

SO₂ 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 (SO₂) to the atmosphere while maintaining or increasing acid production. Utilizing Monsanto cesium-modified catalysts, a number of sulfuric acid producers have effectively reduced their SO₂ 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 SO₂ emissions has required the development of the double absorption contact process for SO₂ 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 SO₂ 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 SO₂ conversion levels near 98 %. Although these plants are operating within authorized conversion limits, many companies are striving to reduce the SO₂ 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 SO₂ 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 SO₂ 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 ($> 430^{\circ}\text{C}/806^{\circ}\text{F}$), 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 SO₂ 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 SO₂ 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 SO₂ 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 % SO₂ feed gas.
- (4) Stack SO₂ 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 % SO₂ fed.
- (4) Stack SO₂ 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 % SO₂ feed gas.
- (4) Stack SO₂ 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 % SO₂ fed.
- (4) Stack SO₂ 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 SO₂ 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 % SO₂ fed.
- (4) Stack SO₂ emissions at 12 lbs./STPD (50 % reduction).

Case 4: Double Absorption Spent Acid Plant

Pre-Cs Data:

- (1) Standard catalyst in all beds; 12 % SO₂ 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 SO₂ 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 SO₂ emissions.

Case 5: Double Absorption Spent Acid Plant

Pre-Cs Data:

- (1) Used conventional catalyst in all beds; 7 % SO₂ 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 SO₂ emissions. Using Cs-110 rings in the bottom pass of double absorption plants, it is possible to reduce the lbs. SO₂ per ton of acid and hence allowing for greater production at the same SO₂ 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 SO₂ 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 SO₂ and O₂ 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 SO₂ and O₂ 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 SO₂ 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 SO₂ levels in 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 SO₂ emissions by bleeding high SO₂ gas directly to the stack or flooding lower pass catalyst beds with SO₂-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: SO₂ 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: SO₂ emissions were approaching permitted limit.

Result: PeGASyS analysis indicated a severe leak in the cold heat exchanger. Following exchanger repair, SO₂ 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 SO₂ 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 SO₂ emissions.

Case 4: Spent Acid Double Absorption Plant

Issue: SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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.

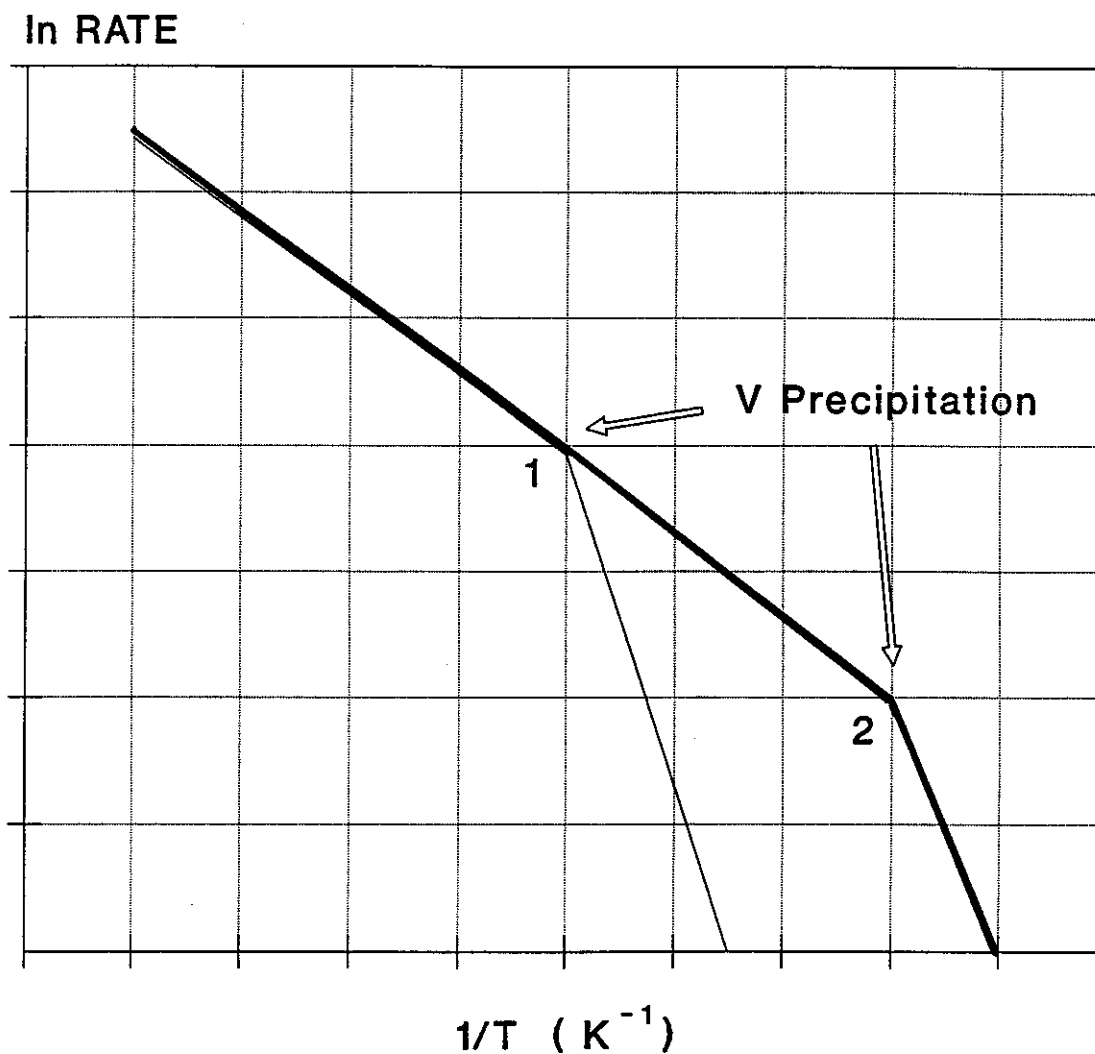
The authors would like to acknowledge the St. Louis R&D Team and the Manufacturing Team in Martinez, CA for their work on the cesium-promoted catalyst development.

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Figure 1

SO₂ OXIDATION RATE VERSUS TEMPERATURE

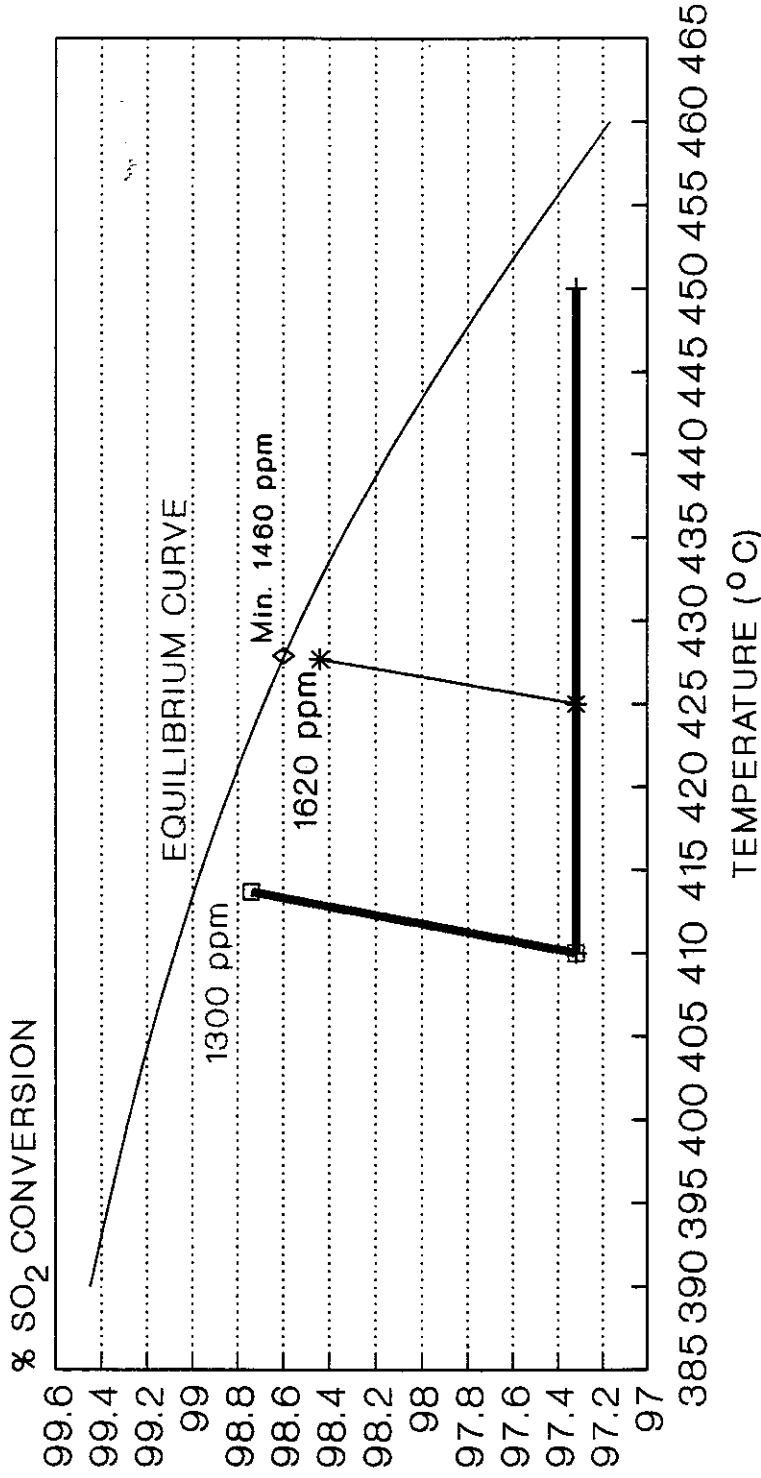


CATALYSTS:

— CONVENTIONAL — *CESIUM-PROMOTED*

Figure 2

SINGLE ABSORPTION: CS ADVANTAGE



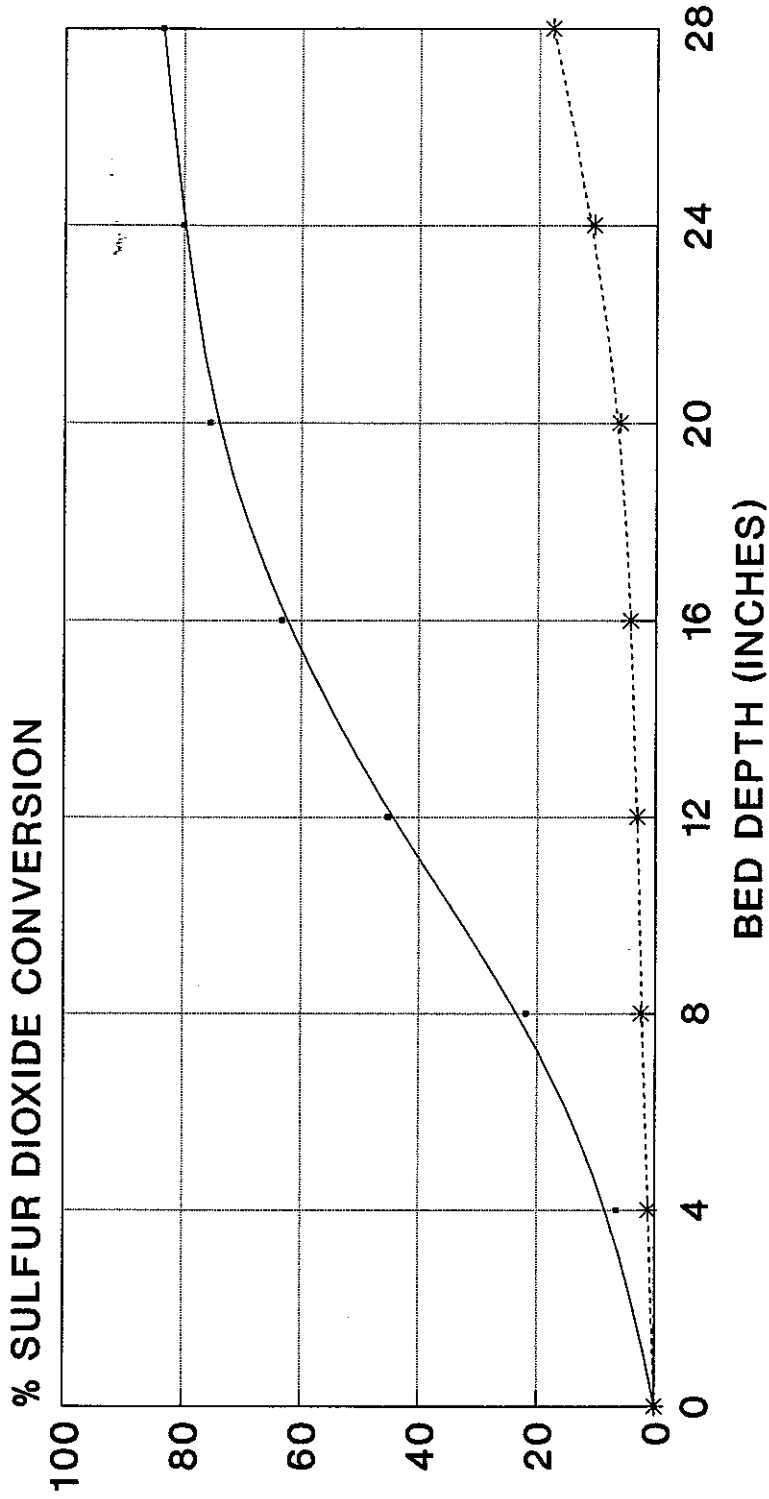
4th PASS CATALYST:

—*— LP-110 —■— Cs-110

FEED GAS = 9 % SO₂, 11.9 % O₂
410°C = 770°F; 425°C = 797°F

Figure 3

FIRST PASS: CAPPED Cs-120 BED SULFUR BURNING; T(INLET)= 380°C/715°F



CATALYST:

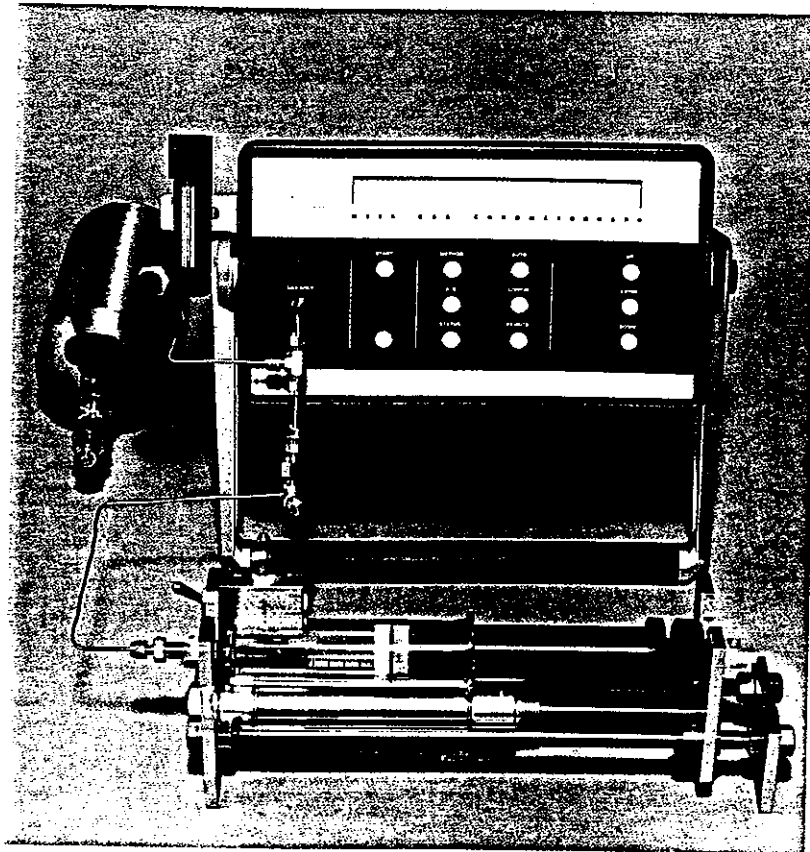
—•— 8 IN. Cs CAP/LP-120 *-*-* STANDARD CATALYST

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

Figure 4

PeGASyS

Portable Gas Analysis System



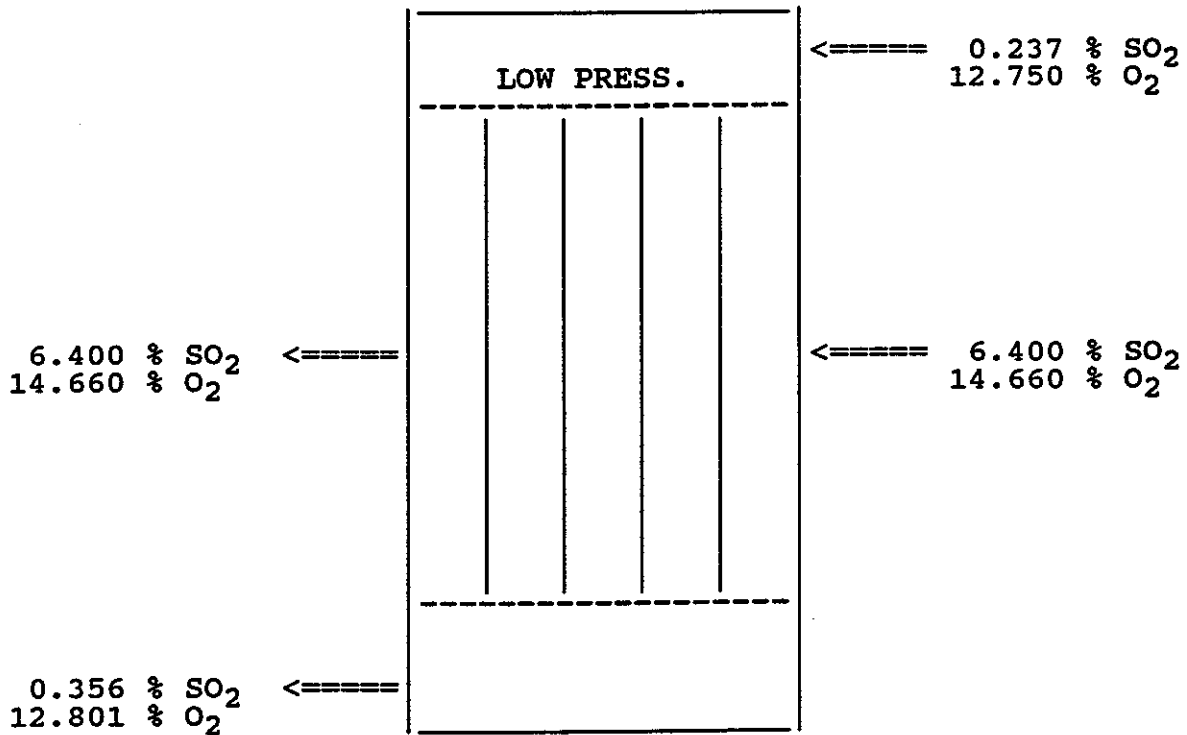
Monsanto Enviro-Chem Systems, Inc.

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