NEW SULFURIC ACID HEAT RECOVERY TECHNOLOGY

HEAT RECOVERY SYSTEM

NAMHAE CHEMICAL CORPORATION

Yeosu, Korea

By JOHN SHEPUTIS

MONSANTO ENVIRO-CHEM

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I. 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 MTPD 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. 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.

FIGURE 1 – HEAT RECOVERY SYSTEM

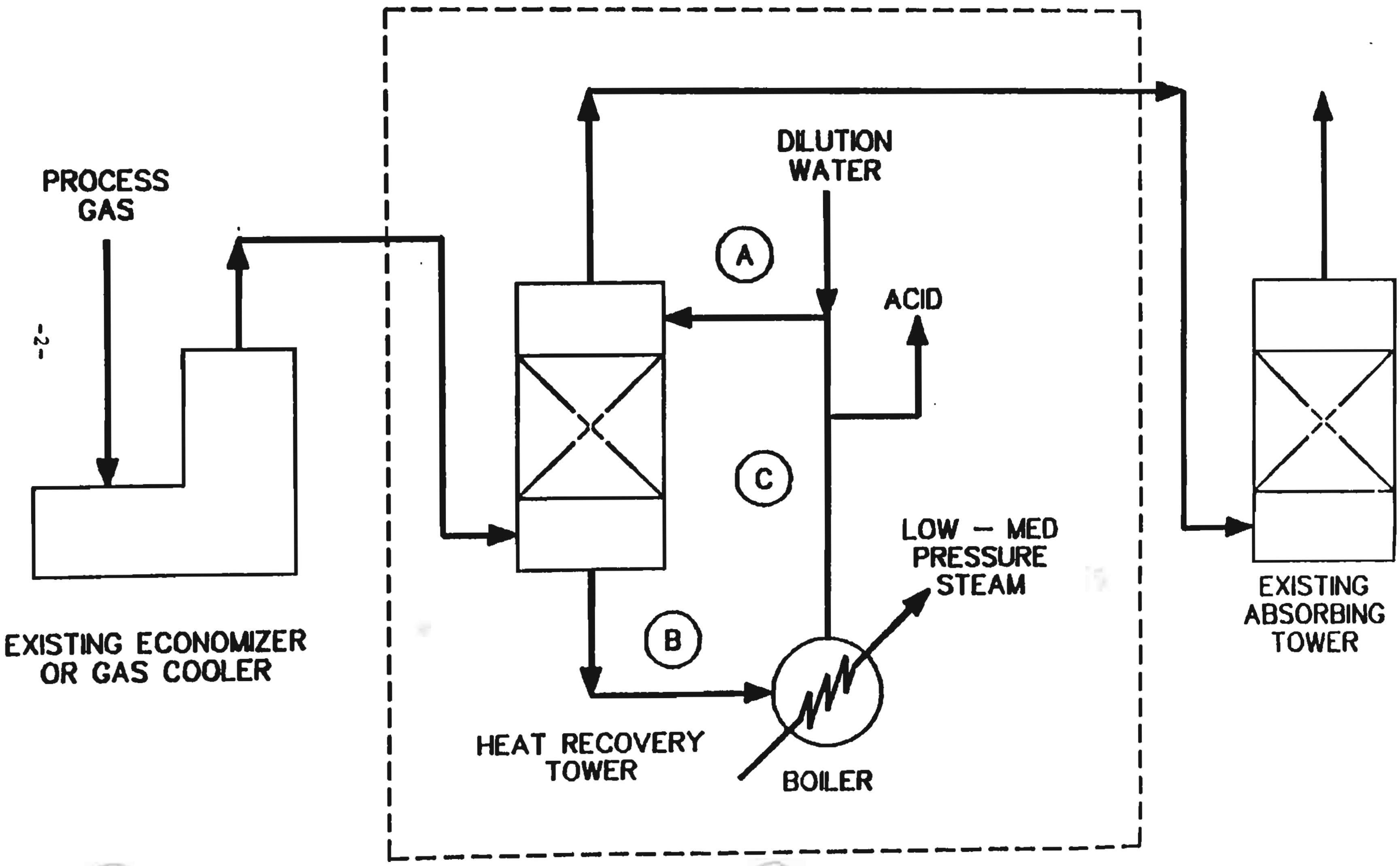
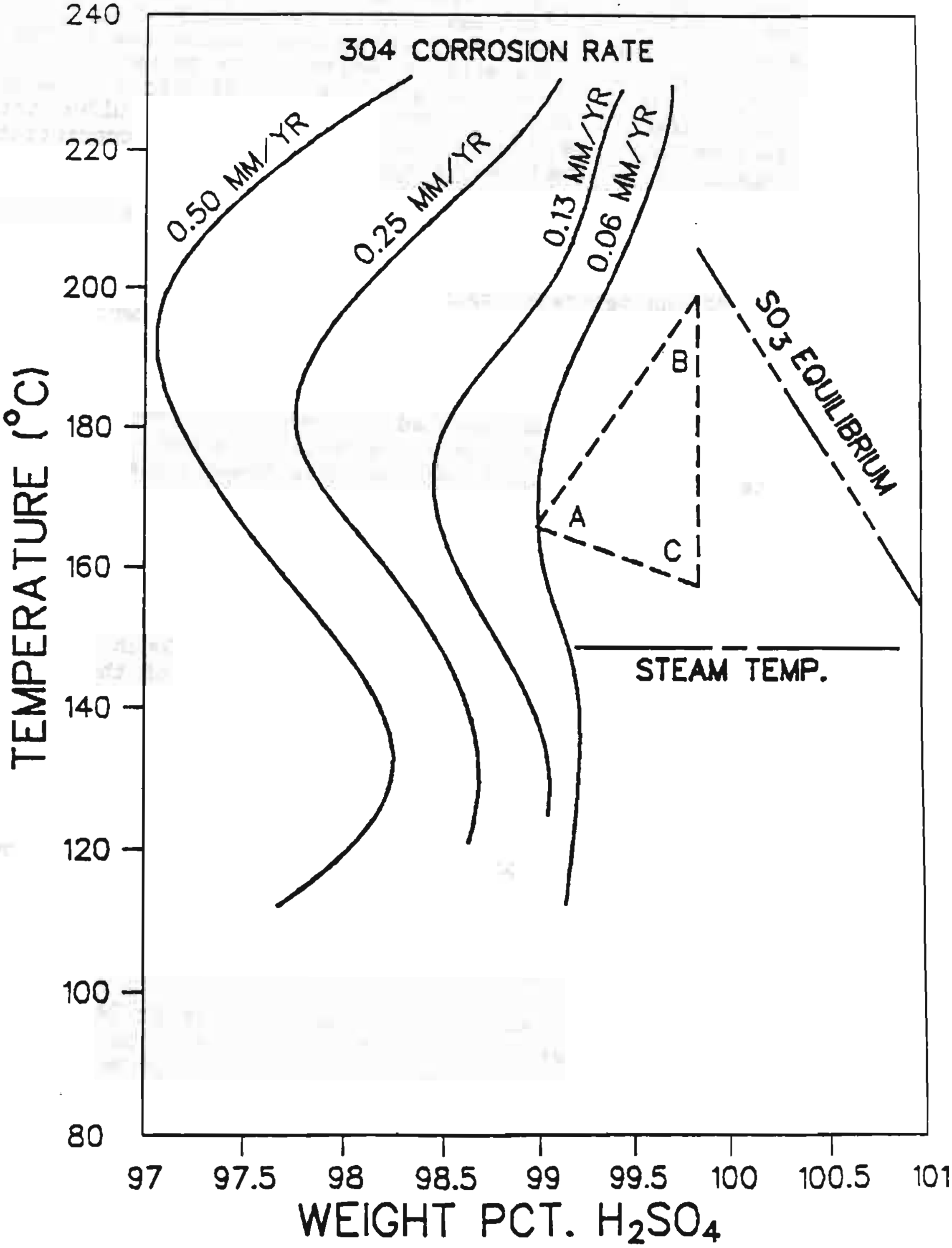


FIG. 2

HRS OPERATING CYCLE



The process is shown on the HRS operating cycle diagram in Figure 2. The curves on the left are isocorrosion lines for 304 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 would be applicable for a 3.5 bar (50 psig) steam system at 144°C steam temperature.

The HRS can generate steam up to 10 bar (150 psig) pressures. When the HRS is installed with other energy enhancements, 90 to 95% of the total available energy generated in a sulfur burning plant can be recovered.

The pilot plant was operated intermittently over a three (3) year period to demonstrate operation reliability and to confirm corrosion rates and steam production at various temperatures and conditions.

II. NAMHAE HRS PROJECT

BACKGROUND

Namhae Chemical Corporation (NCC) of Yeosu, South Korea initiated a project in 1986 to reduce the SO_2 emissions of their two existing, ten year old, single absorption, sulfur burning sulfuric acid 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 MTPD. The original 1100 MTPD capacity had been increased to 1350 MTPD during a previous project using Enviro-Chem LP catalyst and low temperature economizers.
- Increase steam production of the acid plants.

Most of the increased steam production was to be generated by the new HRS. Namhae initiated a separate project to install a new turbine generator dedicated to use only the 10 bar (150 psig) steam produced from the HRS.

In October, 1986, Namhae awarded Monsanto Enviro-Chem Systems, Inc. (MEC) of St. Louis the contract to do a field study of the existing sulfuric acid plants and the front-end engineering to convert the plants to double absorption; add energy enhancements and to incorporate the HRS into the plant. The field study included process review of the existing operations; evaluation of existing equipment and structural examinations of vessels and ductwork. Various design alternates were reviewed and considered; decisions were made and the process design of the plant was essentially set in December, 1986.

Concurrently, Namhae had awarded Sunkyong Engineering and Construction Company of Seoul, Korea the detailed engineering contract for the turbine generator installation as well as for the sulfuric acid plant modifications. Monsanto Enviro-Chem was to provide the front-end engineering design which included flowsheets, equipment specifications, and instrument list with loop diagrams, plant layout, vessel drawings and the ductwork package. In addition, Monsanto Enviro-Chem was to provide sulfuric acid plant design consulting to both Namhae and Sunkyong during the course of the project, review equipment evaluations and selections, inspect special equipment, provide construction quality assurance reviews, write the operating instructions, provide operator training and start-up assistance. Sunkyong was to do the detailed engineering such as foundations, structural support, piping, engineering evaluation, material takeoffs, panel designs and etc.

The final design selected included:

- A Heat Recovery System as the interpass absorption tower. This included a Heat Recovery Tower, with Monsanto ES mist eliminators, to remove interpass 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. This converter contained Monsanto Enviro-Chem LP (Low Pressure Drop) catalyst. Also, some of the catalyst in the existing converter was replaced with LP catalyst to ensure required SO_2 to SO_3 conversion.

- Cold interpass and hot interpass gas to gas shell and tube heat exchangers to heat gas going from the HRS interpass absorption tower to the final catalyst pass.

- Economizers and superheaters to recover additional heat in the form of high pressure steam.

Monsanto Enviro-Chem maximized use of existing equipment to reduce project costs. The existing blower, high pressure boiler, economizers and superheaters were used without costly modifications. The flow sheet is shown in Figure 3.

PROJECT EXECUTION

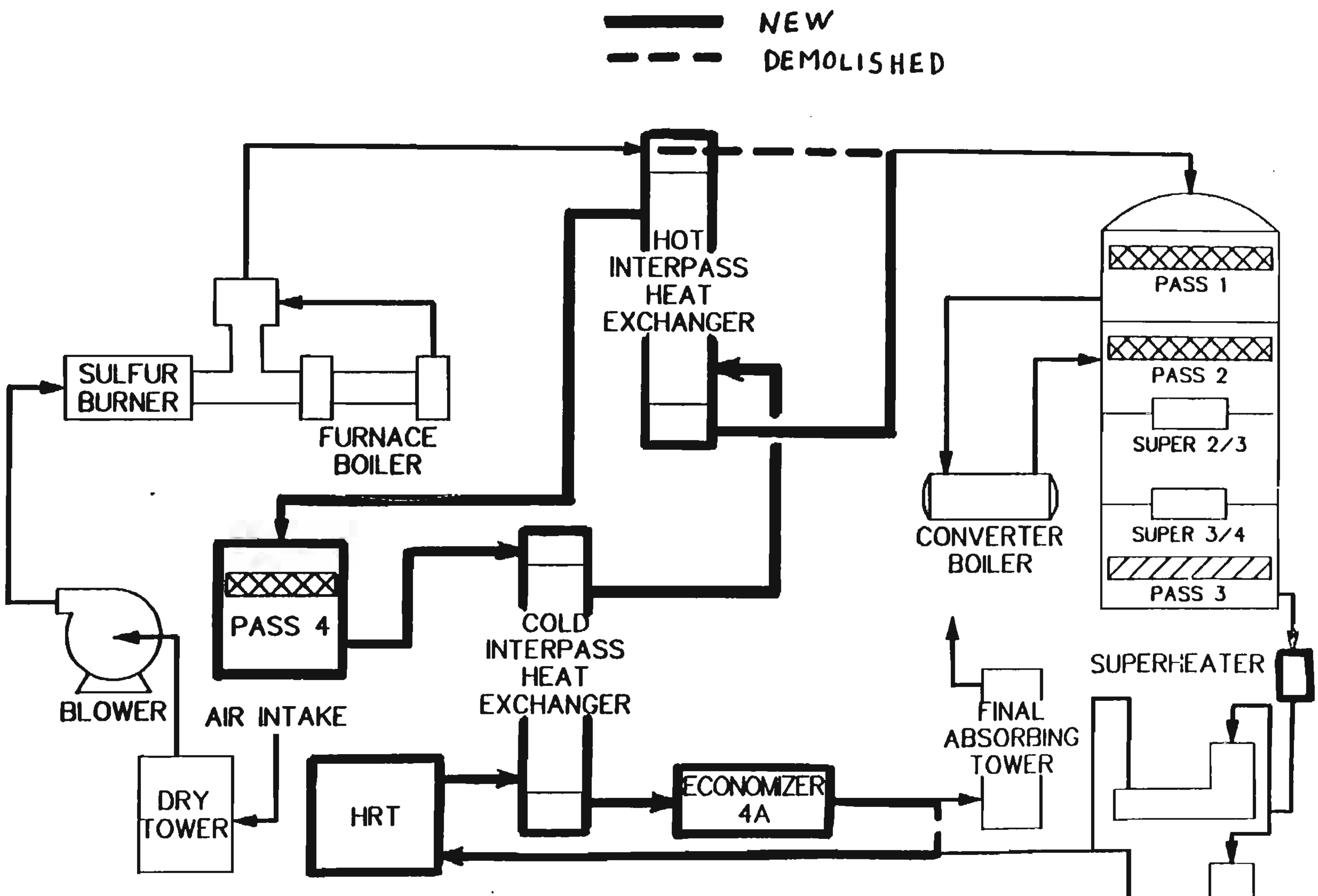
The Namhae project had a fast schedule with the first plant start-up scheduled within one year of contract negotiations. Although there were equipment delivery delays caused by labor strikes, customs clearance procedures and other international purchasing and expediting problems, the first plant came on-line thirteen (13) months after the contract award. The project, which included both plants and a turbogenerator, was designed, procured, installed and demonstrated in fourteen and one-half (14-1/2) months.

KEY MILESTON SCHEDULE DATES

October 13, 1986	Initiate Contract
November 26, 1986	Field Studies/Process Design Complete
February 1, 1987	Enviro-Chem Basic Engineering Complete
June/July, 1987	HRS Equipment Inspected
October 18, 1987	Plant 1 Down for Tie-Ins
November 19, 1987	Plant 1 On-Line
November 27, 1987	Plant 2 Down for Tie-Ins
December 7, 1987	Plant 1 Demonstrated
December 22, 1987	Plant 2 and Turbogenerator On-Line
December 29, 1987	Both Plants and Turbogenerator Demonstrated and Formally Accepted

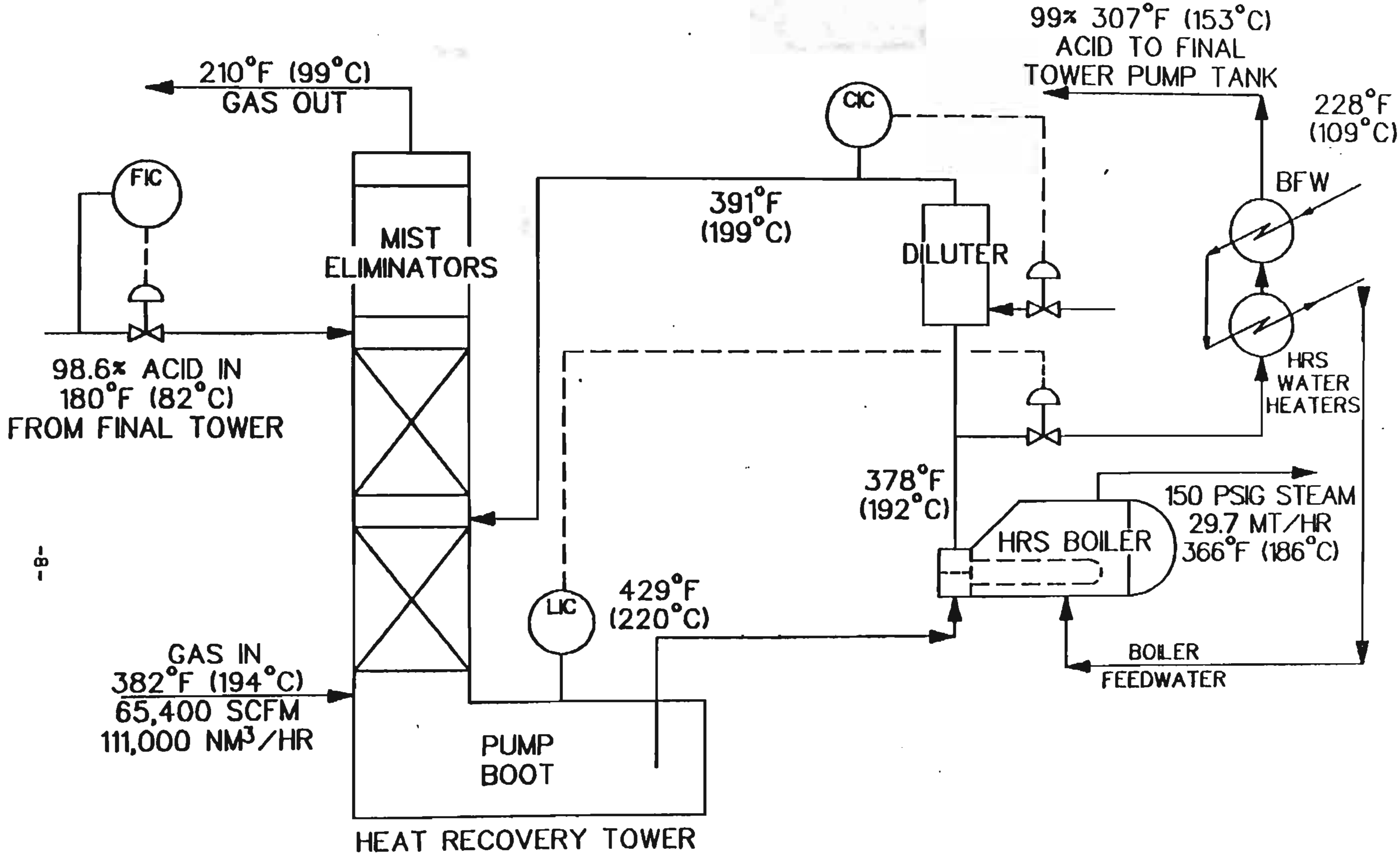
HEAT RECOVERY SYSTEM

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 Namhae HRS flow design is shown in Figure 4.



GAS FLOW DIAGRAM

FIG 3



HEAT RECOVERY SYSTEM

FIGU 4

The main equipment items in an HRS are:

1. Heat Recovery Tower

   This tower is a 310 stainless steel tower with ceramic Intalox packing and Monsanto Enviro-Chem Energy Saver (ES) mist eliminators.

2. HRS Acid Circulation Pump

   This pump is a vertical submerged 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 boiler is a "kettle" type boiler with acid flow through stainless steel tubes. The water side of the boiler is controlled similar to other firetube boilers with redundant level controls, pressure gauges and blowdown connections.

   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 a vessel in which hot dilution water is mixed and absorbed by the hot acid in a turbulent reaction.

5. Instrumentation

   The HRS instrumentation is similar to flow, temperature and pressure instrumentation concepts used in acid plants. However, there are three instrument loops which are not common acid plant design loops:

   A. Concentration Control

      The acid concentration to the tower must be controlled above 98.5% acid to minimize corrosion. If acid concentration goes too high, then SO_3 will slip through the tower thereby reducing steam production and overall SO_2 conversion. Acid concentration can be easily and automatically controlled by use of modern electrodeless torroidal conductivity analyzers. These analyzers have been used in normal absorbing towers for years and have been proven reliable and accurate.

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.

C. Acoustic Leak Monitor (ALM)

The acoustic leak monitor was specially developed by Monsanto and the manufacturer to detect boiler or heater leaks using acoustic emissions. The acoustic wave is transformed into an electric signal and is monitored in the control room.

Boiler or heater leaks cause an increase in the acoustic emission which is detected and alarmed in the control room.

The other materials in an HRS such as pipe, valves, thermowells and etc. are made of stainless steels compatable with high temperature sulfuric acid. Several of these materials were discussed in Paper Number 22 presented by J. E. Neese and D. R. McAlister, both of Monsanto, at the March, 1987, Corrosion Seminar in San Francisco.

The HRS has operated very well since start-up reflecting operator ease in familarizing themselves with the additional interpass absorption and HRS equipment and controls.

HRS START-UP PROBLEMS

As with all chemical plant start-ups, there were some initial problems that developed. The one that caused the most concern was the high corrosion rate of the HRS pump when acid concentration accidently dropped to the 94% to 95% range for about five (5) hours during the first two days of operation. The basic problem, later identified, was that the acid concentration conductivity analyzer installed had a readout in conductivity rather than acid concentration as had been requested but not clearly specified. Conductivity decreases as acid concentration increases, hence, the control actions were reversed on the water control loop.

The consequence was that in the second day of the start-up, when the concentration controller was shifted from manual to automatic, the controller opened the dilution water valve as the conductivity increased (concentration decreased). The error was discovered in about 20 minutes, but the acid had been diluted to about 94% to 95%. A decision was made to keep the plant on-line and about four to six hours were required to increase the acid concentration to above 98%.

Two days later, there was a gas leak at the pump shaft mechanical seal. It is suspected that the hot mechanical seal was damaged when hit with a full stream of cold water from a hose. The pump had to be removed and the pump corrosion was discovered at this time. Corrosion coupons that were installed in various parts of the piping system were removed and examined. The coupons showed higher than normal corrosion, but not as much as on the pump. Namhae and Enviro-Chem were concerned that the pump materials (310 SS and Lewmet) might be velocity sensitive to the acid.

The spare pump was installed and the original pump was returned to the U.S. for further examinations.

Monsanto and Lewis Pump Co. made an extensive investigation of the pump corrosion, which included extensive laboratory corrosion testing. The study conclusion was that the rapid corrosion of the pump was due to erosion-corrosion from the weak acid. There was some galvanic corrosion that was also attributed to the high velocity weak acid. The lab tests and investigation reconfirmed that a pump of 310 SS and Lewmet should provide satisfactory life as long as acid concentrations were properly maintained.

There was some minor corrosion on the recently installed spare pump impeller after a couple of days service. The pump was reinstalled and pulled again after all plant demonstration runs were complete a month later. The corrosion had not noticably progressed in that month. This observation supported the contention that the original specified material of construction selection would provide a satisfactory pump life.

The diluter also presented some problems. The structure supporting the diluter did not allow for the turbulent reaction that occurs in the diluter. The diluter vibrations were readily noticable in the nearby walkway. Eventually, the structural steel supporting the diluter is expected to be reinforced on a more routine schedule.

The diluter water sparger supplied for the project was less structurally sound than was originally specified. The sparger performance, in terms of life and acid mixing, was not as good as desired. Minor design modifications have been made to the sparger and testing for long-term life performance is now in progress.

The corrosion monitor instrumentation required some modification to the electrode probe, but has tracked corrosiveness of the acid well. The acoustic leak monitor (ALM) was too sensitive during the first weeks of operation and alarmed often due to background noises during start-ups and shutdowns. The ALM was recalibrated to reduce the alarm sensitivity to start-up and shutdown background noises with good success. Long-term evaluation on alarm sensitivity is in progress.

Overall, the HRS and instrumentation has performed well since the initial start-up. The major concerns have subsided and only minor design changes will be needed or expected on future Heat Recovery Systems.

RESULTS

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.

RESULTS

	GUARANTEE	EXPECTED	DEMONSTRATED PLANT 1	DEMONSTRATED PLANT 2
Production, MTPD	1350	1350	1442	1430
SO_2 Emission, PPM	500	370	208	152
Steam Production, MT/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

The plants had originally been designed for 1100 MTPD when constructed ten years ago. The capacity had been increased to 1350 MTPD in the early 1980's by use of low pressure drop catalyst and other modifications. However, the 1350 MTPD rate was the maximum rate that had been achieved prior to this project.

The project intent was to keep the 1350 MTPD rate as the design rate. During the demonstration run of each plant, the rate was maintained almost 100 MPTD above the 1350 MTPD guarantee figure to ensure that there were no questions on performance when the data was in and analyzed. The plant ran very well at the higher rates. More production capacity was available but not tested during the formal demonstration period.

All of the HRS steam was directed to the Turbodyne turbogenerator which included an Electric Machine generator. The turbogenerator rated output was designed and demonstrated at 8760 KW with an inlet flow of 57.6 MT/Hr of 150 psig steam. The power generation from the HRS steam was 3.2 MW/1000 MT of acid produced.

The annual gross savings for both plants is 6600 MT of sulfur saved based on a 2.1% SO_2 to SO_3 conversion improvement and a 350 day/year operating schedule at design rate. Also, 73,600 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/MT delivered price and $4.6 million for electrical power based on $0.062/KWH costs. These cost figures are used for illustrations only and not necessarily those used by Namhae.

The design, construction and successful demonstration of the first two commercial Heat Recovery Systems, complete with dedicated turbo-generator, is considered an outstanding success by Namhae and Monsanto.

JOHN SHEPUTIS - PROJECT MANAGER

MONSANTO ENVIRO-CHEM SYSTEMS, INC.

John Sheputis has been with sulfuric acid plants since 1967 when he joined Monsanto.

His career includes catalyst manufacturing, Plant Supervisor, Process Design Supervisor, Mechanical Section Supervisor, Technology Group Leader, Manager of Project Engineering, Proposal Manager and Project Manager in the sulfuric acid plant industry. John is Enviro-Chem's project manager for the Namhae, Korea and Falconbridge, Norway Heat Recovery System projects.