARE BASED ON DRY, SO_3-FREE GAS.

CATALYST BED TEMPERATURES

L/STPD	BED	°F	°C
	1 IN	779	415
31.5	1 OUT	1130	610
	RISE	351	195
	2 IN	824	440
33.0	2 OUT	988	531
	RISE	164	91
	3 IN	831	444
38.5	3 OUT	891	477
	RISE	60	33
	4 IN	795	424
50.5	4 OUT	844	451
	RISE	49	27
	5 IN		
	5 OUT		
	RISE		
	TOTAL R	624	346

Figure 6

MONSANTO ENVIRO-CHEM SYSTEMS, INC.

HEAT EXCHANGER EVALUATION

DATE / TIME: 4-1-91 / 1500 FILE: INTHEX.HEX

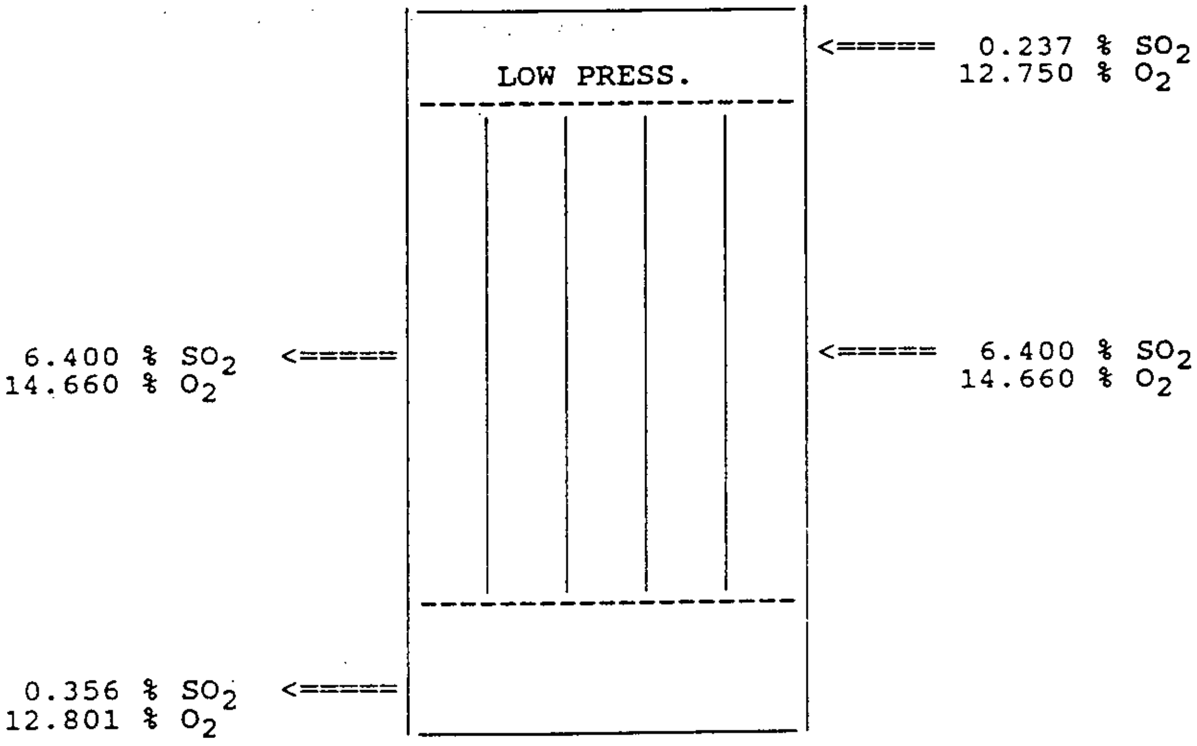
CUSTOMER: EXAMPLE

PLANT LOCATION: U. S. A.

PLANT NUMBER: 1

PLANT TYPE: METALLURGICAL; SINGLE ABSORPTION

HEAT EXCHANGER: INTERMEDIATE HEX



2.0 % OF SHELL SIDE GAS IS LEAKING INTO TUBE SIDE

TUBE SIDE INLET GAS WAS SAMPLED AT:
INLET TO INTERMEDIATE HEX

TUBE SIDE OUTLET GAS WAS SAMPLED AT:
PASS 4 INLET AT CONVERTER

Comparison of Sulfuric Acid Plant Catalysts

by

Leonard J. Friedman

Acid Engineering & Consulting, Inc.
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Introduction

The contact process for the production of sulfuric acid is based on the oxidation of sulfur dioxide to sulfur trioxide in the presence of a vanadium catalyst. From its beginnings in 1831 when Phillips of Bristol, England patented the oxidation of SO2 to SO3 over a platinum catalyst, to the modern plants of today using high activity, low pressure drop, ribbed rings of vanadium catalyst, the contact process and the catalyst it is based on have undergone significant (but subtle) changes, with the vast majority of developments in the last thirty years.

This paper will review the basic principals of the catalytic sulfuric acid process, and using a summary of operating data compare the three catalysts normally used in North America in the areas of conversion efficiency, activity, ignition temperature, loss in activity over time and screening losses. The paper will also review the advantages and problems with extensive plant converter testing using gas chromatography, Reich or other test methods.

Background

Before 1900, essentially all sulfuric acid was produced by the "Chamber" process, where nitrogen oxides were used to catalyze the oxidation of sulfur dioxide to sulfur trioxide. Plant size was small, unusually less than 50 STPD, and product acid strength limited to 65% to 75% sulfuric acid. The development of the chemical (dye) industry and the need for gun powder in the late 1800's necessitated a process to produce high strength sulfuric acid and Oleum. Early work (1870's - 1910) based on platinum as a solid catalyst, usually as platinum impregnated asbestos gauze, was the first technical and economic application of the "Contact" process. The high cost of platinum and its susceptibility to poisoning by many materials (notably arsenic present in the roaster gas streams of the day), led to the development of vanadium pentoxide based catalysts using alkali metal prompters on a porous silica carrier in the early 1900's (BASF patent of 1913). This is essentially the vanadium based catalyst used today. The following table shows the transition from the Chamber to Contact process:

Transition to the Contact Process

	1910	1930	1950	1960	1980
Contact Process %	20	27	75	85	100
Chamber Process %	80	73	25	15	0

Vanadium Catalyst

Vanadium catalyst usually contains 6% - 9% vanadium pentoxide with alkali metal promoters. The promoters are potassium sulfate with an atomic ratio of potassium to vanadium of 2 - 4 and a small amount of sodium sulfate to adjust (lower) the eutectic melt temperature of the mixture. The active components are supported on a highly porous silica base (diatomaceous earth).

In 1948 Topsoe & Nielsen demonstrated catalyst at operating temperatures exists as a melt within the pores of the silica support. The melt consists of vanadium sulfur complexes dissolved in pyrosulfates. In other words, the oxidation of sulfur dioxide to sulfur trioxide is a homogeneous reaction in the liquid film covering the surfaces of the support and not the heterogeneous reaction it would appear to be. The activity of the catalyst is from active species of vanadium pentoxide (V2O5), with the mechanism involving changes in the valence of vanadium.

The reaction rate is the result of many factors, including; the solubility of SO2, SO3 and oxygen in the melt, mass transfer limitations, the concentration of the active catalyst components and their solubility's in the melt, the porosity and pore size distribution of the silica support, as well as other less obvious factors (manufacturing process, etc.). The effect and interaction of each variable is not completely defined, so changes leading to improvements are more by trial and error than science. The difference between conversion predicted by rate equations and conversion actually obtained is accounted for by adding a so called "catalyst effectiveness factor" or fudge factor to the rate equation. The reaction rate can be described by the following relationship:

$$r = k\,[p(SO2)^{l}\,p(O2)^{m}\,p(SO3)^{-n}]\ K\,act\ \ K\,eff$$

r = reaction rate - g mole SO2/g catalyst, sec
k = rate constant - function on catalyst properties
$p()^{x}$ = partial pressure of components
K act = adjustment factor for catalyst activity
K eff = adjustment factor for system unknowns

The acknowledgment of the reaction taking place in the liquid melt leads to an understanding of catalyst ignition temperature as the temperature at which the melt first forms. The decrease in activity at low temperature is explained by the precipitation of some of the vanadium compounds reducing the concentration of the vanadium in the melt. The loss in catalyst activity at high temperature is attributed to the melt exceeding the capacity of the catalyst pores, with the liquid melt forming large inactive globules. The "old wives tale" of catalyst having a memory - once operated at high temperature, it must always be operated at high temperature - is explained by the loss in activity from melt components flowing out of the catalyst.

Sulfur dioxide to sulfur trioxide equilibrium is determined by the following equation:

$$Kp = \frac{p(SO3)}{p(SO2)\,p(O2)^{.5}}$$

A typical equilibrium curve showing operating lines for a four bed single or double absorption system is shown in Figure 1. The figure shows the change in the equilibrium curve resulting from the removal of SO3 in the interstage absorber (upper equilibrium line), and the reason the double absorption process increases conversion of SO2 to SO3 from 98.5% to 99.7%.

A review of the equilibrium equation indicates increasing pressure will increase equilibrium conversion. Figure 2 shows the effect of increasing pressure. In the example shown, increasing pressure from 1.3 bar (3.8 psi) to 10 bar (127 psi) will increase equilibrium conversion in a first catalyst stage from 63% to 75%. In the late 1960's, I did extensive work developing and evaluating a pressure process for sulfuric acid production - looking at single absorption at pressure versus double absorption. The conclusion of that work indicated double absorption could not be avoided at reasonable pressures to meet 99.7% conversion, eliminating the pressure process from economic consideration. In the mid 1970's, Krebs built a plant at PCUK in France based on the pressure process. The plant was a double absorption unit operating at 70 psi. Analysis indicated capital cost savings compared to the conventional double absorption route to be small (< 10%), with the plant experiencing extremely high corrosion and low energy efficiency.

Another route to increased conversion is to increase the oxygen concentration in the converter gas by using enriched air or pure oxygen. Analysis indicates improved conversion efficiency, but not enough to eliminate double absorption. A process using pure oxygen was evaluated in the late 1960's as an alternate to double absorption. The system was not economically sound due to the continuing cost of oxygen. No plants based on pure oxygen have been built. A number of spent acid regeneration plants use enriched air to overcome capacity limitations in the gas cleaning sections of the plant, and oxygen use to enrich the gas in the contact section is being used in a few places. The cost is a balance of the need for additional capacity versus the continuing cost of oxygen.

Catalyst Shape and Composition

In the 1960's and early 1970's catalyst was in the form of pellets, usually 1/4" and 5/32" diameter by 0.3" to 0.6" long (6 mm & 4 mm diameter by 8 mm - 15 mm long). The catalyst normally contained 6% to 8% V2O5, and was sold in North America by many vendors:

Stauffer
Cyanamid
BASF
Catalyst & Chemicals

Allied
Monsanto
Topsoe
Imperial Smelting

In the mid to late 1970's lower pressure drop through the catalyst bed was achieved by the use of a larger diameter pellet, 8 mm in diameter or 5/16" rather than 6 mm diameter. This size pellet was heavily promoted by Monsanto as 516 catalyst. At about the same time Topsoe introduced the ring shape catalyst to the North American market. Topsoe claimed significantly lower pressure drop and greater dust holding capacity. Initial installations used ring catalyst to top off the pellets in the first catalyst bed. Data showed lower initial pressure drop, and lower rate of pressure drop build-up (greater dust holding capacity). Complete first beds of ring catalyst showed acceptable activity and conversion while maintaining the low pressure drop and pressure drop build-up. Ring catalyst allowed an increase in operating time between turnarounds from 12 months to 18 - 24 months. It took a number of years for ring catalyst to be accepted and used in the entire converter. Now the three principal catalyst suppliers to North America (Topsoe, BASF, Monsanto) all offer ring shaped catalyst - with pellet and 516 catalyst essentially obsolete. The most recent change in catalyst shape has been the ribbed ring, offered by Topsoe as "Daisy" and BASF as "Star" rings, providing about 20% lower pressure drop than the normal 10 mm rings.

In addition to catalyst shape changes, in the last twenty years catalyst composition changes have provided improved performance permitting 99.7% conversion in a double absorption plant with increasing SO_2 gas strengths (9.5% - 10% in the 1970's to 11.5% - 11.75% today). A catalyst with 6% - 8% V_2O_5 is used in the first and second beds of the converter to attain resistance to activity loss at high temperature and maintain high temperature strength (reduced screening loss). The lower vanadium content - lower activity is offset by the higher average operating temperature of the upper beds, resulting in a high reaction rate and acceptable catalyst loading and approach to equilibrium. A catalyst with 7% to 9% V_2O_5 is used in the third and fourth catalyst beds to provide higher activity, lower ignition temperature and high reaction rate at the lower average operating temperature. The higher vanadium, lower bed catalyst has 10% to 20% greater activity than the 6% - 8% V_2O_5 upper bed catalyst.

The most recent catalyst development (re-invention of a 1948 discovery) is the so called "Cesium Catalyst". Cesium catalyst is really a 6% - 8% V_2O_5 catalyst with the formulation adjusted by substituting cesium for a portion of the potassium promoter. The use of cesium doubles the activity of the catalyst in the low temperature region, permitting continuous operation at bed inlet temperatures in the 720 F - 730 F region. The high cost of cesium promoted catalyst (about 2.5 times standard catalyst) limits its use to special applications.

The various catalyst shapes are shown in Figures 3 and 4. The following tables compare catalyst size and composition.

Shape

		Pellet	Pellet	Ring	Ribbed Ring
Diameter	mm	6	8	10	12
Length	mm	8	12 - 15	9 - 14	10
Pressure Drop	"H2O	1.0	0.9 - 0.95	0.5	0.4

Composition

	V2O5 Content	Comments
Upper Bed Catalyst	6% to 8%	High Temperature Operation Hardness & Temperature Resistance
Lower Bed Catalyst	7% to 9%	Low Temperature Operation High Activity - Softer Catalyst
Cesium Catalyst	6% to 8%	High Activity at Low Temperature (720 F) Can be Sticky at High Temperature

Catalyst Operation Analysis

Over the last ten years Acid Engineering & Consulting, Inc. has been involved with the operation of over one-hundred sulfuric acid plants around the world. In many cases data collected included information on various catalysts, including conversion efficiency, ignition temperature, loss in activity, screening loss, pressure drop and pressure drop build-up. A statistical analysis was performed on the data and the resulting observations are presented below. The analysis was made for the three main North America catalyst suppliers, Topsoe, BASF, and Monsanto, identified and supplier "A", "B", and "C". Note: If the analysis is on target, acid plant operators should be able to connect the supplier with their performance data.

Conversion Efficiency - The data suggests little significant difference in overall conversion efficiency between the three suppliers. Conversion efficiency analysis was complicated by many operating plants with more than one manufacturers catalyst in the converter, and many with two or three suppliers catalyst in a particular bed. Although there was some statistical difference, one could not use the conversion efficiency difference to tell which catalyst was in a particular converter.

Loss in Activity - The reduction in activity of a particular catalyst over time was determined by a review of catalyst suppliers activity test results and operating data showing changes in bed inlet and exit temperatures and conversions over time. The results were based on plants operating with high converter inlet SO2 concentrations resulting in bed 1 exit temperatures of 1140 F to 1160 F. The table below summarizes the activity loss over an 18 month to 24 month period for ring catalyst.

Loss in Activity (18 - 24 Months)

	Supplier "A"	Supplier "B"	Supplier "C"
Bed 1	20% - 35%	9% - 12%	9% - 13%
Bed 2	8% - 12%	5% - 8%	5% - 8%
Bed 3	< 5%	< 5%	< 5%
Bed 4	< 5%	< 5%	< 5%

The data indicates supplier "A" upper bed catalyst looses activity at a significantly higher rate than the others, about 2 to 3 times the activity loss between turnarounds. This would suggest a formulation problem resulting in the melt solution leaving the pores of the catalyst when operating at high temperature. The data is consistent over many years, eliminating the possibility of a bad batch or run of catalyst causing the results. In fact, for many years this supplier recommended limiting first bed exit temperature to less than 1125 F.

Screening Loss - Data for screening loss was based on ring catalyst, vacuum screened per suppliers instructions, usually by the same two commercial catalyst screening companies. The wide variation in the data for a particular supplier is attributed to operating time at high temperature, screening rate and the amount of broken pieces returned to the converter.

Screening Loss (% of Bed)

	Supplier "A"	Supplier "B"	Supplier "C"
Bed 1	25% - 40%	10% - 15%	11% - 16%
Bed 2	20% - 30%	9% - 15%	10% - 15%
Bed 3	15% - 20%	8% - 14%	8% - 14%
Bed 4	12% - 17%	8% - 12%	8% - 12%

The data is consistent, indicating a problem with supplier "A" catalyst, especially in the high temperature area, suggesting a formulation problem (high screening loss and loss in activity). The data is from many plants over a number of years with more data points for beds 1 and 2, and limited data for beds 3 and 4.

Pressure Drop Build-up - Data for sulfur burning plants was analyzed to determine differences in the rate of pressure drop build-up over an 18 month operating period between turnarounds. The analysis was complicated by unknown variations in the ash content of the sulfur and the amount of broken pieces returned to the converter after screening. After some adjustment for bed area, gas velocity, etc., the data indicated no significant difference in the rate of pressure drop build-up between the three catalysts.

Comparison Summary

Overall the catalyst comparison indicates supplier "A" has a problem with its upper bed ring catalyst when operated at high gas strength - high temperature (exit temperatures above 1130 F), resulting in excessive loss of activity over time and screening losses two to three times the others. In fact, the high screening loss and subsequent make-up with fresh catalyst obscures the activity loss problem, so overall plant conversion efficiency is maintained. Based on the analysis, supplier "B" and "C" catalyst are close in all aspects studied, with supplier "A" upper bed catalyst of lower overall performance.

Cesium Promoted Catalyst

Cesium promoted catalyst is offered by the three North American suppliers. The high cost, about 2.5 - 3 times conventional catalyst, has limited use to special situations. Cesium catalyst is rarely used in sulfur burning plants, but has found some advantages in spent acid regeneration and metallurgical plants. The catalyst has been used as a top layer of the first catalyst bed to provide operation at 720 F - 730 F, reducing gas heat exchanger requirements, while allowing restart of the plant when the catalyst bed is at 600 F.

Early installations of cesium promoted catalyst experienced severe pressure drop build-up. Pressure drop in some plants increased 30" to 60" H2O in a few months. Investigation indicated the plants experiencing the problem were operating at first bed inlet temperature of 780 F to 820 F, while plants without problems operated at 720 F to 740 F. The operating data indicates the cesium catalyst becomes very sticky at elevated temperatures. Recently, Topsoe has reformulated their cesium catalyst so it can be operated at low or high temperature without the pressure drop build-up problem. The other suppliers are expected to produce an adjusted formulation in the near future.

Converter Testing

Traditionally catalyst performance evaluations are made by reviewing bed inlet temperatures and temperature rise, inlet SO2 gas strength and overall conversion efficiency. Changes in these operating variables, although small from day to day, are good indicators of catalyst bed performance over time. Recently, one catalyst supplier has offered portable gas chromatograph testing of converter systems. The tests provide the composition of gas into and out of each catalyst bed. Comparing actual bed conversion with calculated conversion and equilibrium would be a superior way of determining catalyst activity - performance.

Acid Engineering & Consulting, Inc. has reviewed the results of a number of gas chromatograph tests of converter systems. In most cases, the test data was consistent with evaluations based on traditional methods, and was a useful tool in determining catalyst activity - replacement requirements for an upcoming turnaround. In a number of cases, the test results were obviously incorrect and the interpretation of the results flawed and self-serving. Objectivity comes into question when the one doing the testing is selling catalyst or testing his own catalyst to show how good it is, or how bad a competitors is. In one case, the test data indicated 7% to 8% conversion of SO2 to SO3 in the sulfur furnace - well above equilibrium. This was coupled with extremely low conversion in the first catalyst bed, indicating low catalyst activity and the need for additional replacement catalyst. In another case, a spent acid regeneration plant was experiencing conversion efficiency problems (very low first bed temperature rise) after a major plant modification. The catalyst in the first bed was changed, but the same problem persisted. Gas chromatograph tests (purchased with the replacement bed of catalyst) were run at various O2/SO2 ratios (0.72 to 0.92) and SO2 gas strengths (9.4% - 10.7%). Note: Most sulfur burning plants operate at O2/SO2 ratios of 0.75 to 0.77 and SO2 gas strengths of 11.5% - 11.75%. The test results are summarized below:

Plant Test Data

	Run 1	Run 2	Run 3
O2/SO2 Ratio	0.72	0.86	0.92
Overall Conversion	90.8%	94.2%	95.4%
Bed 1 Catalyst Activity	104%	83%	82%

Note: Catalyst activity dropped 22% between test runs 1 and 3. This was reported as "catalyst activities are in the normal range".

The conclusion presented by the testing company - catalyst supplier was the plant design at 0.75 O2/SO2 ratio and 97% conversion in a single absorption plant was not possible with the catalyst type, volume and O2/SO2 ratio. However, the catalyst supplier - testing company would be happy to study ways to achieve plant conversion and capacity, although they stated "there are no clear cut, low cost ways to do this". Note: Acid Engineering & Consulting, Inc. adjusted plant operating conditions and in four hours the plant was able to meet design capacity at an O2/SO2 ratio of 0.75 with conversion exceeding 98%. In this case, knowledge and experience was able to do what blind or self-serving testing could not do - get the plant operating at or above design without additional catalyst or costly modifications.

Conclusion

This work was intended to provide an understanding of sulfuric acid plant catalysts and to present a comparison of the three catalysts used in North America. Data from many plants over a number of years was reviewed, adjusted and evaluated to obtain comparative catalyst performance. The data indicated suppliers "B" and "C" catalyst to be about equal in each of the areas examined, with supplier "A" catalyst of lower performance (activity loss over time and high screening loss).

If some have a better understanding of sulfuric acid plant converter operation and catalysts, and supplier "A" is encouraged to improve their catalyst, the time and effort spent on this work will have been justified.

Figure 1

Converter Equilibrium

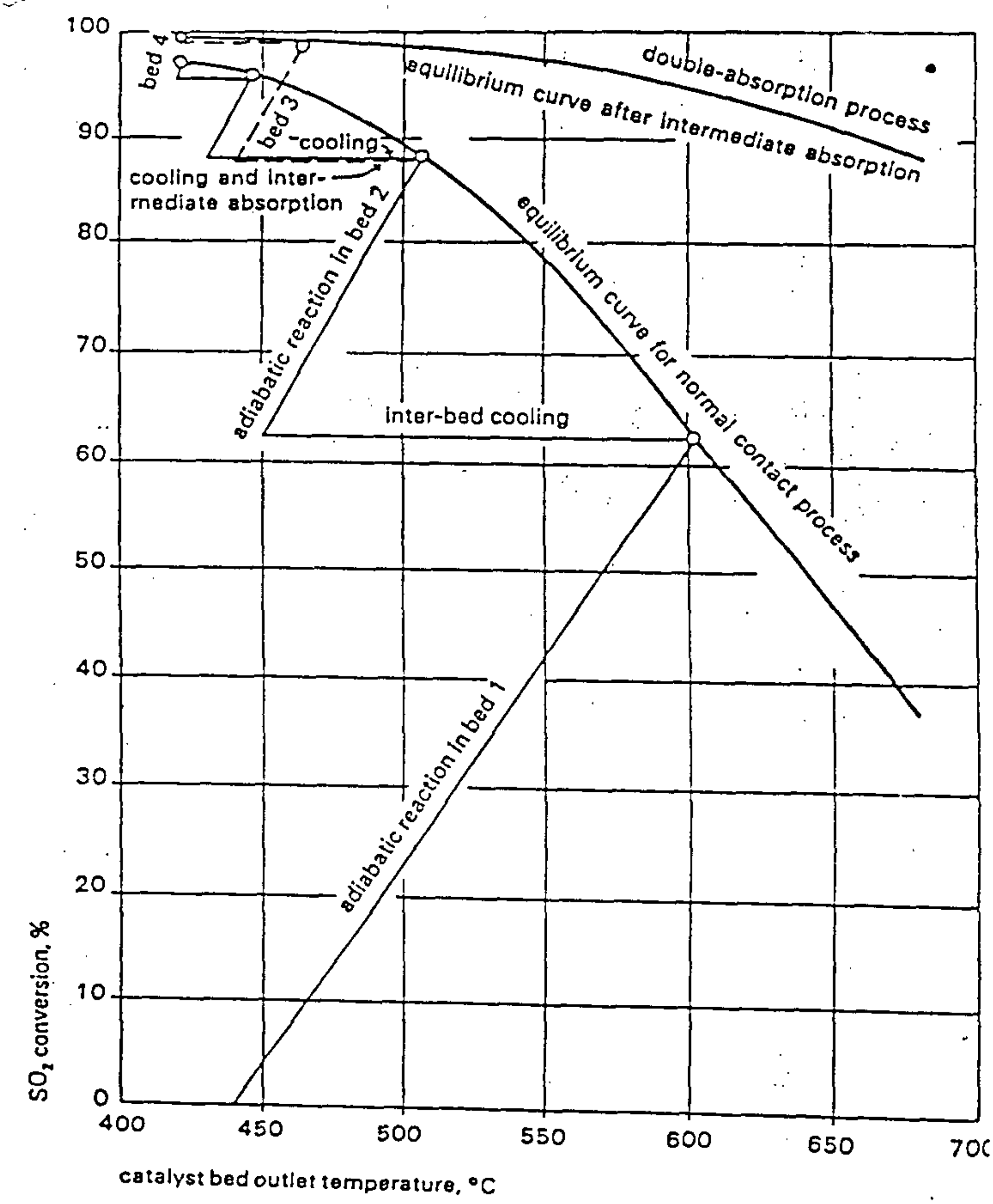

Figure 2

Pressure Effect on Equilibrium

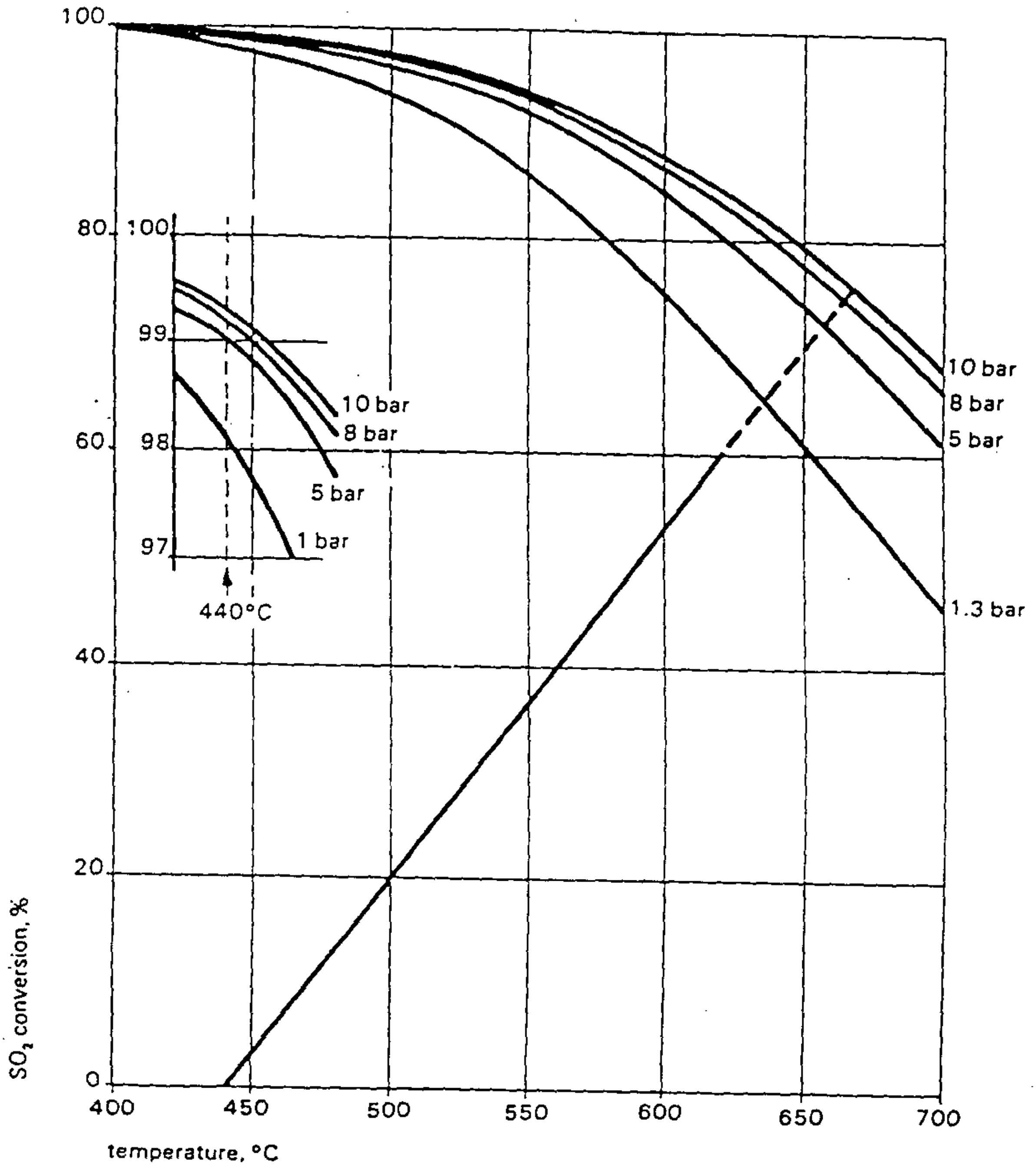

Figure 3

Catalyst Shapes & Sizes

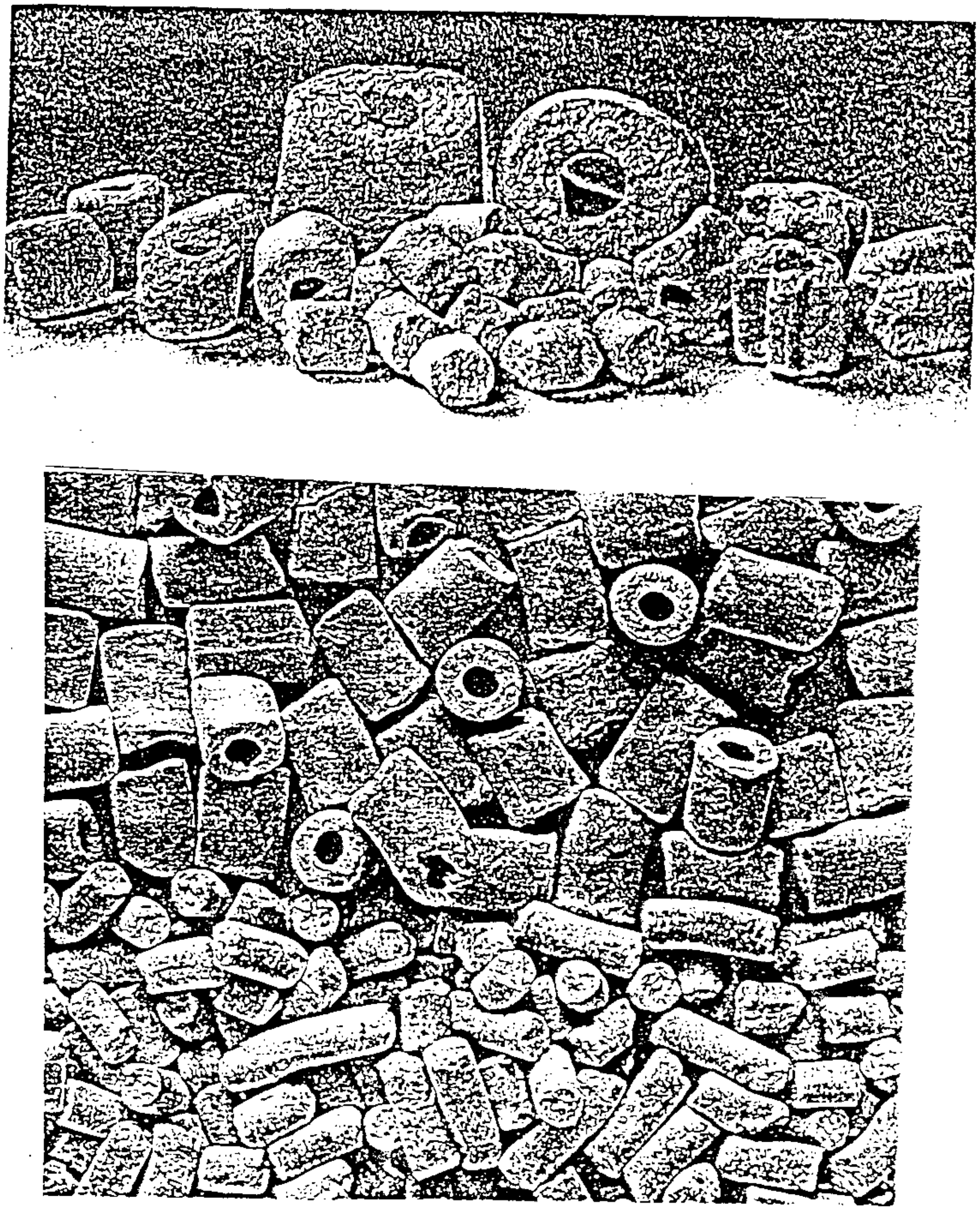

Figure 4

Catalyst Shapes & Sizes