1 of 2

A NOVEL CARBON-BASED PROCESS FOR FLUE-GAS CLEANUP

FINAL REPORT

**S. K. Gangwal
G. B. Howe
W. J. McMichael
J. J. Spivey**

Work Performed Under Contract No.: DE-AC22-91PC91345

For

**U.S. Department of Energy
Office of Fossil Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236-0940**

By

**Research Triangle Institute
P. O. Box 12194
Research Triangle Park, NC 27709-2194**

October 1993

This report was prepared by the Research Triangle Institute (RTI) as an account of work sponsored by the U.S. Department of Energy. RTI makes no warranty or representation, expressed or implied, with respect to the information contained in this report, or that the use of any apparatus, method or process disclosed in this report may not infringe privately owned rights. Furthermore, RTI assumes no liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

ABSTRACT

A low-temperature process employing activated carbon-based catalysts and operating downstream of the electrostatic precipitator (ESP) was evaluated jointly by Research Triangle Institute (RTI) and the University of Waterloo (Waterloo). The RTI-Waterloo process was projected to be capable of removing more than 95% SO_2 and 75% NO_x from coal combustion flue gas. In the process, the flue gas leaving the ESP is first cooled to approximately 100 °C. The SO_2 is then catalytically oxidized to SO_3 which is removed as medium-strength sulfuric acid in a series of periodically flushed trickle-bed reactors containing an activated carbon-based catalyst. The SO_2 -free gas is then reheated to approximately 150 °C and NH_3 is injected into the gas stream. It is then passed over a fixed bed of another activated carbon-based catalyst to reduce the NO_x to N_2 and H_2O . The clean flue gas is then vented to the stack. The feasibility of the process has been demonstrated in laboratory-scale experiments using simulated flue gas. Catalysts have been identified that gave the required performance for SO_2 and NO_x removal with <25 ppm NH_3 slip. Potential for producing up to 10 N sulfuric acid by periodically flushing the SO_2 removal reactor and further concentration to industrial strength 93.17% sulfuric acid was also demonstrated. Using the results of the experimental work, an engineering evaluation was conducted. Cost for the RTI-Waterloo process was competitive with conventional selective catalytic reduction (SCR) - flue gas desulfurization (FGD) process and other emerging combined SO_2/NO_x removal processes.

ACKNOWLEDGMENT

This study was sponsored by the U.S. Department of Energy (DOE) under contract No. DE-AC22-91PC91345. The authors would like to acknowledge with gratitude the guidance provided by the DOE Contracting Officer's Representative, Ms. Diane Revay Madden, of the Pittsburgh Energy Technology Center (PETC). Helpful discussions were also held with other PETC personnel, particularly Charlie Drummond and Chuck Schmidt. Calgon Carbon, Degussa Corporation, and DMT (Germany) provided a number of carbon samples for testing free of charge. David Biscan of Calgon Carbon arranged a presentation of the RTI-Waterloo process to Calgon personnel in Pittsburgh.

TABLE OF CONTENTS

Section	Page
Abstract	iii
Acknowledgment	v
List of Figures	ix
List of Tables	xi
Executive Summary	xiii
1.0 Introduction	1-1
2.0 Process Background	2-1
3.0 NO _x Removal	3-1
3.1 Experimental	3-1
3.2 Results and Discussion	3-5
4.0 SO ₂ Removal Experiments	4-1
4.1 Experimental	4-1
4.2 Results and Discussion	4-2
5.0 Process Evaluation	5-1
6.0 Conclusions and Recommendations	6-1
7.0 References	7-1
Appendix	
1 University of Waterloo Final Report	

LIST OF FIGURES

Number		Page
1-1	RTI-Waterloo process	1-2
3-1	RTI NO _x reduction reactor system	3-2
3-2	Comparison of catalyst C2 with commercial carbon catalysts for NO conversion (1,400 scc/cc·h, NH ₃ /NO = 1.22)	3-8
3-3	NO conversion on modified carbon catalyst (space velocity = 1,370 scc/(cc·h) [3,005 scc/(g·h)]; inlet NO = 530 ppmv)	3-9
3-4	NO conversion on modified carbon catalyst (space velocity = 1,370 scc/(cc·h) [3,005 scc/(g·h)]; inlet NO = 530 ppmv; NH ₃ /NO = 1.42)	3-10
3-5	NO conversion on modified carbon catalyst (space velocity = 1,758 scc/(cc·h) [3,948 scc/(g·h)]; inlet NO = 530 ppmv; NH ₃ /NO = 1.25)	3-11
3-6	NO conversion on various carbon-based catalysts (85 cc bed; 1,400 scc/(cc·h); 15.7 psia; 5% O ₂ , 10% CO ₂ , 10% H ₂ O, 75% inert; 530 ppm NO in; NH ₃ /NO = 1.26)	3-14
4-1	Outlet temperature and SO ₂ concentration versus run time (MCCI catalyst, Run 2 of Table 4-2, Cycle 6 of Table 4-4, inlet temperature 80 °C)	4-7
4-2	Outlet temperature and SO ₂ concentration versus run time (MCCI catalyst, Run 3 of Table 4-2, Cycle 3 of Table 4-5, inlet temperature 130 °C)	4-7

LIST OF TABLES

Number		Page
1-1	Advantages of RTI-Waterloo Process	1-3
3-1	Nominal Simulated Flue Gas Composition for NO _x Reduction Experiments (vol %)	3-3
3-2	NO _x Conversion on Commercial Carbon-Based Catalysts	3-6
3-3	Modified Carbon Catalyst II (MCCII) NO _x Removal Performance	3-12
3-4	Modified Carbon Catalyst III (MCCIII) NO _x Removal Performance	3-12
3-5	Modified Carbon Catalyst IV (MCCIV) NO _x Removal Performance	3-13
3-6	Feed Gas Composition for NO Removal Test of MCCII	3-15
3-7	NO Removal with MCCII at 150 °C in the Presence of 106 ppm SO	3-15
4-1	Simulated Flue Gas for RTI SO ₂ Removal Experiments at 80 to 130 °C	4-1
4-2	SO ₂ Removal Runs of MCCI Catalyst	4-2
4-3	SO ₂ Removal Test Results (38.75 g of modified carbon catalyst, 80 °C, 1,400 scc/(cc·h) flue gas containing 2,550 ppmv SO ₂ , 10% CO ₂ , 10% H ₂ O, 5% O ₂ , and balance N ₂)	4-3
4-4	SO ₂ Removal Test Results (37.22 g of MCCI, 80 °C, 1,475 scc/(cc·h) flue gas containing 2,550 ppm SO ₂ , 450 ppm NO, 10% CO ₂ , 10% H ₂ O, 5% O ₂ , and balance N ₂)	4-6
4-5	SO ₂ Removal Test Results (37.22 g of MCCI, 130 °C, 1,475 scc/(cc·h) flue gas containing 2,550 ppm SO ₂ , 450 ppm NO, 10% CO ₂ , 10% H ₂ O, 5% O ₂ , and Balance N ₂ , 200 cc 4.32 N H ₂ SO ₄ flush after each cycle)	4-8
5-1	Process Assumptions	5-3
5-2	Economic Assumptions	5-3
5-3	Capital Requirements: SO ₂ /NO _x Removal Process Basis: 100 MW Power Plant, 65% Capacity Factor, 1991 Dollars	5-5
5-4	Operating Costs: SO ₂ /NO _x Removal Process Basis: 100 MW Power Plant, 65% Capacity Factor, 1991 Dollars	5-6
5-5	Levelized Busbar Costs: SO ₂ /NO _x Removal Process Basis: 100 MW Power Plant, 65% Capacity Factor, 1991 Dollars	5-7
5-6	RTI-Waterloo Process Economic Performance (100-MW Power Plan, 65% Capacity Factor)	5-8
5-7	Cost of SO ₂ /NO _x Removal	5-9
5-8	Effect of Contingency on the Estimated Capital and Levelize Busbar Costs for the RTI-Waterloo Process (100-MW Power Plant, 65% Capacity)	5-10

EXECUTIVE SUMMARY

Coal-burning power plants produce a flue gas containing sulfur dioxide (SO_2) and nitrogen oxide (NO_x) which are precursors to acid rain. New source performance standards (NSPSs) mandate a 90% reduction in SO_2 and require a ceiling on NO_x emission of 0.6 lb NO_2 per million Btu of coal input. The Clean Air Act requires significant reduction in these acid-rain precursors for existing coal-burning power plants as well. The U.S. Department of Energy (DOE), Pittsburgh Energy Technology (PETC) is aggressively pursuing the development of super-clean processes for application in the year 2000 and beyond with the objective of reducing the SO_2 and NO_x in flue gas to even lower levels than those mandated by NSPS. To this end DOE issued a Program Research and Development Announcement (PRDA) [PRDA No. DE-RA22-90PC89802] in 1990, entitled *Advanced Separation Technology for Flue Gas Cleanup*. In addition to 95% SO_2 reduction and 75% NO_x reduction, the PRDA required the development of flue-gas cleanup processes that cost 20% less than conventional technology and produce no waste material.

This report addresses the requirements of this PRDA in a study entitled *A Novel Carbon-Based Process for Flue-Gas Cleanup*. The work, performed by Research Triangle Institute (RTI) and the University of Waterloo (Waterloo), seeks to develop an activated carbon-based process (hereafter referred to as the RTI-Waterloo process) that operates at low temperature ($<150^\circ\text{C}$) to convert SO_2 to industrial strength sulfuric acid and reduce NO_x to N_2 and H_2O . The process concept is shown in Figure ES-1.

The hot flue gas after the electrostatic precipitator (ESP) is first cooled in a heat exchanger and then brought into a series of 2 to 3 periodically flushed trickle-bed reactors containing an activated carbon catalyst. In these reactors, SO_2 is catalytically oxidized to SO_3 which is retained on the carbon bed. A periodic short duration aqueous or acid flush is used to remove the SO_3 from the carbon as H_2SO_4 , which then leaves the system. The key to the process is that periodic (rather than continuous) flush simultaneously regenerates the carbon and produces a stronger sulfuric acid at lower pressure drop than would be possible with conventional contacting schemes. The gas continues to flow at all times, even during the periodic flush. After the SO_2 is removed from the flue gas, the gas is reheated by the heat exchanger to 130°C or higher temperature. NH_3 is then injected into the gas as it enters

Figure ES-1. RTI-Waterloo process.

another activated carbon-based catalytic reactor to reduce NO_x to N_2 and H_2O prior to being vented to the stack. The principal novelty of the NO_x converter compared to a conventional selective catalytic reduction (SCR) reactor is that it operates at lower temperatures with essentially no particulates or SO_2 in the gas. This minimizes catalyst degradation and ammonium sulfate salt formation. The advantages of the RTI-Waterloo process are summarized in Table ES-1.

The RTI-Waterloo process is based on the demonstrated ability of activated carbons to catalyze SO_2 oxidation and NO_x reduction at low temperatures. The objective of this work is to obtain sufficient experimental data for the process to enable a preliminary economic evaluation to be conducted. The minimum targets to be achieved in the project are

- 95% or greater SO_2 removal,
- production of at least 2 molar (4 normal) sulfuric acid,
- pressure drop of less than 30 in. of water in the SO_2 removal process,
- 75% or greater removal of NO_x , and
- 25 ppmv or less NH_3 slip.

Table ES-1. Advantages of RTI-Waterloo Process

SO_2 Removal

• Easier retrofit	- Downstream of ESP where space is more readily available
• No waste product	- Sulfuric acid is potentially marketable
• Low temperature	- Reduced equipment stress, nonenergy intensive, no hazards including carbon combustion
• Simple regeneration	- No carbon loss
• Periodic operation	- Low pressure drop, concentrated sulfuric acid

NO_x Removal

• High catalyst life	- Low temperature operation in the absence of SO_2 and particles significantly increases catalyst life
• Low salt/ SO_3 formation	- Due to complete SO_x removal upstream, the acid dew point of the gas is very low and salt formation is avoided
-

The RTI-Waterloo project was conducted over 26 months (June 1991 to July 1993). To carry out the project expeditiously, the work was divided between RTI and Waterloo as follows. Waterloo's work dealt only with the SO₂ removal portion of the project. The emphasis of Waterloo's work was to study the periodic operation, including primarily the effect of variables such as liquid and gas velocities, period cycle time, flush duration, and liquid acid strength on SO₂ removal efficiency, pressure drop, and acid strength produced using one selected activated carbon catalyst. For convenience, the major portion of Waterloo's experimental study was conducted at room temperature (21 °C) with a few experiments at 80 °C. Waterloo also developed a mathematical model for the three-phase trickle-bed SO₂ reactor/scrubber. The RTI portion of the work dealt with SO₂ removal at higher temperature (80 to 130 °C) with emphasis on catalyst screening to develop catalysts that could give very high removal efficiency and enable production of higher strength acid. The RTI portion of the work also dealt with all of the NO_x removal experiments with emphasis on catalyst screening to find catalysts that gave the required performance of >75% NO_x removal with <25 ppmv NH₃ slip at reasonably high space velocities. RTI was also responsible for conducting the technical and economic evaluation of the process at scales of 100 MW and 1 MW.

A number of activated carbon-based catalysts were tested and developed for both the SO₂ removal and NO_x removal parts of the process using laboratory-scale reactor systems. The NO_x removal experiments demonstrated that more than 90% NO_x removal can be achieved in the RTI-Waterloo process at temperatures below 150 °C and space velocities up to 3,500 scc/(cc·h). The presence of traces of SO₂ appears to slowly poison the NO_x reduction catalyst with formation of an ammonium-sulfur salt which stays on the bed. The salt could be easily removed by washing or heating to >400 °C. The NO_x reactor acts as a guard bed for any SO₂ slippage from the upstream SO₂ removal bed and provides 100% SO₂ removal. The SO₂ removal experiments with periodic flushing demonstrated that more than 98% SO₂ removal can be achieved while producing a medium strength sulfuric acid of up to 10 N. This can be concentrated to 93.17% sulfuric acid using an evaporator. A preliminary technical and economic evaluation of the RTI-Waterloo process indicated that the process could achieve the required performance of SO₂ and NO_x removal and produce a 93.17% acid product at costs that are comparable to existing and emerging combined SO₂/NO_x removal processes. With a total process and project contingency of 80%, 93.17% acid could be produced at a capital cost of \$171 to \$188 per kW and a levelized cost of 7.4 to 8.3 mil/kWh.

The following recommendations are provided for further development of the RTI-Waterloo process. The process should be scaled up to an integrated SO_2/NO_x bench-scale skid-mounted reactor system. After demonstration of the integrated process with simulated flue gas, the system should be tested with real flue gas at a boiler. The effect and fate of air toxics, particularly mercury, benzene, and hydrogen chloride, should be addressed. In parallel to the bench-scale demonstration, catalyst optimization/development should be carried out. Catalysts with higher efficiency at lower costs should be developed. The question of pressure drop in the process should be investigated further and structured catalyst packing should be developed to reduce pressure drop. Also in parallel to the integrated demonstration, a process model should be developed, particularly for the three-phase periodic trickle-bed reactor process for SO_2 removal, to allow scale-up to pilot-scale operation.

1.0 INTRODUCTION

The report presents the results of a study titled "A Novel Carbon-Based Process for Flue Gas Cleanup." The work was performed by the Center for Process Research (CPR) at the Research Triangle Institute (RTI) and the Chemical Engineering Department at the University of Waterloo (Waterloo) under Contract No. DE-AC22-91PC91345 for the Pittsburgh Energy Technology Center (PETC), U.S. Department of Energy (DOE).

The RTI-Waterloo project was awarded based on a proposal in response to DOE's Program Research and Development Announcement (PRDA) [PRDA No. DE-RA2290PC89802], titled "Advanced Separation Technology for Flue Gas Cleanup." The objective of this PRDA was to develop flue gas cleanup processes that had the following attributes:

- 95% to 98% removal of SO_2 and 75% to 90% removal of NO_x from coal combustion flue gas cleanup streams,
- Cost reduction of at least 20% compared to the combined cost of SO_2 and NO_x removal using a limestone scrubber and a selective catalytic reduction (SCR) process, and
- Production of salable byproducts in a process concept that produces no waste material.

This work seeks to develop a novel activated carbon-based process (hereafter referred to as the RTI-Waterloo process) that operates at low temperature ($<150^\circ\text{C}$) to convert SO_2 to industrial strength sulfuric acid and reduce NO_x to N_2 and H_2O . The process concept is shown in Figure 1-1.

The hot flue gas after the electrostatic precipitator (ESP) is first cooled in a heat exchanger and then brought into a series of 2 to 3 periodically flushed trickle-bed reactors containing an activated carbon catalyst. In these reactors, SO_2 is catalytically oxidized to SO_3 which is retained on the carbon bed. A periodic short duration aqueous or acid flush is used to remove the SO_3 from the carbon as H_2SO_4 , which then leaves the system. The key to the process is that periodic (rather than continuous) flush simultaneously regenerates the carbon and produces a stronger sulfuric acid at lower pressure drop than would be possible with conventional contacting schemes. The gas continues to flow at all times, even during the

Figure 1-1. RTI-Waterloo process.

periodic flush. After the SO₂ is removed from the flue gas, the gas is reheated by the heat exchanger to 130 °C or higher temperature. NH₃ is then injected into the gas as it enters a second activated carbon-based catalytic reactor to reduce NO_x to N₂ and H₂O prior to being vented to the stack. The principal novelty of the NO_x converter compared to a conventional selective catalytic reduction (SCR) reactor is that it operates at lower temperatures with essentially no particulates or SO₂ in the gas. This minimizes catalyst degradation and ammonium sulfate salt formation. The advantages of the RTI-Waterloo process are summarized in Table 1-1.

The RTI-Waterloo process is based on the demonstrated ability of activated carbons to catalyze SO₂ oxidation and NO_x reduction at low temperatures as discussed in detail in the Process Background Section (Section 2.0). The objective of this work is to obtain sufficient experimental data for the process to enable a preliminary economic evaluation to be conducted. The minimum targets to be achieved in the project are

Table 1-1. Advantages of RTI-Waterloo Process

SO₂ Removal	
• Easier retrofit	- Downstream of ESP where space is more readily available
• No waste product	- Sulfuric acid is potentially marketable
• Low temperature	- Reduced equipment stress, nonenergy intensive, no hazards including carbon combustion
• Simple regeneration	- No carbon loss
• Periodic operation	- Low pressure drop, concentrated sulfuric acid
NO_x Removal	
• High catalyst life	- Low temperature operation in the absence of SO ₂ and particles significantly increases catalyst life
• Low salt/SO ₃ formation	- Due to complete SO _x removal upstream, the acid dew point of the gas is very low and salt formation is avoided

- 95% or greater SO₂ removal,
- production of at least 2 molar (4 normal) sulfuric acid,
- pressure drop of less than 30 in. of water in the SO₂ removal process,
- 75% or greater removal of NO_x, and
- 25 ppmv or less NH₃ slip.

The RTI-Waterloo project was conducted over 26 months (June 1991 to July 1993). To carry out the project expeditiously, the work was divided between RTI and Waterloo as follows. Waterloo's work dealt only with the SO₂ removal portion of the project. The emphasis of Waterloo's work was to study the periodic operation, including primarily the effect of variables such as liquid and gas velocities, period cycle time, flush duration, and liquid acid strength on SO₂ removal efficiency, pressure drop, and acid strength produced using one selected activated carbon catalyst. For convenience, the major portion of Waterloo's experimental study was conducted at room temperature (21 °C) with a few experiments at 80 °C. Waterloo also developed a mathematical model for the three-phase trickle-bed SO₂ reactor/scrubber. The RTI portion of the work dealt with SO₂ removal at higher temperature (80 to 130 °C) with emphasis on catalyst screening to develop catalysts that could give very high removal efficiency and enable production of higher strength acid. The RTI portion of the work also dealt with all of the NO_x removal experiments with emphasis on catalyst screening to find catalysts that gave the required performance of >75% NO_x removal with <25 ppmv NH₃ slip at reasonably high space velocities. RTI was also responsible for conducting the technical and economic evaluation of the process at scales of 100 MW and 1 MW.

The Waterloo work is described in its entirety as a stand-alone report in Appendix 1. The main body of the report (Sections 3.0 through 6.0) thus describes the RTI work. A number of publications and presentations have resulted from this project. These are listed below:

- Gangwal, S.K., and P.L. Silveston, 1991. In *Proceedings of the 7th Annual Coal Preparation, Utilization, and Environmental Control Contractor's Conference*, DOE/PETC, Pittsburgh, July.
- Gangwal, S.K., and P.L. Silveston, 1992. In *Proceedings of the 8th Annual Coal Preparation, Utilization, and Environmental Control Contractor's Conference*, DOE/PETC, Pittsburgh, July.
- Gangwal, S.K., G.B. Howe, J.J. Spivey, P.L. Silveston, R.R. Hudgins, and J.G. Metzinger, 1992. "Low-Temperature Carbon-Based Process for Flue-Gas Cleanup," Summer National AIChE Meeting, Minneapolis, Minnesota, August 9-12.

- Gangwal, S.K. 1992. In *Proceedings of the U.S.-Japan Technical Exchange Workshop*, San Francisco, October.
- Gangwal, S.K., W.J. McMichael, G.B. Howe, J.J. Spivey, and P.L. Silverston, 1993. Low-Temperature Carbon-Based Process for Flue-Gas Cleanup, In *Proceedings of Desulfurization III, Institution of Chemical Engineers, IChemE Symposium Series 131*, Sheffield, England, March.
- Gangwal, S.K., G.B. Howe, J.J. Spivey, P.L. Silverston, R.R. Hudgins, and J.G. Metzinger, 1993. *Environmental Progress*, 12(2):128.
- Gangwal, S.K., and P.L. Silverston, 1993. In *Proceedings of the 9th Annual Coal Preparation, Utilization, and Environmental Control Contractor's Conference*, DOE/PETC, Pittsburgh, July.

2.0 PROCESS BACKGROUND

The RTI-Waterloo process is based on the demonstrated ability of activated carbon-based catalysts to promote SO_2 oxidation and NO_x reduction using NH_3 below 150°C . The SO_2 removal part of the process uses a novel periodically flushed concurrent or countercurrent trickle-bed of an activated carbon-based catalyst to produce an acid product and low SO_2 levels in the gas discharge. Activated carbon is among the most efficient of all well-known oxidation catalysts (Davtyan and Ovchinnikova, 1955). Use of activated carbons for stripping SO_2 out of gas streams has been studied extensively. It is not clear from the literature when the catalytic properties of activated carbon for the reactions $\text{SO}_2 + (1/2) \text{O}_2 \rightarrow \text{SO}_3$ or $\text{SO}_2 + (1/2) \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ were first discovered. A detailed description of the mechanism of SO_2 oxidation over activated carbon is provided by various authors (Hartman et al., 1971; Hartman and Coughlin, 1972; and Siedlewski, 1965). Catalytic oxidation involves the reaction between SO_2 chemisorbed on active centers with chemisorbed molecular oxygen to form SO_3 which is then adsorbed on the surface and can be subsequently removed by washing with water or by heating to temperatures above 400°C (Davtyan and Ovchinnikova, 1955).

Water plays an important role in the oxidation of sulfur dioxide over activated carbon (Davtyan and Ovchinnikova, 1955). The presence of water vapor in the gas phase, together with oxygen and sulfur dioxide, increases the sulfur dioxide reactive capacity of a carbon bed. Sulfur dioxide oxidation is also favored by the presence of liquid water in the carbon at concentrations up to 0.3 g/g carbon (Davtyan and Ovchinnikova, 1955). At low temperature, most of the sulfur trioxide formed is present at the surface of the catalyst as sulfuric acid. Sulfuric acid, however, suppresses the ionization of dissolved sulfur dioxide, decreasing its solubility. The solubility of oxygen in water is also reduced by the presence of sulfuric acid. The sulfuric acid thus must be removed to continue the reaction at a reasonable rate. By periodic flushing, the sulfuric acid is removed and the sites are regenerated for additional reaction.

The comprehensive review paper by Hartman et al. (1971) reports preliminary experiments on stripping SO_2 from a simulated flue gas in both trickle-bed and slurry reactors. No attempt was made to optimize either the slurry or the trickle-bed process. Nevertheless,

Hartman et al. (1971) achieved 70% SO₂ removal and generated a 0.1 M acid. Slurry contacting was pursued by Seaburn and Engel (1973) and later by Komiyama and Smith (1975). Seaburn and Engel (1973) were interested in comparing the performance of different activated carbons, while Komiyama and Smith (1975) were concerned with kinetics and mass transfer interference. They concluded that catalytic oxidation in a three-phase system is controlled by O₂ mass transfer rate to the surface. A thinner liquid film, as would be achieved by periodic flushing in the RTI-Waterloo process, would result in a lower mass transfer resistance and consequently a higher oxidation rate.

The results of previous studies showed that the rate of oxidation of SO₂ to SO₃ and the formation of sulfuric acid vary greatly with the particular type of activated carbon used. Research on SO₂ adsorption and oxidation in a trickle-bed has continued since the Hartman-Coughlin work in the early 1970s. These include papers by Mata and Smith (1981), Goto and Smith (1978), Pavko and Levec (1981), and Herskovitz (1981). Although these investigators discuss the relevance of the work to flue-gas desulfurization, the main interest has been studying mass transfer and wetting in trickle-beds and development of theoretical models.

Work in the subcontractor's laboratory at University of Waterloo began in the early 1980s and was directed at improving rates of reaction in trickle-beds by operating in the partially wetted state. Higher rates of mass transfer, it was reasoned, should raise the rate of reaction. Berruti et al. (1984) explored the use of hydrophobic surface treatment, while Haure et al. (1989) examined pulsing of the water flow. In both cases, SO₂ oxidation over activated carbon was used as the test reaction. The latter study led to the RTI-Waterloo process.

Haure et al.'s (1989) objective was to see if periodically starting and stopping liquid flow in a trickle-bed would raise the rate of reaction by reducing mass transfer resistance. SO₂ oxidation over activated carbon was used as a test reaction following the lead of previous investigators. The experimental results were remarkable: increases in the rate of oxidation of 40% to 60% were obtained. Although no optimization efforts were made, it was observed that moderately strong acid, almost 0.2 M, could be produced while still achieving a 40% to 60% increase in the oxidation rate at room temperature. This formed the basis for the RTI-Waterloo process. A patent has been obtained on the novel periodic operation feature of the process (Canadian Patent No. 1299843).

In the RTI-Waterloo process, NO_x is reduced using NH_3 at 130 to 150 °C in a separate reactor. SCR of NO_x using NH_3 is a proven catalytic process with numerous catalysts reported in the literature based on Fe, V, Cr, Mo, Co, Ni, Cu, Ba, and noble metals on alumina, titania, and silica supports (Siddiqi and Tenini, 1981; Andersen, et al., 1961; and Ayen and Amirnazi, 1980). The reaction stoichiometry is generally believed to be $4 \text{ NO} + 4 \text{ NH}_3 + \text{O}_2 \rightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O}$ although other reactions not involving O_2 are also reported. By far most of the literature deals with vanadia-based SCR catalysts. However, in nearly all cases, the catalysts described have been tested at temperatures much higher (200 to 400 °C) than is relevant to this study. One exception is the activated carbon or "coke" catalyst. Such a catalyst is used in the commercial Mitsui process and is active at 130 °C, converting some 85% of the NO_x at a space velocity of 400 h^{-1} (Mitsui Corporation, 1991). Since much of the SO_2 is removed before the NO-NH_3 reaction takes place, the Mitsui process catalyst, similar to the RTI-Waterloo process, does not have to promote this reaction in the presence of high levels of SO_2 . However, the space velocity of the Mitsui process is quite low presumably due to the low activity of the carbon catalyst employed. This results in large beds and thus high costs associated with the process. A significant incentive thus exists for finding more active low-temperature carbon-based (or other) catalysts.

A number of studies corroborate that activated carbons could be modified by impregnation or other surface treatment to increase their activity. Kusakabe et al. (1988) studied the reduction of NO on activated coke catalysts which were modified by sulfuric acid treatment at 400 °C. This treatment increased the N_2 formation rate by up to 2.6 times that of the untreated catalyst. Kuehl et al. (1986) showed that treatment by an "active nitrogen" increased the activity of the carbon catalyst. [Tests were carried out at 100 to 160 °C, 0% to 15% H_2O , 5% O_2 , NO, and NH_3 concentrations below 100 ppm.] An ammonium oxide/carbon catalyst was found to be active for NO reduction using ammonia at temperatures as low as 100 °C (Seki et al., 1975). These same authors also described in a patent (U.S. Patent 4,184,373) the impregnation of carbon with halogens (Br, Cl, I) and a "promoter" to increase the activity of carbon for the NO-NH_3 reaction.

Other studies have dealt with the interaction of NO and NH_3 , with various forms of activated carbon. The adsorption of NH_3 and NO, as single compounds, was measured by Kareko et al. (1988) on activated carbon fibers prepared from pitch. At 30 °C, NO adsorption

was 6 wt % at a partial pressure of 60 kPa, and NH_3 adsorption was 5 wt % at the same partial pressure, on the fiber having the highest capacity. Measurements at flue-gas concentrations around 200 ppm (0.15 kPa partial pressure) were not made, but the results suggest that NO and NH_3 have appreciable affinity for the carbon surface at low temperatures.

3.0 NO_x REMOVAL

In this section, the details of the NO_x removal experimental facility and experimental conditions are provided followed by results and discussion.

3.1 Experimental

A schematic of the RTI NO_x reduction reactor system is shown in Figure 3-1. The system consisted of a convective oven (Varian 3700 Gas Chromatograph Oven) to control the reaction temperature. This provided excellent control at the low operating temperatures (typically 130 to 160 °C). Earlier attempts with a vertical split-tube single-zone furnace had failed to provide the desired temperature control. A number of Pyrex reactor tubes of different diameters ranging from 2 to 4 cm and lengths ranging from 8 to 32 cm were prepared to allow a wide range of space velocities to be tested. The material of construction for the entire path of gas flow was either Teflon or glass to provide the degree of inertness needed to carry out the experiments with trace amounts of gases without loss due to metal surfaces. Two 1/16-in. thermocouples were positioned in the reactors that were tested, one at the inlet and one at the outlet. Each end of the reactor tube was reduced to 1/2 in. to allow the use of standard fittings. The carbon catalyst bed was positioned in the center with glass wool supports on the two ends. The wool acted as a flow distributor as well as an additional preheater to bring the gases to the desired temperature.

The carbon catalysts used were industrial granulated materials ranging in size from 1/16-in. (0.16 cm) to 1/8 in. (0.32 cm). Many of these catalysts were proprietary to RTI and thus their physical properties and chemical compositions are withheld from this report. Space velocities in the 1,000 to 4,000 scc/(cc·h) range were used. The gases leaving the reactor passed through a condenser/water knockout pot and a pressure control valve prior to being vented to a hood through a soap bubble flow meter.

The gas feed including steam and NH₃ was prepared as follows. Two sets of differential flow controllers rated for high and low flows were used to provide the wide range of space velocities tested. The flow was measured and calibrated using rotameters and filters were provided upstream to prevent fine particle contamination/plugging. The gases typically blended together included helium, certified NO/helium mixture, and certified CO₂/O₂ mixture

obtained from a commercial gas vendor. It is important to note here that no N_2 was used in the feed gas. This was essential to provide the N_2 balance following the NO reduction reaction. The NO/helium, CO_2/O_2 and the helium were certified to contain <5 ppmv N_2 . Analysis of these gases confirmed this. Another important point to note is that NO and O_2 were kept in different cylinders to prevent NO oxidation, a known process at low temperature. After blending the dry gases in the desired proportion, the gases passed through a preheater which consisted of a glass tube filled with glass balls and surrounded with heat tapes controlled by variable transformers. At the middle of the preheater a desired NH_4OH -water solution was injected using a syringe pump to provide a wet gas nominally containing the composition shown in Table 3-1. The NH_3/NO ratio was varied by adjusting the strength of the NH_4OH-H_2O mixture. Most of the experiments were conducted without SO_2 in the gas since the SO_2 is removed upstream in the RTI-Waterloo process. In a few experiments, the effect of SO_2 slip from the upstream SO_2 removal part of the RTI-Waterloo process was also tested. For these tests, SO_2 at a 110 ppm level was generated by using a gas containing a mixture of CO_2 , O_2 , and SO_2 . For some catalysts, activation was carried out with activation gas using proprietary techniques whose details are withheld. All of the lines past the preheater and prior to the condenser were heated with heat tapes.

The analytical system consisted of a chemiluminescent NO/ NO_2 analyzer, an NH_3 slip measurement system consisting of a midget impinger and an Orion ion specific electrode, and a gas chromatograph (GC) with a thermal conductivity detector (TCD). The continuous NO/ NO_2 analyzer (TECO Series 10) is based on the gas phase reaction of NO with ozone to produce NO_2 , oxygen, and light. The light is detected and converted to an electrical signal with a photomultiplier tube. Ozone for reaction with NO is produced by UV irradiation of O_2 in air. To measure NO_2 in the gas, NO_2 is reduced to NO in a catalytic reactor contained within

Table 3-1. Nominal Simulated Flue Gas Composition for NO_x Reduction Experiments (vol %)

He	balance	NO	500 ppmv
H_2O	10	NH_3	500 to 750 ppmv
CO_2	10	SO_2	0 to 110 ppmv
O_2	5		

the analyzer. Total NO_x is then measured as NO and the NO_2 concentration is obtained by subtraction of the previously measured NO concentration (without the catalytic reduction) from this value.

The Orion ion specific electrode for ammonia was calibrated with standards prepared from ammonium chloride. To test for ammonia during a run, sample gas was extracted before the condenser at a flow rate of 50 sccm and passed through a midjet impinger containing 25 mL of deionized/distilled water. The ammonia electrode was then used to determine the ammonia concentration in solution, from which the gas phase ammonia concentration was calculated. This method was tested by sampling from a 1,050 ppm NH_3 in N_2 standard for 30 minutes at 50 sccm. The concentration based on analysis of the impinger catch with the ammonia electrode was 1,112 ppm (+5.9% difference).

The Carle GC with a TCD was calibrated for measuring CO_2 , O_2 , and N_2 from the test system. Two columns were installed for performing the required separations. The first column was a 9 ft x 1/8 in. stainless steel (SS) tube packed with Hayesep R porous polymer. The second column was a 6 ft x 1/8 in. SS column packed with 40/60 mesh molecular sieve 5A. A Carle 10-port gas switching valve was used for injection of gas samples and to control the sequence of columns used during the analysis. After injection of a 1 mL sample loop, O_2 and N_2 passed through the Hayesep column and into the molecular sieve. CO_2 was retained in the Hayesep. After 1 minute, the Carle valve was switched to reverse the column sequence. CO_2 eluted from the Hayesep column first and was detected by the TCD. O_2 and N_2 are separated on the molecular sieve column and then passed through the Hayesep column to the TCD. A Hewlett-Packard 3392A integrator was used for data acquisition and for controlling valve switch timing through an HP-19405A sampler/event control module.

Sample flow through the NO/ NO_2 analyzer, impinger, and GC sample loop was provided by adjusting the pressure control valve located just before the bubble flow meter to produce sufficient system pressure (~1 psig).

Prior to beginning the experiments, the N_2 mass balance was tested. Also formation of NO_2 and N_2O was investigated. NC and N_2O were not detected at the temperatures of the experiments (typically 130 to 160 °C). It is noteworthy that at other higher operating

temperatures, e.g., in conventional SCR and selective noncatalytic reduction (SNCR), N_2O formation may occur. Also, the mass balance of the N_2 ranged from 95% to 108% using the input N_2 due to NO and NH_3 and the output N_2 due to unreacted NO, NH_3 slip, and the N_2 formed. This was deemed quite satisfactory to conduct the experiments for collecting process data of NO reduction.

3.2 Results and Discussion

A number of commercial catalyst materials were first tested followed by a number of proprietary catalysts. These proprietary catalysts were prepared by modifying some of the commercial materials. RTI investigated the patentability of these materials and at present has decided not to pursue the patent. Rather, it has been elected to withhold the details of the proprietary material and data from publication.

The NO_x conversion results of the commercial carbon-based materials are shown in Table 3-2. The Calgon BPL carbon was the baseline carbon from which improvements were sought. None of these materials gave the required performance of >75% NO conversion. Of the various commercial materials tested, the Degussa Pt-impregnated carbons gave the best performance. It was found that adsorption of NO occurred at 120 °C or lower temperatures. Thus, the results at these temperatures could be influenced by adsorption.

CarboTech carbon gave a better performance than Calgon BPL. The Calgon BPL and the CarboTech materials were unpromoted and were derived from a bituminous coal and a lignite, respectively. The higher activity of the CarboTech carbon (which is presumably used in the Mitsui process) was probably due to the higher activity of the parent coal from which it was derived. The Degussa parent carbon was wood based. The unimpregnated wood-based Degussa carbon was also tested. The results, not shown in Table 3-2, indicated that the activity of this carbon was even lower than the Calgon BPL carbon. The order of activity of various carbons was thus determined to be promoted carbon > bituminous coal-based carbon > lignite-based carbon > wood-based carbon.

A number of modified proprietary catalysts were prepared and tested. These included catalysts C2, MCCI, MCCII, MCCIII, and MCCIV. Catalyst C2 was an unpromoted carbon

Table 3-2. NO_x Conversion on Commercial Carbon-Based Catalysts

Catalyst	Bed size (g)	Bed volume (cc)	Bed ID (cm)	Space velocity (scc/(cc·h))	Temperature (°C)	NO In (ppmv)	NH ₃ /NO (nominal)	NO conversion (%)
Calgon BPL 10x16	12	27	2.1	8274	150	420	1.25	0
	12	27	2.1	4467	150	350	1.43	2.9
	12	27	2.1	4422	98	400	1.26	7.5 ^a
Calgon BPL 6x16	52	110	3.4	1081	150	530	1.00	18.9
	52	110	3.4	1086	104	505	1.03	26.7 ^a
Calgon BPL 4x6	42.3	85	3.0	1412	82	500	1.03	29.0 ^a
	42.3	85	3.0	1412	152	500	1.03	24.0
Degussa 0.5% Pt/Carbon, 2.5 - 4.5 mm	37.8	85	3.0	1419	82	470	1.06	36.2 ^a
	37.8	85	3.0	1419	153	470	1.06	55.3 ^b
	37.8	85	3.0	1384	121	470	1.06	14.9
	37.8	85	3.0	1390	137	480	1.04	33.3
	37.8	85	3.0	1390	153	480	1.04	56.2 ^b
	37.8	85	3.0	1390	168	480	1.04	58.3
Degussa 1.0% Pt/Carbon, 2.5 - 4.5 mm	38.8	85	3.0	1412	82	485	1.03	35.1 ^a
	38.8	85	3.0	1412	153	485	1.03	55.7 ^b
	38.8	85	3.0	1390	122	490	1.02	23.5 ^a
	38.8	85	3.0	1390	137	490	1.02	46.9
	38.8	85	3.0	1390	168	490	1.02	61.2 ^b
Calgon BPL 18x20	41.3	85	3.0	1376	122	480	1.04	17.7 ^a
	41.3	85	3.0	1376	137	480	1.04	16.7
	41.3	85	3.0	1376	152	480	1.04	14.6
	41.3	85	3.0	1376	167	480	1.04	14.6
CarboTech D52/4 3/16" extrudes	49.5	85	3.0	1369	123	460	1.09	39.1 ^a
	49.5	85	3.0	1369	137	460	1.09	37.0
	49.5	85	3.0	1369	152	460	1.09	37.0
	49.5	85	3.0	1369	166	460	1.09	37.0
CarboTech D52/4 5 mm extrude	58.5	85	3.0	1400	140	530	1.22	32.0
	58.5	85	3.0	1400	150	530	1.22	35.0
	58.5	85	3.0	1400	160	530	1.22	40.0

^aResult could be influenced due to adsorption which is dominant below 120 °C.

^bConversion could be limited due to unavailability of sufficient NH₃.

whereas the MCC materials were promoted carbons with different types and levels of promoters.

The NO_x conversion performance of the unpromoted carbon catalyst C2 is compared to the Calgon BPL carbon and CarboTech carbon in Figure 3-2. As seen, catalyst C2 gave better performance but not the desired performance of $>75\%$ NO_x removal. The results of the MCC promoted carbon materials are described below.

The MCCI carbon catalyst was tested the most. Results of NO_x conversion performance of this catalyst were taken over a 267-hour longevity test and are shown in Figures 3-3 to 3-5. The catalyst showed no signs of deactivation over the long-term test. The data show that the required 75% removal with 25 ppmv NH_3 slip can be obtained on this catalyst at a space velocity of about 1,300 to 1,800 $\text{scc}/(\text{cc}\cdot\text{h})$ [3,000 to 4,000 $\text{scc}/(\text{g}\cdot\text{h})$] at 135 to 140 $^\circ\text{C}$, with an NH_3 to NO_x inlet ratio of about 1.25. No NO_2 , N_2O , or other nitrogen compounds (except molecular N_2) were detected in the outlet and the reaction suggested (based on mass balance) an overall stoichiometry in which nearly 1.5 mol of NH_3 was consumed for every mole of NO fed. As will be evident, this is believed to be due to a competing reaction of NH_3 oxidation to N_2 in addition to the NH_3 - NO - O_2 reaction.

The results of the MCCII, MCCIII, and MCCIV carbon catalysts are shown in Tables 3-3 to 3-5. All of these MCC catalysts appear capable of at least 75% NO removal at around 135 $^\circ\text{C}$. The best performance was provided by MCCIV which consistently converted 90% to 93% of the NO at temperatures from 130 to 160 $^\circ\text{C}$. This catalyst was prepared toward the tail end of the experimental work and funds did not permit a complete investigation.

Looking further at data in Table 3-3 for MCCII, it is seen that ammonia slip and NO conversion are strong functions of the independent variables (space velocity, temperature, and inlet NH_3/NO ratio). The first five data lines of Table 3-3 show essentially no NH_3 slip, i.e., the reaction is starved for NH_3 . As temperature is decreased a meager 5 $^\circ\text{C}$ at a space velocity of 1717 $\text{scc}/(\text{cc}\cdot\text{h})$, ammonia slip increases from 6.2 ppmv to 121 ppmv but the NO conversion only drops by 5% from 88% to 83%. This suggests that NH_3 is not only consumed by reaction with NO but also by reaction with O_2 . Because no other nitrogen products (except N_2 itself) were observed in the effluent, it is concluded that some of NH_3 is oxidized to N_2 by O_2 .

Figure 3-2. Comparison of catalyst C2 with commercial carbon catalysts for NO conversion (1,400 scc/cc·h, $\text{NH}_3/\text{NO} = 1.22$)

Figure 3-3. NO conversion on modified carbon catalyst
(space velocity = 1,370 scc/(cc·h) [3,005 scc/(g·h)]; Inlet NO = 530 ppmv).

Figure 3-4. NO conversion on modified carbon catalyst
(space velocity = 1,370 scc/(cc·h) [3,005 scc/(g·h)]; Inlet NO = 530 ppmv; NH₃/NO = 1.42).

Figure 3-5. NO conversion on modified carbon catalyst
(space velocity = 1,758 scc/(cc·h) [3,948 scc/(g·h)]; Inlet NO = 530 ppmv; NH₃/NO = 1.25).

Table 3-3. Modified Carbon Catalyst II (MCCII) NO_x Removal Performance

Temp. (°C)	Space velocity scc/(cc·h)	Inlet NH ₃ /NO	NO conversion (%)	NH ₃ slip (ppm)
140	1412	1.36	85.9	0.2
150	1414	1.36	87.9	0.2
130	1408	1.26	77.8	4.0
135	1408	1.26	81.5	0.8
135	1717	1.41	88.0	6.2
130	1717	1.41	83.0	121
140	3354	1.42	92.9	77.6
135	3354	1.42	87.9	220

Table 3-4. Modified Carbon Catalyst III (MCCIII) NO_x Removal Performance

Temp. (°C)	Space velocity scc/(cc·h)	Inlet NH ₃ /NO	NO conversion (%)	NH ₃ slip (ppm)
140	3301	1.17	46.9	NA
140	3342	1.33	46.9	NA
140	3367	1.43	46.9	NA
150	3367	1.43	71.4	NA
158	3367	1.43	89.8	NA
140	1683	1.09	35.6	NA
140	1720	1.35	35.6	NA
150	1720	1.35	71.1	NA
160	1720	1.35	90.4	NA
155	1720	1.35	84.6	42.5

NA = Not available.

Table 3-5. Modified Carbon Catalyst IV (MCCIV) NO_x Removal Performance

Temp. (°C)	Space velocity scc/(cc·h)	Inlet NH ₃ /NO	NO conversion (%)	NH ₃ slip (ppm) (estimated)
130	1464	1.38	93.3	<10
140	1464	1.38	90.0	<10
150	1464	1.38	91.1	<10
160	1464	1.38	92.2	<10

in the gas and this reaction competes with the NH₃-NO or NH₃-NO-O₂ reactions. Comparing the fifth data line of Table 3-3 with the last data line, it is seen that, with all other conditions constant as space velocity is nearly doubled from 1717 to 3354 scc/(cc·h), the NO conversion is hardly affected, but the NH₃ slip increases significantly presumably due to the NH₃-O₂ reaction occurring to a lesser extent. This result indicates that the NH₃-O₂ reaction is much slower than the NH₃-NO reaction. The data further indicate that it is very likely that NH₃ slip can be controlled to the desirable limit of 25 ppm at a space velocity of 3,354 scc/(cc·h) by slightly increasing the bed temperature.

The performance of the MCCI and II and C2 catalysts are compared to CarboTech and BPL carbons in Figure 3-6. The results indicate the BPL carbon to be the worst performer. The MCCI and II and C2 catalysts perform significantly better than the CarboTech and BPL catalysts. The NO_x removal results demonstrate the feasibility of the RTI-Waterloo process to achieve the desired performance at space velocities of nearly 3,500 scc/(cc·h). However, further catalyst development/screening should be carried out to optimize the NO_x removal with respect to cost and efficiency.

Finally the effect of SO₂ on the NO_x removal performance of MCC materials was tested. A batch of MCCII was used for these tests with nominally 100 ppm SO₂ in the feed gas whose composition is summarized in Table 3-6.

The reactor was operated at a temperature of 150 °C and a space velocity of 1,480 scc/(cc·h). Results of a 24-hour deactivation test are shown in Table 3-7. Based on these

Figure 3-6. NO conversion on various carbon-based catalysts (85 cc bed; 1,400 scc/(cc·h); 15.7 psia; 5% O₂, 10% CO₂, 10% H₂O, 75% Inert; 530 ppm NO In; NH₃/NO = 1.26).

Table 3-6. Feed Gas Composition for NO Removal Test of MCCII

Component	Feed concentration
NO	500 ppm
SO ₂	106 ppm
NH ₃	783 ppm
Steam	11.7%
CO ₂	10%
O ₂	5%

Table 3-7. NO Removal with MCCII at 150 °C in the Presence of 106 ppm SO₂

Time on stream (hr)	NO conversion (%)
2	79
4	79
6	78
8	71
10	69
12	68
14	68
16	64
18	74
20	74
22	66
24	66

results, there did appear to be some deactivation of the catalyst over the 24-hour period, as conversion decreased from 79% to 66%; however, the reason for the cycling up at 18 hours is not clear.

Before SO_2 was introduced into the feed gas at the beginning of the test, the NO conversion was near 100%. When the SO_2 was added, the increase in the outlet NO concentration was equivalent to the feed gas SO_2 concentration. This suggests that ammonia preferentially reacts with SO_2 , thus making it unavailable for reduction of NO. This explains the need for a higher NH_3/NO ratio in the feed (1.57) compared with what was needed previously (1.26) to achieve >75% NO reduction with no SO_2 present. However, the overall process shows capability for 100% SO_2 removal and this may need to be traded with any potential catalyst deactivation. If $(\text{NH}_4)_2\text{SO}_4$ formation on the catalyst is the cause of deactivation, then it may be possible to wash it off to reactivate the catalyst. A moving-bed system might be employed in this scenario.

To summarize the NO_x removal experiments, more than 90% NO_x removal can be achieved in the RTI-Waterloo process at temperatures below 150 °C and space velocities up to 3,500 scc/(cc·h). The presence of traces of SO_2 probably slowly poisons the NO_x reduction catalyst with formation of ammonium-sulfur salt which stays on the bed. However, the NO_x reactor acts as a guard bed for SO_2 slippage from the upstream SO_2 removal bed and provides 100% SO_2 removal. Further catalyst development/optimization is recommended with respect to cost, efficiency, SO_2 tolerance, and regenerability. The process at this point is ready to be scaled up to the bench-scale level.

4.0 SO₂ REMOVAL EXPERIMENTS

In this section, the results of the SO₂ removal experiments at RTI are described. Additional SO₂ removal experiments were conducted at Waterloo as described in Appendix 1. The emphasis of the Waterloo work, as stated earlier, was to evaluate the effect of a number of experimental variables associated with periodic operation. The Waterloo experiments were carried out only on the baseline carbon (Calgon BPL) at 21 °C with a few experiments at 80 °C. The RTI work on SO₂ removal emphasized catalyst screening at 80 to 130 °C with an objective to develop high activity catalysts that can achieve >95% SO₂ removal at space velocities >1000 scc/(cc·h) and produce acid of up to 10 N strength upon flushing. No attempt was made to optimize the periodic operation in the RTI work.

4.1 Experimental

For SO₂ removal experiments at 80 to 130 °C at RTI, the RTI NO_x reduction reactor system (Figure 3-1) was modified to allow SO₂ removal experiments. The modification was rather straightforward. N₂ and N₂/SO₂ mixture were substituted for He and He/NO mixture. The NH₄OH-water solution was replaced with water. Finally, a Dupont 400 continuous UV photometric analyzer was installed to monitor SO₂ on a slipstream past the condenser.

The simulated flue gas composition used for the SO₂ removal experiments is shown in Table 4-1. In initial experiments, NO was not included in the flue gas. In later experiments, up to 500 ppmv NO was also included.

The experiments were carried out in a cyclic manner as follows. The carbon catalyst of interest was loaded in a desired reactor size (typically, an 85-cc bed) and was brought to temperature with N₂ gas flow. The gas was then switched to the simulated flue gas of

Table 4-1. Simulated Flue Gas for RTI SO₂ Removal Experiments at 80 to 130 °C (vol %)

CO ₂	10	N ₂	balance
O ₂	5	SO ₂	2,500 ppmv
H ₂ O	10	NO	0 to 500 ppmv

interest. After SO₂ breakthrough, arbitrarily defined when the outlet SO₂ reached 5% of the inlet value (i.e., 125 ppmv), the carbon bed was taken off-line. With the bed held in a vertical position, 200 cc of liquid (either water or sulfuric acid of desired strength) was allowed to flow through it under the action of gravity. The sulfuric acid concentration of the liquid after the flush was determined by measuring its density. The density of water and density of H₂SO₄ were used to find the acid strength of the liquid by interpolation. This entire process was referred to as a cycle. This cycle was then repeated as often as desired. For many catalyst materials, however, 95% SO₂ removal was not achieved. In these cases, the adsorption portion of the cycle was arbitrarily run for about 2 hours prior to flushing.

4.2 Results and Discussion

Five different proprietary carbon-based catalyst materials were tested for their ability for SO₂ removal and conversion to sulfuric acid. These included MCCI, MCCII, C2, MCCV, and MCCVI. MCCI, MCCII, and C2 had also been previously tested for their ability for NO removal (Section 3.0). MCCI was found to be the most successful and was tested in detail as described below.

Three different runs were conducted with MCCI. The basic differences in conditions of these runs are shown in Table 4-2. Each run is discussed in detail below.

The results of Run No. 1 are shown in Table 4-3. The experiment was conducted using a 38.75-g (85-cc) bed of the modified carbon catalyst at a space velocity of 1,400 scc/(cc-h) with simulated flue gas containing 2,550 ppmv SO₂.

Table 4-2. SO₂ Removal Runs of MCCI Catalyst

Run No.	No. of cycles	Temperature (°C)	Simulated gas NO content
1	10	80	0
2	10	80	450
3	3	130	450

Table 4-3. SO₂ Removal Test Results (38.75 g of modified carbon catalyst, 80 °C, 1,400 scc/(cc-h) flue gas containing 2,550 ppmv SO₂, 10% CO₂, 10% H₂O, 5% O₂, and balance N₂)

Cycle	Breakthrough time (h) ^a	SO ₂ removal (%)	SO ₂ converted (g) ^b	Breakthrough extent ^c	Cold flushing liquid (200 cc)	Acid strength achieved, N
1	9.94	98.6	20.2	Complete	Water	1.02
2	5.76	>99.9	12.0	5%	Water	0.54
3	5.84	99.6	12.3	5%	Water	0.71
4	7.84	99.8	16.1	5%	4.32 N H ₂ SO ₄	5.24
5	4.04	99.8	8.4	5%	4.32 N H ₂ SO ₄	5.19
6	3.10	98.1	6.4	5%	4.32 N H ₂ SO ₄	4.94
7	3.60	99.6	7.4	5%	8.31 N H ₂ SO ₄	8.81
8	d	64.5	NA	NA	e	NA
9	2.5	99.3	5.3	5%	4.32 N H ₂ SO ₄	4.78
10	2.92	97.2	6.0	5%	4.32 N H ₂ SO ₄	5.08

^a 5% breakthrough.

^b Per 100 g carbon at 5% breakthrough.

^c At liquid flush.

^d Conversion stayed constant at 64.5%. Run terminated after 3 h.

^e 200 cc water followed by 200 cc 4.32 N H₂SO₄.

NA = Not analyzed.

The cycle in Table 4-3 refers to the operation involving flue gas exposure followed by liquid flush. After this operation during each cycle, the bed was ready for the next exposure/cycle.

Except for Cycle 1 and Cycle 8, each of the cycles involved exposure of the bed at 80 °C to flue gas until a bed outlet SO₂ concentration (monitored by a continuous SO₂ analyzer) of 125 ppmv (~5% of inlet) was reached, followed by a liquid flush. The liquid flush was done off-line while maintaining the bed hot.

The results for SO₂ removal and acid strength achieved are highly promising as seen in Table 4-3. The catalyst shows no signs of deactivation and the cycle-to-cycle variations are believed to be due to the somewhat variable batch liquid flush procedure employed and not due to changes in catalyst.

The points of interest to note from Table 4-3 are as follows:

- The catalyst maintains over 97% SO₂ removal and high capacity with up to 4.32 N H₂SO₄ flushes, while producing up to 5 N H₂SO₄.
- When flushing liquid strength is increased to 8.31 N H₂SO₄, an 8.81 N H₂SO₄ is produced; however, the SO₂ removal drops to 64.5% for the next cycle.
- The loss of catalyst activity after the 8.31 N H₂SO₄ flush is reversible, i.e., the activity is restored by flushing again with lower strength solutions.
- The loss of catalyst activity with the higher strength acid flush is believed to be due to the lower solubility of O₂ in H₂SO₄. However, even with a 64.5% conversion, a two-bed trickle reactor process can be developed to produce nearly a 10 N H₂SO₄ while still achieving nearly 100% SO₂ removal.

The results of Run 2 of Table 4-2 in which NO was included in the simulated gas are shown in Table 4-4. These results show consistent SO₂ removal and capacity (especially over the last 8 cycles) and no decay in catalyst performance. Also, about the same breakthrough time was measured as in the earlier test of the same catalyst without nitric oxide present. There was, however, one difference observed in the performance of MCCI under these test conditions. In the previous test, with no NO in the feed, the SO₂ conversion reached >95% within a few minutes after the reactor was placed on-line and remained high

until breakthrough. In test 2, however, with NO present in the feed, the conversion initially was greater than 95%, but would decrease to about 87% and then return to greater than 95% over a 1- to 2-hour period, before beginning to break through. This behavior may have been partially caused by the presence of NO in the feed leading to competitive adsorption between NO and SO₂. However, it may have also been partly caused because of a drop in reactor downstream temperature due to evaporation of water that remained from the previous cycle. This behavior is illustrated for Cycle 6 of Test 2 (Table 4-4) in Figure 4-1. As seen in this figure, the reactor outlet temperature stays at about 66 °C with the inlet at 80 °C for about 125 minutes. The SO₂ removal efficiency drops from nearly 100% to about 87% and then increases back to over 95% prior to breakthrough. The outlet temperature begins to increase after the SO₂ removal efficiency goes back up and then slightly overshoots the inlet temperature probably because of the exothermicity of SO₂ oxidation.

To test whether this maxima in SO₂ outlet concentration could be prevented, a 3-cycle test (Run 3 of Table 4-2) was performed on MCCI at 130 °C. The results of this test, shown in Table 4-5, indicate that SO₂ removal at the beginning of exposure is >97%, but that breakthrough occurs in about one-third of the time observed previously in 80 °C tests. However, the period of time in which conversion is >95% is about the same as that observed at 80 °C and the percent SO₂ removal does not decrease in the early part of the cycle as shown in Figure 4-2. One potential reason why the maxima in the SO₂ outlet concentration is not observed at 130 °C is that NO is not adsorbed at this temperature. Operating the reactor at 130 °C offers the advantage of sustained high SO₂ removal efficiency with a breakthrough time which is feasible for the periodic flush process. Because the overall breakthrough time is shorter, the results suggest that the optimum temperature may be closer to 100 °C with respect to both capacity and SO₂ removal efficiency.

The results of the MCCI catalyst for SO₂ removal and acid production by flushing are highly promising. The catalyst shows the potential for as much as 98% to 99% SO₂ removal and production of up to 10 N sulfuric acid with two periodically flushed trickle-bed reactors in series. MCCI was a promoted carbon catalyst. As mentioned earlier, several other catalysts were also tested. They were not as successful as the MCCI catalyst. However, cost of some of these other catalysts is projected to be lower than MCCI, thus a tradeoff exists. Sensitivity

Table 4-4. SO₂ Removal Test Results (37.22 g of MCCI, 80 °C, 1,475 scc/(cc·h) flue gas containing 2,550 ppm SO₂, 450 ppm NO, 10% CO₂, 10% H₂O, 5% O₂, and balance N₂)

Cycle	Breakthrough time (h) ^a	Percent SO ₂ removal	SO ₂ converted (g) ^b	Breakthrough extent (%)	Cold flushing liquid (200 cc)
1	0.6	99.7	1.39	5	4.32 N H ₂ SO ₄
2	8.95	99.4	20.62	5	4.32 N H ₂ SO ₄
3	3.22	97.4	7.27	5	4.32 N H ₂ SO ₄
4	3.42	97.7	7.74	5	4.32 N H ₂ SO ₄
5	2.83	93.9	5.93	5	4.32 N H ₂ SO ₄
6	2.92	97.1	6.35	5	4.32 N H ₂ SO ₄
7	3.17	97.8	7.03	5	4.32 N H ₂ SO ₄
8	3.30	98.6	7.21	5	4.32 N H ₂ SO ₄
9	3.33	98.1	7.24	5	4.32 N H ₂ SO ₄
10	3.25	98.3	7.24	5	4.32 N H ₂ SO ₄

^a 5% breakthrough

^b Per 100 g carbon at 5% breakthrough.

^c At liquid flush.

Figure 4-1. Outlet temperature and SO₂ concentration versus run time (MCCI catalyst, Run 2 of Table 4-2, Cycle 6 of Table 4-4, Inlet temperature 80 °C).

Figure 4-2. Outlet temperature and SO₂ concentration versus run time (MCCI catalyst, Run 3 of Table 4-2, Cycle 3 of Table 4-5, Inlet temperature 130 °C).

Table 4-5. SO₂ Removal Test Results (37.22 g of MCCI, 130 °C, 1,475 scc/(cc·h) flue gas containing 2,550 ppm SO₂, 450 ppm NO, 10% CO₂, 10% H₂O, 5% O₂, and Balance N₂, 200 cc 4.32 N H₂SO₄ flush after each cycle)

Cycle	Breakthrough time (h) (at 5%)	SO ₂ removal (%)	SO ₂ converted (g)
1	1.75	99.6	3.83
2	0.8	97.8	1.67
3	1.1	99.7	2.32

of process economics to catalyst cost is investigated in Section 5.0. The results of all other catalysts besides MCCI are presented briefly below.

The other catalysts tested besides MCCI were C2, MCCII, MCCV, and MCCVI. C2 was an unpromoted carbon material. This catalyst was exposed to simulated flue gas (without NO) at 80 °C at conditions identical to Run 1 of MCCI catalyst. In the first cycle, 99.3% SO₂ removal was achieved and 5% breakthrough occurred after 2.22 hours. A total of 3.62 g of SO₂ was removed per 100 g of carbon. Upon flushing with 200 cc of 4.32 N H₂SO₄, a 4.52 N H₂SO₄ was produced. Mass balance indicated that a much greater portion of the SO₂ was strongly retained on the C2 carbon as opposed to MCCI. The strong SO₂ retention partially poisoned the C2 carbon as is evident in the second cycle in which only 50% SO₂ removal was achieved. Cycle 2 was run for 2.4 hours. An attempt was made to restore the activity of the catalyst by flushing with pure water rather than 4.32 N H₂SO₄ after the second cycle. Flushing with 200 cc of water produced a 0.93 N sulfuric acid. However, the activity could not be restored to the original level as is evident from the third cycle in which again only about 50% SO₂ removal was achieved. This confirmed the conclusion that some of the SO₂ was very strongly retained on the catalyst after the first cycle and partially poisoned the catalyst.

MCCII catalyst was similarly tested for three cycles with simulated flue gas (without NO), at 1,454 scc/(cc·h) and 80 °C, the catalyst removed over 99% SO₂ in the first cycle but 5% breakthrough of the 2,550 ppm SO₂ feed occurred in only about 1.63 hours. After flushing the reactor with 200 cc of 4.32 N sulfuric acid, it was placed back on line at 80 °C. The highest SO₂ removal in the second cycle over 2 hours was 76%, indicating poisoning of the catalyst in

the first adsorption or due to the acid flush. After flushing the reactor again with 4.32 N sulfuric acid, an attempt was made to see if SO₂ removal could be increased by increasing temperature. However, in the third cycle at 105 °C, an SO₂ removal of only 63.9% was achieved.

Two other promoted catalysts (MCCV and MCCVI) projected to be significantly cheaper than MCCI were also tested with simulated flue gas containing NO. In the first cycle of MCCV, a 98.8% SO₂ removal was achieved but 5% breakthrough occurred after only 5 minutes. After flushing with 200 cc of 4.32 N H₂SO₄, only 94.6% SO₂ removal was achieved in the second cycle. In the first cycle of MCCVI, a 98.3% SO₂ removal was achieved and 5% breakthrough occurred after 28 minutes. After flushing with 200 cc of 4.32 N H₂SO₄, only 82.3% SO₂ removal was achieved in the second cycle.

None of the other catalysts (besides MCCI) exhibited the high efficiency and capacity for SO₂ removal as MCCI. However, some of them, as stated earlier, are projected to be significantly cheaper than MCCI, so a tradeoff exists. It is noteworthy to mention here that Waterloo also carried out a few experiments at 80 °C with the baseline carbon (Calgon BPL). Their results in Appendix 1 show about 70% SO₂ removal under conditions similar (except for a 2 N H₂SO₄ flush as opposed to 4.32 N) to those used for the proprietary materials presented above.

Pressure drop considerations for SO₂ removal have been addressed in detail by Waterloo (Appendix 1). Their calculations show projected pressure drop to be much less than 17 in. of water with efficient catalysts at 80 °C. The development and use of structured catalyst packing, e.g., monolithic catalysts, should further reduce this number.

To summarize the SO₂ removal work, more than 98% SO₂ removal (100% with a subsequent NO_x reduction reactor) can be achieved in the RTI-Waterloo process while producing a medium-strength sulfuric acid product. Further optimization of catalysts should be carried out with respect to cost, pressure drop, and efficiency. The process is ready to be scaled up for bench-scale demonstration using a multibed trickle-bed reactor system integrated with a NO_x reduction reactor downstream.

5.0 PROCESS EVALUATION

In this section a cost comparison of several alternative configurations of the RTI-Waterloo process is developed. In addition, the costs associated with these alternatives are compared to the capital costs and operating expenses that have been reported for processes with which the RTI-Waterloo process may compete in the implementation of advanced control processes.

The economic analysis reported herein was carried out using the Technical Assessment Guide (TAG) Methodology (TAG, 1989). This methodology was developed by the Electrical Power Research Institute (EPRI) to systemize the comparison of capital requirement and operating costs for alternative power producing systems. The TAG methodology was applied to a base case configuration of the RTI-Waterloo process in order to determine baseline operating and capital costs. The sensitivity of these costs to variations in catalyst costs and life expectancy, product acid strength, and number of stages required to achieve desired SO_2 removal were examined.

A simplified flowsheet for base case configuration of the RTI-Waterloo process has been shown previously in Figure 1-1. As can be seen from this figure, flue gas at 150°C is cooled to 105°C prior to being passed to the three-stage SO_2 reactor system. In the SO_2 reactor system SO_2 is adsorbed from the flue gas onto packed bed of carbon based catalyst where the SO_2 is converted to SO_3 and remains on the catalyst as SO_3 or H_2SO_4 .

The packed beds are flushed periodically. As shown in Figure 1-1, the liquid wash flows concurrent with respect to flue gas within each reactor stage but overall has a countercurrent motion with respect to the flue gas. In this way, pressure drop in the reactors is minimized and driving forces for SO_2 adsorption and reaction are maximized. The wash water leaving the top stage will contain approximately 32% H_2SO_4 which is about the strength of battery acid. Approximately 95% removal of SO_2 from the flue gas will be achieved. The flue gas leaving the SO_2 reactor system will be reheated to 135°C and passed to the NO_x converter.

There are several options for operating the SO_2 reactor/heat exchange system. One option might be to humidify the outlet gas from the SO_2 reactor system with a small flow of

water in order to control temperature swings that would be induced in the system by periodic flushing of the SO_2 reactor beds without the humidification step.

The flue gas leaving the SO_2 reactor system is mixed with a small flow of NH_3 and passed to the NO_x converter. The NH_3/NO_x molar ratio is maintained at 1.35. The NO_x converter is a packed bed of carbon based catalyst. Approximately 85% of the NO_x will be removed from the flue gas.

The 32% sulfuric acid leaving the SO_2 reactor system can be increased in strength by evaporation. For the purpose of the present economic evaluation, the evaporation is carried out in a single stage evaporation using high-pressure steam as the heating medium. In the various subcases of the RTI-Waterloo process addressed in the economic evaluation of the process, concentration of the 32% acid to 77.67 and 93.17% was considered.

Materials of construction were assumed to be carbon steel. In the situation where contact with acid was considered likely, it was assumed that the carbon steel was glass lined. Such glass-lined equipment items included the SO_2 reactor system, acid storage tank, and the evaporator.

In the economic evaluation of the RTI-Waterloo process a number of process and economic assumptions were made. These are outlined in Tables 5-1 and 5-2, respectively. Some of the more important process assumptions include space velocities for the SO_2 and NO_x reactors which were extrapolated from laboratory scale data. Most of the economic assumptions shown in Table 5-2 were developed based on information in the TAG methodology manual. For example, the critically important contingency factors, while very high, are in the mid-range of those recommended by the TAG methodology for the scale at which experimental process data are available and the detail of design that has been carried out.

In Table 5-2 the credit available for H_2SO_4 byproduct for the 77.67% and 93.17% acid were taken from the March 27, 1992, issue of *Chemical Prices*. As can be seen from Table 5-2, the price of these acids per ton is directly proportional to acid content. The byproduct credit value for the 32% acid was obtained by assuming that the cost of the 32%

Table 5-1. Process Assumptions

Power plant capacity	--	100 MW and 1 MW, 65% capacity factor
Coal type	--	Illinois #6, 2.8% sulfur
Flue gas composition	--	72.6% N ₂ , 4.5% O ₂ , 12.6% CO ₂ , 10% H ₂ O, 2,300 ppm SO ₂ , 530 ppm NO _x
SO ₂ converter	--	2 or 3 stages, 10,000 h ⁻¹ in each stage
NO _x converter	--	1 stage, 3500 h ⁻¹ , NH ₃ /NO _x = 1.35, promoted carbon catalyst, \$20/lb
Acid storage	--	24 hours

Table 5-2. Economic Assumptions

In-service date	=	Mid 1991
Average future apparent escalation rate	=	6%/year
Steam cost		
190 psig	=	\$3.71/1000 lb
1500 psig	=	\$5.62/1000 lb
Cost of raw water	=	\$0.64/100 gal
Total contingency allowance	=	80% (30% project and 50% process)
Recovered sulfuric acid credit		
32% acid	=	\$24/ton
77.67% acid	=	\$58/ton
93.17% acid	=	\$70/ton
Cost of NH ₃	=	\$150/ton

acid was also proportional to its acid content. This extrapolation probably overestimates the price of the weak acid.

Detailed results of the economic evaluation carried out for one RTI-Waterloo process alternative are shown in Tables 5-3, 5-4, and 5-5. In Table 5-3, the capital requirements for the major equipment items were based on cost figures reported for the respective items by Peters and Timmerhaus (1968). These costs were extrapolated to mid-1991 dollars using the *Chemical Engineering Index*. Supporting process items such as insulation, instrumentation and controls, piping, and electrical were estimated as a percent of the total cost of the major equipment items. These percentages were 8%, 13%, 31% and 5%, respectively, as recommended by Peters and Timmerhaus (1968). General facilities and home office fees were taken to be 10% and 15%, respectively, of total process capital as recommended by the TAG methodology. Royalty allowance was taken to be 0.5% of the total process capital; preproduction and land costs were assumed to be 9% and 1% of the total plant cost, respectively. Costs of initial charges of catalyst for the SO₂ and NO_x reactors were calculated based on the cost of catalyst for both reactors being \$20/lb. As can be seen from Table 5-3, the total capital requirement for the RTI-Waterloo process in the case where 93.17% acid is produced is \$187.74/kW.

Table 5-4 lists the operating costs for the RTI-Waterloo process alternative described above. The operating labor was determined by a standard technique described by Peters and Timmerhaus (1968) assuming \$21/hr wages and benefits. Maintenance labor and material costs per year per kW were calculated as 2% and 1.8% of the total plant cost (see Table 5-2) respectively. Administration and support labor was taken as 50% of the operating labor as recommended by Peters and Timmerhaus (1968). The variable operating costs shown in Table 5-4 were computed based on the economic assumptions described in Table 5-1 by multiplying the cost of an item by its usage. In the present alternative for the RTI-Waterloo process the catalyst was assumed to cost \$20/lb and have a useful life of 6 years. Byproduct credit for spent catalyst was assumed to be 50% of the market value of the promoter which in this case worked out to be \$3.20/lb of spent catalyst. The total operating cost for the RTI-Waterloo process alternative under present consideration came to \$8.49/year per kW as shown in Table 5-4.

Table 5-3. Capital Requirement: SO₂/NO_x Removal Process
Basis: 100 MW Power Plant, 65% Capacity Factor, 1991
Dollars

Process Capital	\$/KW
Heat exchange	19.38
Three-stage SO ₂ reactor	7.26
NO _x reactor	6.29
Acid storage	1.65
Evaporator	2.29
Insulation	2.95
Instrumentation and controls	4.79
Piping	11.43
Electrical	1.84
Total Process Capital	57.88
General facilities	5.79
Engineering and home office fees	8.68
Subtotal of Process Capital and Cost of Facilities and Engineering	72.35
Project contingency (30% of subtotal)	21.71
Process contingency (50% of subtotal)	36.18
Total Plant Cost	130.24
Royalty allowance	0.29
Preproduction costs	11.72
Initial catalyst and sorbents	44.19
Land	1.30
Total Capital Requirement	187.74

Table 5-4. Operating Costs: SO₂/NO_x Removal Process
Basis: 100 MW Power Plant, 65% Capacity Factor, 1991
Dollars

Fixed Operating Costs	\$/yr/kW
Operating labor	3.06
Maintenance labor	2.60
Maintenance material	2.34
Administrative and support labor	1.53
Subtotal	9.53
Total Fixed Operating Cost at 65% of Subtotal	6.19
Allocated variable operating cost 35% of subtotal	3.34
Variable Operating Costs	
Utilities	
Water	0.10
Power	0.03
Steam	7.56
Catalysts, sorbents, and chemicals	
Catalysts	7.37
NH ₂	1.96
Allocated variable operating costs (from above)	3.34
Byproduct credit	
93.17% sulfuric acid	(16.88)
Spent catalyst	(1.18)
Total Variable Operating Costs	2.30
Total Net Operating Costs (fixed + variable)	8.49

**Table 5-5. Levelized Busbar Costs: SO₂/NO_x Removal Process
Basis: 100 MW Power Plant, 65% Capacity Factor, 1991 Dollars**

Capital Costs	mil/kWh
Process capital	1.75
General facilities	0.18
Engineering and home office fees	0.27
Project contingency	0.64
Process contingency	1.10
Total Plant Cost	3.94
Royalty allowance	0.01
Preproduction cost	0.35
Initial catalyst and sorbents	1.34
Land	0.04
Total Capital Requirement	5.68
Operating Costs	
Fixed operating cost	1.90
Variable operating cost	0.70
30-Year Levelized Busbar Cost	8.28

Table 5-5 shows the computation of the 30-year levelized busbar cost which in the present case came to 8.28 mil/kWh.

Economic evaluations, similar to the one described above, have been carried out on a number of variations of the RTI-Waterloo process. The results of these analyses are shown in Table 5-6. The table shows that the capital requirement and operating costs for the RTI-Waterloo process are sensitive to catalyst cost and life, and acid strength desired.

The required strength of acid byproduct also greatly affects the levelized cost of RTI-Waterloo process; however, the capital requirement for the process is not significantly affected by acid strength. These points are illustrated by comparing Cases 4 and 6 of Table 5-6. It can be seen that increasing acid strength from 77.67% to 93.17% increases the levelized cost of the control process by about 14%. The reasons for this increase are due mainly to the

**Table 5-6. RTI-Waterloo Process Economic Performance
(100-MW Power Plant, 65% Capacity Factor)**

SO₂ Conversion						
Case No.	Stages (-)	Catalyst cost (\$/lb)	Catalyst life (yr)	Acid product strength (wt %)	Capital cost (\$/kW)	Levelized cost (mil/kWh)
1	3	20	3	32	179	8.2
2	2	20	3	32	162	6.8
3	3	20	3	77.67	188	9.0
4	3	20	6	77.67	188	7.3
5	2	20	6	77.67	171	6.4
6	3	20	6	93.17	188	8.3
7	2	20	6	93.17	171	7.4
8	3	3	2	77.67	169	6.3
9	3	3	2	93.17	169	7.0

requirement of using 1,500 psig steam to produce 93.17% acid versus 190 psig steam to produce 77.67% acid.

A comparison of Cases 3 and 4 in Table 5-6 shows that, if the life of \$20/lb SO₂ catalyst can be extended from 3 to 6 years, the levelized cost of the control process can be reduced by nearly 19%. In addition, Case 8, where a cheap, expendable catalyst is utilized, further illustrates this point.

The capital requirement and levelized cost for the RTI-Waterloo process are compared to the costs associated with other advanced SO₂/NO_x control systems in Table 5-7. It can be seen that the RTI-Waterloo process compares favorably with other control technologies. In addition, the closeness of the cost estimates for processes similar to the RTI-Waterloo process in comparison to the costs obtained by RTI for the RTI-Waterloo process lends credibility to the economic evaluation carried out by RTI.

As more experimental data are obtained on larger scale equipment, and more detailed designs and costs are developed for the RTI-Waterloo process the high contingency factors

Table 5-7. Cost of SO₂/NO_x Removal

Process	MW	Capital cost (\$/kW)	Levelized cost (mil/kWh)
Conventional FGD/SCR	500	200	8.8
Advanced FGD/SCR	500	170	7.8
NOXSO	500	215/260/300	8/11.8/17
SNOX	500	330/375/430	8.8/10.4/13
E-Beam	500	310/400/440	9/13.2/15.3
RTI-Waterloo	100	162 to 188	6.3 to 9.0

Estimates except for RTI-Waterloo process from Cichanowicz et al. (1992)

required by the TAG methodology in the economic evaluation of the process should be reduced. With reduced contingencies the RTI-Waterloo process should be very competitive with alternative technologies.

In order to obtain a hint of the effect of contingency on the total capital requirement and levelized busbar cost, the economic evaluation of several configurations of the RTI-Waterloo process shown in Table 5-6 were reworked using 50% of the contingencies used to develop Table 5-6. The result of these further calculations is shown in Table 5-8. As can be seen from Table 5-8, the total capital requirement and the levelized busbar cost are both reduced by about 18% when the process and project contingencies are reduced by 50%.

As can be seen from Table 5-6, the effect of increasing product acid strength from 77.67% to 93.17% increases the levelized busbar cost by roughly 11% to 14% while the total capital requirement remains virtually the same. The increase in the levelized costs is due primarily to the amount and quality of steam required to operate the evaporator. Another factor that would have a great impact on steam usage is the strength of acid that can be obtained directly from the SO₂ reactors. In the various configurations of the RTI-Waterloo process discussed above, the average acid strength exiting the SO₂ reactors was assumed to be 32% or about 8 N sulfuric acid. The economic analysis for Cases 8 and 9 of Table 5-8 were carried out again assuming the average acid strength from the SO₂ reactor system was 10 N or about 38% H₂SO₄ and the total contingency was 40%. The capital requirement for

Table 5-8. Effect of Contingency on the Estimated Capital and Levelize Busbar Costs for the RTI-Waterloo Process (100-MW Power Plant, 65% Capacity)

SO ₂ conversion					Total contingency 80%		Total contingency 40%	
Case no.	Stages (-)	Catalyst cost (\$/lb)	Catalyst life (yr)	Acid product strength (wt %)	Capital cost (\$/kW)	Levelized cost (mil/kWh)	Capital cost (\$/kW)	Levelized cost (mil/kWh)
4	3	20	6	77.67	188	7.3	156	6.0
5	2	20	6	77.67	171	6.4	141	5.1
6	3	20	6	93.17	188	8.3	156	7.0
7	2	20	6	93.17	171	7.4	141	6.2
8	3	3	2	77.67	169	6.3	137	4.9
9	3	3	2	93.17	169	7.0	137	5.9

the 8 N and 10 N acid cases was \$137/kW and \$136/kW, respectively. This decrease in capital requirement is due primarily to the minor change in the cost of the evaporator. The levelized busbar cost was reduced by 4% by increasing the acid strength from the SO₂ reactor from 8 N to 10 N in case 8 where 77.67% acid is produced. A decrease of 2% in levelized busbar cost was obtained in Case 9 where the acid strength was 93.17%.

The capacity of a process is well known to affect the costs associated with the process due in most instances to economy of scale. In order to determine the effects of economy of scale for the RTI-Waterloo process, the base case for the RTI-Waterloo process, which was summarized in Tables 5-3, 5-4, and 5-5 and sized for a capacity of 100 MW, was carried out again based on a 1-MW power plant. For a capacity of 1 MW the capital requirement for the RTI-Waterloo process was \$950/kW versus \$188/kW for the 100 MW case. The levelized busbar costs associated with the RTI-Waterloo process for the 1-MW plant capacity sailed to 46.8 mil/kWh compared to 8.3 mil/kWh for the 100-MW plant.

To summarize, technical/economic evaluation of the RTI-Waterloo process shows it to be attractive and competitive with conventional SCR/flue gas desulfurization (FGD) and other SO₂/NO_x control processes. The advantages over SCR/FGD include potential for higher SO₂ removal and production of a salable rather than a waste product. Thus, a direct comparison is not possible at this time. A more detailed evaluation should be carried out after data are available at a larger bench-scale of operation which demonstrates SO₂/NO_x removal in an integrated manner.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The RTI-Waterloo process has been demonstrated at laboratory scale to be capable of removing more than 95% SO_2 and more than 85% NO_x while producing a medium-strength sulfuric acid product. The process has the potential to remove 100% of the SO_2 using a downstream regenerable NO_x reduction reactor as a guard bed. Furthermore, catalyst optimization could lead to more than 90% NO_x removal. The optimum operating temperature for SO_2 removed is around 100 °C whereas it is around 135 to 150 °C for NO_x removal. A preliminary engineering evaluation shows that the medium-strength sulfuric acid product from a 2- or 3-reactor trickle-bed SO_2 removal system can be upgraded to industrial strength sulfuric acid of 93.17% concentration using an evaporator. Furthermore, this configuration of the process producing 93.17% sulfuric acid is attractive and cost competitive with conventional SCR/FGD and emerging SO_2/NO_x removal processes.

The following recommendations are provided for further development of the RTI-Waterloo process. The process should be scaled up to an integrated SO_2/NO_x bench-scale skid-mounted reactor system. After demonstration of the integrated process with simulated flue gas, the system should be tested with real flue gas at a boiler. The effect and fate of air toxics, particularly mercury, benzene, and hydrogen chloride should be addressed. In parallel to the bench-scale demonstration, catalyst optimization/development should be carried out. Catalysts with higher efficiency at lower costs should be developed. The question of pressure drop in the process should be investigated further and structured catalyst packing should be developed to reduce pressure drop. Also in parallel to the integrated demonstration, a process model should be developed, particularly for the three-phase periodic trickle-bed reactor process for SO_2 removal, to allow scale-up to pilot-scale operation.

7.0 REFERENCES

- Andersen, H.C., W.J. Green, and D.R. Steele, 1961, *Ing. Eng. Chem.*, 53(3):199-204.
- Ayen, R.J., and A. Amirnazi, 1980, *Ind. Eng. Chem. Proc. Des. Dev.*, 9(2):247-254.
- Berruti, F., R.R. Hudgins, and E. Rhodes, 1984, *Can. J. Chem. Eng.*, 62:644.
- Cichanowicz, J.E., et al., 1991, Engineering Evaluation of Combined SO₂/NO_x Removal Processes, Electric Power Research Institute.
- Davtyan, O.K., and E.N. Ovchinnikova, 1955, *Dokl. Akad. Nauk SSR*, 104:857.
- Goto, S., and J.M. Smith, 1978, *AIChE Journal*, 24:286.
- Hartman, M., and R.W. Coughlin, 1972, *Chem. Eng. Sci.*, 27:867-880.
- Hartman, M., J. Polek, and R.W. Coughlin, 1971, *Chem. Eng. Prog. Symp. Ser.*, 115(67):7-22.
- Herskowitz, M., 1981, *Chem. Eng. J.*, 22(2):167.
- Haure, P., R.R. Hudgins, and P.L. Silveston, 1989, *AIChE Journal*, 35:1437.
- Kareko, K., Y. Nakahigashi, and K. Nagata, 1988, *Carbon*, 26(3):327-333.
- Komiyama, H., and J.M. Smith, 1975, *AIChE Journal*, 21:664.
- Kuehl, H., E. Richter, K. Knoblauch, and H. Juengtgn, 1986, *Carbon '86*, Bergbau-Forschung, Essen, Germany, pp. 351-353.
- Kusakabe, K., M. Karhima, S. Morook, and K. Shigeharu, 1988, *Fuel*, 67(5):714-718.
- Mata, A.R., and J.M. Smith, 1981, *Chem. Eng. J.*, 22:229.
- Mitsui Corporation, 1991, Private communication, with S. Gangwal Research Triangle Institute.
- Pavko, A., and J. Levec, 1981, In *Proc. 2nd World Congress of Chem. Eng.* (Montreal), Vol. iii, 156.
- Peters, M.S., and K.D. Timmerhaus. 1968. *Plant Design and Economics for Chemical Engineers*, McGraw Hill, NY.
- Seaburn, J.T., and A.J. Engel, 1973, *Chem. Eng. Prog. Symp. Ser.*, 134(69):71.
- Seki, M., Y. Sakurai, and K. Yoshida, 1975, *Am. Chem. Soc. Div. Env. Chem. Reprints*, 15(2):28-31, Chicago Meeting, August 24-29.
- Siddiqi, A.A., and J.W. Tenini, 1981, *Hydrocarbon Processing*, 60(10):113.

Siedlewski, J, 1965, *Intern. Chem. Eng.*, 5:297.

TAG, 1989, *TAG Technical Assessment Guide, Electrical Supply* 1989, EPRI P-6587-L, Volume 1, Rev. 6, Report prepared by the Electrical Power Research Institute, Palo Alto, CA, September.

APPENDIX 1

**UNIVERSITY OF WATERLOO
FINAL REPORT**

Final Report

Prepared for
Center for Process Research
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709

Subcontract No. 1-96U-5055/Contract No. DE-RA22-91PC91345

A Novel Carbon-Based Process for Flue-Gas Cleanup

James Metzinger, B.A.Sc
Research Engineer

P.L. Silveston, Ph.D., P. Eng
Principal Investigator

Reaction Engineering Laboratory
Department of Chemical Engineering
University of Waterloo

April 1, 1993

Abstract

Activated carbon is a well-known low-temperature catalyst for SO_2 oxidation. This investigation uses a periodically operated trickle bed reactor, operating with a simulated flue gas at both 20 and 80 °C, to investigate the potential of this system as an FGD device.

The objective of this work was to develop a novel activated carbon based process that operates at low temperature ($<150^\circ\text{C}$) to convert SO_2 to industrial strength sulfuric acid. Our targets were to achieve 95% or greater removal of SO_2 , production of at least 2 molar sulfuric acid and a pressure drop of at most 30 inches of water (7468.3 Pa).

At 20 °C, steady state operation was found to be superior to periodic operation for scrubbing stack gas. This unexpected result indicates that with SO_2 in the 0 to 2500 ppm range SO_2 removal and conversion to acid is reaction rate controlled at these conditions. Even though factorial experiments indicated that steady state operation was superior at removing SO_2 from the gas stream at 20 °C, periodic operation is superior for converting the SO_2 removed from the gas to sulfuric acid.

Experiments conducted at 80 °C demonstrate that this process should be operated at 80 °C or better (rather than 20 °C). Removal approximately tripled and conversion of the SO_2 removed from the simulated flue gas to acid almost doubled on average. The required bed height and therefore the pressure drop would be significantly lower operating at 80 °C. At 80 °C, evaporation occurred within the reactor with simulated flue gas. Thus, hot flue gas offers a means of concentrating the acid circulating through the trickle bed.

Table of Contents

Abstract	ii
1.0 Introduction	1
1.1 Work Statement.....	1
1.2 Report Introduction.....	1
2.0 Literature Review	3
2.1 Activated Carbon as SO ₂ Oxidation Catalyst.....	3
2.2 Regeneration of Activated Carbon Following SO ₂ Oxidation.....	4
2.3 Oxidation of SO ₂ in a Trickle Bed Reactor.....	5
2.4 Characteristics of a Trickle Bed Reactor.....	6
2.4.1 Flow Patterns.....	6
2.4.2 Effect of Gas and Liquid Flow Rates.....	7
2.4.3 Wetting Efficiency	8
2.4.4 Liquid Holdup	9
3.0 Experimental Equipment	10
3.1 Experimental Set-Up	10
3.1.1 Reactor.....	10
3.1.2 Preparation of Liquid Phase	15
3.1.3 Preparation of Gas Phase	17
3.1.4 Computer Interface.....	19
3.2 Catalyst.....	20
3.3 Equipment Operation Procedures	20
3.4 Analysis Method.....	24
3.4.1 SO ₂ Gas Analyzer	24
3.4.2 Wet Chemistry	27
3.4.2.1 Total Acidity Determination	27
3.4.2.2 Sulfurous Acid Determination.....	28
3.4.3 SO ₂ Removal and Conversion Calculations.....	28
3.4.3.1 SO ₂ Removal	28
3.4.3.2 SO ₂ Conversion	29
3.4.3.3 Sulfur Balance.....	30
4.0 Experimental Design.....	31
4.1 Low Temperature Experiments.....	31
4.1.1 Experimental Layout.....	32
4.1.2 Factorial Design Interpretation.....	34
4.2 High Temperature Experiments	34

5.0 Scrubber Model	36
5.1 Model Development	36
5.2 Quantitative Development for Oxygen Transport Controlling	41
5.3 Quantitative Development for Surface Reaction Controlling	42
5.4 Pressure Drop Model	43
5.5 Comments	44
6.0 Results and Discussions	45
6.1 Comparing Periodic and Steady State	45
6.2 Factorial Design Interpretation	52
6.2.1 SO ₂ Removal	57
6.2.2 Conversion of SO ₂ Removed	59
6.2.3 Product Increase in Sulfuric Acid Concentration	60
6.2.4 Product Sulfurous Acid Concentration	60
6.2.5 Conclusions from Factorial Design	61
6.3 80°C Experiments	62
6.4 Pressure Drop and Required Bed Depth for 95% SO ₂ Removal	65
6.5 Temperature Profiles within the Reactor	70
6.6 SO ₂ Removal Profiles	74
6.7 Liquid Maldistribution	77
7.0 Conclusions and Recommendations	79
7.0 Conclusions	79
7.2 Recommendations	81
Appendix A : Calculating Experimental Variation Between Titrated Samples	82
Appendix B : Sample Calculations	86
Appendix C : Measured and Calculated Results	92
Appendix D : Factorial Design Interpretation	102

Table of Figures

3.1: 20°C Experimental Equipment Schematic.....	11
3.2: 80°C Experimental Equipment Schematic.....	12
3.3: SO ₂ Oxidation Reactor	13
3.4: Sampling System for SO ₂ Gas Analyzer.....	26
5.1: Mass Transfer Around a Catalyst Particle.....	36
5.2: O ₂ and SO ₂ Concentration Profiles Around a Catalyst Particle	37
5.3: Sulfuric Acid Concentration Profile in a Catalyst Particle	38
5.4: Flow of Gas and Liquid Co-currently Through a Reactor	40
6.1: Periodic and Steady State SO ₂ Removal at Various Superficial Liquid Velocities ($v_g = 1000$ scc/cchr)	47
6.2: Periodic and Steady State SO ₂ Removal at Various Superficial Liquid Velocities ($v_g = 2850$ scc/cchr).....	48
6.3: Periodic and Steady State SO ₂ Conversion at Various Superficial Liquid Velocities ($v_g = 1000$ scc/cchr).....	49
6.4: Periodic and Steady State SO ₂ Conversion at Various Superficial Liquid Velocities ($v_g = 2850$ scc/cchr).....	50
6.5: Periodic and Steady State Product Sulfuric Acid Concentraions at Various Superficial Liquid Velocities ($v_g = 1000$ scc/cchr).....	53
6.6: Periodic and Steady State Product Sulfuric Acid Concentraions at Various Superficial Liquid Velocities ($v_g = 2850$ scc/cchr).....	54
6.7: Periodic and Steady State Product Sulfurous Acid Concentraions at Various Superficial Liquid Velocities ($v_g = 1000$ scc/cchr).....	55
6.8: Periodic and Steady State Product Sulfurous Acid Concentraions at Various Superficial Liquid Velocities ($v_g = 2850$ scc/cchr).....	56
6.9: Typical Axial Reactor Temperature Profile for 20°C Experiments	71

6.10: Typical Axial Reactor Temperature Profile for 80°C Experiments	73
6.11: Typical SO ₂ Outlet Concentration Profile for 20°C Experiments	75
6.12: Typical SO ₂ Outlet Concentration Profile for 80°C Experiments	76
6.13: Typical Variation in Product Total Acidity Concentration for 80°C Experiments.....	78

List of Tables

2.1 Efficiency of Oxidation Catalysts at 20°C.....	3
3.1 Bottled Gas Grade and Quality.....	18
3.2 Properties of Activated Carbon	21
3.3 Properties of Catalytic Bed	21
4.1 Levels of Variables Studied in Factorial Experiments	32
4.2 Conditions for Each Experiment.....	33
4.3 Level of Variables Studied at High Temperature	35
6.1 Results of Factorial Experiments	58
6.2 Results of High Temperature Experiments	64
6.3 Estimated Bed Height and Pressure Drop for 95% SO ₂ Removal Assuming Oxygen Transport Controls.....	66
6.4 Estimated Bed Height and Pressure Drop for 95% SO ₂ Removal Assuming Oxidation Rate Controls	67
6.5 Estimated Bed Height and Pressure Drop for 95% SO ₂ Removal at 80°C Assuming Oxygen Transport Controls	68
6.6 Estimated Bed Height and Pressure Drop for 95% SO ₂ Removal at 80°C Assuming Oxidation Rate Controls	68
6.7 Pressure Drop / m Depth of Reactor Bed for Periodic Operation.....	70
6.8 Pressure Drop / m Depth of Reactor Bed for Steady State Operation	70
A.1 Random Total Acidity Samples	83
A.2 Random Sulfurous Acid Titration Samples	85
B.1 Sample Data from Experiment R1-3	86

1.0 Introduction

1.1 Work Statement

The objective of this work was to develop a novel activated carbon based process that operates at low temperature ($<150^{\circ}\text{C}$) to convert SO_2 to industrial strength sulfuric acid. Our targets were to achieve 95% or greater removal of SO_2 , production of at least 2 molar sulfuric acid and a pressure drop of at most 30 inches of water (7468.3 Pa).

1.2 Report Introduction

Flue gas desulfurization (FGD) is considered to be the most commercially developed means of continuous control of SO_2 emissions from coal-fired boilers. FGD systems can be grouped into two main categories, regenerable and non-regenerable (also known as throwaway) systems. The vast majority of FGD systems use an alkaline sorbent to absorb the SO_2 in the flue gas. In this type of non-regenerable system, the sulfur dioxide is permanently bound to the alkaline sorbent and must be disposed of as waste or sold as a by-product, such as gypsum. In a regenerable system the SO_2 is released in a regeneration process following the absorption/adsorption process. The regenerated absorbent/adsorbent is then recycled to the scrubbing step. The recovered SO_2 from the regeneration step can then be processed to obtain sulfuric acid or elemental sulfur. This experimental investigation deals with a FGD system based on water which produces a saleable product - sulfuric acid. It can be considered regenerable because the carbon is reused, but SO_2 is converted to sulfuric acid and in that sense it is a non-regenerable process.

Our work is based on the well-known low-temperature catalytic properties of activated carbon for SO_2 oxidation, but uses a novel periodically flushed co-current trickle bed to produce a moderately concentrated sulfuric acid. Haure (1989) was investigating if periodically starting and stopping the liquid flow in a trickle bed reactor would raise the rate of reaction by reducing mass transfer resistance. SO_2 oxidation was used as the test reaction with remarkable results. Increases of 40 to 60% in the rate of SO_2 oxidation were achieved while producing a moderately strong sulfuric acid, almost 0.2 mole/L. This work suggested that periodic flow interruption could be applicable to FGD.

A test reactor, similar to that used by Haure, was constructed in order to test the response of this novel periodically flushed scrubber with a simulated flue gas. In this investigation, a comparison of SO_2 removal, conversion, and product sulfurous and sulfuric acid concentrations are made between continuously flushing the trickle bed with water (steady state operation) and periodically flushing the bed operating at 20 °C. Under periodic operation, the effect on the system performance was measured. Experiments were also conducted at 80°C using periodic operation to determine if there is an advantage to operating at higher temperature. From these experimental results the bed height and pressure drop were estimated for 95% removal of SO_2 from the simulated stack gas.

2.0 Literature Review

2.1 Activated Carbon as SO₂ Oxidation Catalyst

In 1955 Davtyan and Ovchinnikova conducted the first studies on the catalytic oxidation of sulfur dioxide. They reported that at 20°C, activated carbon is among the most efficient of all well-known oxidation catalysts in terms of quantity of sulfur trioxide formed per gram of catalyst (Table 2.1). Seaburn and Engel (1973) tested eight commercially available activated carbons for their ability to adsorb and also to catalyze SO₂ oxidation. Their study showed that type BPL is a fairly good catalyst although it is only a mediocre adsorbent.

Table 2.1 Efficiency of oxidation catalysts at 20°C

Catalyst	Catalytic Efficiency
Platinum	0.090
Activated Carbon	0.070
V ₂ O ₅	0.050
Graphite	0.025
Cr ₂ O ₃	0.010
Fe ₃ O ₃	0.009

Carbons developed for catalyst applications, which are usually synthesized by thermal decomposition of organic matter, followed by an activation process which increases

porosity, typically possess specific surfaces as large as $1000 \text{ m}^2/\text{g}$ (Hartman et al., 1971). High temperature steam and H_3PO_4 treatment are well-known activation processes.

Previous investigators at the University of Waterloo, (Haure et al., 1989; Hasokowati 1993) used type BPL activated carbon with reasonable results. The properties of this carbon are shown in Table 3.2.

2.2 Regeneration of Activated Carbon Following SO_2 Oxidation

Hartman et al. (1971), Hartman and Coughlin (1972), and Siedlewski (1965) provide a detailed description of the mechanism of SO_2 oxidation over activated carbon. Catalytic oxidation involves the reaction between SO_2 chemisorbed on active centres with chemisorbed molecular oxygen (Otake et al., 1971) to form SO_3 which is then adsorbed on the surface.

The SO_3 formed on the catalyst surface does not desorb spontaneously at low temperature. There are two methods to desorb the SO_3 in order to regenerate the active sites on the carbon: thermal desorption or water flushing. Thermal desorption at temperatures above 400°C , as practiced in the Mitsui process, can regenerate the catalyst. However, repeated adsorption-desorption cycling will lead to carbon loss through CO_2 formation. The SO_2 conversion activity and adsorption capacity will also decrease as a result of a decrease in the surface area caused by pore coalescence.

The second method, discussed by Davtyan and Ovchinnikova (1955), involves washing the catalyst with water. This method results in the removal of adsorbed SO_3 from the catalyst as sulfuric acid. According to these authors, the presence of water vapour in the gaseous

phase, together with oxygen and SO_2 , increases the capacity of a carbon bed for SO_2 capture. SO_2 oxidation is favoured by the presence of liquid water in the carbon at concentrations up to 0.3 g/g carbon. Further increases in water concentration do not increase sulfuric acid formation. Since water flushing does not result in the degradation of the catalyst, this method of operation would be preferred for industrial applications.

2.3 Oxidation of Sulfur Dioxide in a Trickle Bed Reactor

A trickle bed reactor (TBR) is a three-phase reactor with the catalyst contained in a fixed bed and the gas and liquid phases usually flowing co-currently over the bed to minimize the reactor pressure drop.

In a comprehensive review paper by Hartman et al.(1971), preliminary results are reported on SO_2 removal from an air stream containing 0.5% SO_2 in a counter-current trickle bed reactor. They achieved SO_2 removals as high as 70% and sulfuric acid concentrations up to 0.1 molar.

Komiyama and Smith (1975) studied the kinetics and mass transfer effects of the SO_2 oxidation reaction in a slurry reactor using type BPL activated carbon as a catalyst. They found that the intrinsic reaction rate is first order with respect to oxygen and zero order in SO_2 . They concluded that the catalytic oxidation of SO_2 in a three-phase system is controlled by the rate of O_2 transfer to the surface.

Mata and Smith (1981) investigated SO_2 oxidation in a TBR using type BPL activated carbon catalyst. They ran experiments using water saturated with air and partially deoxygenated water. They found that when the concentration of O_2 in the liquid feed was

changed, the average rate changed dramatically. The results of experiments using partially deoxygenated water indicated that the rate of O_2 transfer from the gas into the liquid phase was not rapid enough to increase the liquid concentration significantly. They also confirmed a zero-order dependence of SO_2 on the intrinsic reaction rate.

Haure et al.(1989) used the oxidation of SO_2 on type BPL activated carbon in a TBR to demonstrate that periodically starting and stopping the liquid flow would raise the rate of reaction by reducing liquid film resistance. The results showed an increase of 40 to 60% in the rate of oxidation. It was also found that sulfuric acid concentrations of almost 0.2 M, could be produced while achieving a 40 to 60% increase in the oxidation rate at room temperature.

2.4 Characteristics of a Trickle Bed Reactor

2.4.1 Flow Patterns

There are four distinct flow regimes observed in trickle bed reactors. At low gas and liquid rates, the liquid flows over the catalyst in a laminar film or in rivulets. The gas flows continuously through the voids in the bed. This is known as the low interaction regime (also known as the gas continuous flow or homogeneous region) as the gas does not affect the flow of the liquid rivulets. If the gas flow is increased while the liquid flow is kept constant, the flow pattern changes. The gas phase is still continuous; however, the liquid phase is now dispersed as a heavy mist in the gas. This is known as the spray flow regime. If the liquid flow is now increased the reactor is brought into the pulsing or slug flow regime. This regime is characterized by the fact that the composite gas-liquid mixture flowing through the bed changes its spatial-average density periodically. This is

also known as the high interaction regime. If the gas flow is then decreased, the liquid phase becomes continuous and the gas passes through the reactor in bubbles. This is known as the dispersed bubble flow regime.

Herskowitz and Smith (1983) have reported that most laboratory, pilot and industrial TBR's operate in the gas continuous or pulsing flow regimes. Transitions from one flow regime to another have been determined by sharp increases in pressure fluctuations (Chou et al., 1977; Sicardi et al., 1979), sudden changes in the gas-liquid mass transfer coefficients (Fukushima and Kusaka, 1977) and in appearance (Talmor, 1977). Several flow regime maps are available (Sicardi et al., 1979; Talmor, 1977; Charpentier and Favier, 1975). Unfortunately, very little experimental work has been done on the development of general correlations for predicting transitions from the gas continuous to the pulsing flow regimes.

2.4.2 Effect of Gas and Liquid Flow Rates

Herskowitz and Mosseri (1983) studied the effect of gas and liquid rates on the hydrogenation of α -methyl styrene to cumene in a TBR. They varied the gas and liquid rates over a wide range in the gas continuous flow regime and found that increasing the liquid and gas rates increased the rate of reaction. Berruti et al.(1984) studied the influence of gas and liquid flow rates on SO_2 oxidation in a TBR with type BPL activated carbon as a catalyst. This study also reported that increasing the liquid and gas rates increased the rate of reaction. Increasing the liquid and/or gas flow enhances the rate of gas to liquid mass transfer.

Studies carried out by Haure et al.(1989), Bellut (1985), Mata and Smith (1981) (studying SO₂ oxidation in a TBR) and Herskowitz et al., (1979) (studying α -methyl styrene hydrogenation) report measured global rates of reaction that decrease with increased liquid flow rate, reach a minimum and then increase with further increases in the liquid flow. This type of behaviour is expected if the liquid-solid mass transfer resistance is significant over the range of liquid flow rates.

2.4.3 Wetting Efficiency

The wetting efficiency (f) is defined as the fraction of the particle external surface covered by a moving film of liquid. In trickle beds the pores of the catalyst are normally filled with liquid. However, for a reactor operating at low liquid flow rates (gas continuous flow regime), a condition may occur where the catalyst is only partly covered by liquid and hence the wetting efficiency is less than 100%. This partial wetting leads to direct contact between the gas and the catalyst.

For reactions in which the intrinsic rate is controlled by a non-volatile reactant, reduced wetting efficiency leads to reduced global rates. If the limiting reactant is in the gas phase, and mass transport resistances are significant, partial wetting results in increased global reaction rates. This occurs because the mass transfer resistance on the non-wetted surface is less than on the surface covered with flowing liquid (Herskowitz and Smith 1983).

Research conducted by Herskowitz (1981) and Mata and Smith (1981) show that wetting efficiency decreases with a decrease in liquid flow rate. Herskowitz and Mosseri (1983) report that the wetting efficiency decreases with increasing gas flow rate, especially at low

liquid rates. Specchia et al. (1978) and Sicardi et al. (1981), however, observed the opposite trend.

2.4.4 Liquid Holdup

The total liquid holdup is the fraction of the total volume of the bed filled with liquid and consists of the static holdup plus the dynamic holdup. The static holdup is the volume fraction of the liquid that remains after the bed is drained. For porous particles the static holdup consists of the intraparticle holdup and the interparticle static holdup. The intraparticle holdup consists of liquid within the pores of the catalyst particles. The interparticle static holdup consists of liquid held outside the catalyst pores in the bed volume. The internal pores of the catalyst are normally filled with liquid as a result of capillarity forces. The interparticle holdup which is the sum of the dynamic and interparticle static holdup, affects the pressure drop in the column since it reduces the effective void fraction (Herskowitz and Smith, 1983).

3.0 Experimental Equipment

This section describes the experimental equipment, the procedures followed and the analytical methods used.

3.1 Experimental Set up

The equipment constructed for this work is based on equipment used in previous studies by Berruti(1984), Bellut(1985) and Haure(1987).

A schematic of the apparatus is shown in Figure 3.1 and Figure 3.2. The difference between the two schematics is that Figure 3.1 represents the equipment used for experiments at 20 °C, and Figure 3.2 represents the equipment used for experiments at 80 °C. The apparatus consists of four main parts: 1) the reactor, 2) preparation of the liquid phase, 3) preparation of the gas phase, and 4) the computer and interface system.

3.1.1 Reactor

The reactor is constructed from 5 cm ID, thick walled glass. The liquid phase (de-ionized water or dilute sulfuric acid) and the gas phase (a simulated flue gas described in Section 3.1.3) enters the top of the reactor flowing co-currently downward through the reactor. The phases are separated at the bottom and removed separately. A detailed drawing of the reactor is given in Figure 3.3. The reactor is made up of a 50 cm long glass cylinder with two glass caps. The top cap adding an additional 5 cm and the bottom 15 cm to the overall height. The caps are flanged and contain o-ring seals. They are joined to the

Figure 3.1: 20 °C Experimental Equipment Schematic

Figure 3.2: 80 °C Experimental Equipment Schematic

NOTES

- 1) THE REACTOR IS CONSTRUCTED FROM 5 cm DIAMETER THICK WALLED GLASS
- 2) ALL CONNECTIONS ARE 1/4"

N.T.S.

ALL DIMENSIONS IN cm

Figure 3.3: SO₂ Oxidation Reactor

cylinder with conventional glass clamps. The upper cap contains a 6 mm glass tube at the top for the introduction of the liquid feed. The main glass cylinder contains three 6 mm connections. The uppermost for the introduction of the gas feed and two others for manometer connections. The lower glass cap contains a 6 mm connection on one side for the gas outlet and a 6 mm connection on the very bottom for the liquid outlet.

As shown in the figure the upper part of the reactor is filled with 1.6 mm glass beads as a prepacking. The purpose of the prepacking is to improve the distribution of the liquid flow. It also provides mixing of the liquid and gas phases so that they enter the bed at or very near equilibrium.

The catalyst bed which is activated carbon, rests on a Teflon support screen. Pressure drop is measured using manometer ports located above and below the bed. Separate measurements using glass beads only permit correction so pressure drop across the activated carbon alone are measured.

A thorough understanding of the performance requires temperature profile measurements. For this purpose 0.8 mm Type K thermocouples covered by 1.6 mm Teflon tubing are used and inserted into the reactor as shown in Figure 3.2. At each of the three levels, three thermocouples are used in a skewed arrangement so that the axial profiles are measured at different radial and angular positions in the bed. The thermocouple depth is variable to permit us to determine the radial temperature profile at three levels. The thermocouples at each level are randomly inserted at three different depths of 8, 17.5 and 25 mm.

3.1.2 Preparation of the Liquid Phase

For these experiments both de-ionized water and 2N sulfuric acid are used as the liquid phase. 2N sulfuric acid is prepared by diluting laboratory grade 95% sulfuric acid (2.8 litres of 95% H_2SO_4 to 47.2 litres of water). The strength of the diluted acid is measured by titration with a standard solution of analytical grade 0.1 N NaOH (titration method described in detail in Section 3.2). 50 litres of 2N acid are made up at a time.

The liquid phase passes through a glass liquid-air contactor that is made of 5 cm ID glass and is 1.22 m in length. As with the reactor, the saturator is built from three sections, two glass caps and a glass cylinder. The top cap contains a 6 mm connection for the liquid feed. Near the top of the main cylinder there is a 6 mm connection for the air inlet. The bottom cap contains a 6 mm connection where both the air and liquid exit. The main section of the saturator is filled to a height of 80 cm with 6 mm glass ballotini supported on a Teflon support screen. This is similar to the equipment used by Haure (1987) which was found to be adequate for saturation of the liquid phase with air. This saturator reduces the interference of mass transfer between the air and the water in the reactor.

The liquid and air exiting the liquid saturator are lifted via the air pressure in the saturator to the overhead gravity feed tank. For low temperature experiments the overhead feed tank was a Nalgene 10 litre poly-propylene jug. Currently a 23 litre borosilicate jug is used for two reasons. Firstly, poly-propylene is not very corrosion resistant to 80°C sulfuric acid. Secondly, it is necessary to heat the liquid to 80°C using a stirrer/hot plate. The overhead tank is supported six feet above the reactor. The overhead tank is open to the atmosphere and also functions as a liquid/air separator. A liquid overflow line is also provided near the top of the tank to ensure that a constant liquid head is maintained for

flow to the reactor. The liquid phase passes from the bottom of the overhead tank through a Teflon rotameter, which controls the liquid flow rate, into the top of the reactor. A peristaltic pump is used on occasions when the overhead feed tank does not provide enough head. This occurs for experiments at high gas and liquid flow rates. The liquid flow rate to the reactor is periodically turned on by energizing either the solenoid or the peristaltic pump on the liquid inlet line to the reactor. This action is controlled by a timer through the computer control system.

The overflow from the overhead tank flows into the top of a Nalgene 50 litre poly-propylene holding tank. This tank is filled with the liquid to be used during an experimental run. The liquid leaves the bottom of the holding tank and is pumped through a peristaltic liquid recirculation pump to the glass liquid phase saturator.

There was a small operational difference between low and high temperature experiments. For low temperature experiments, liquid from the holding tank is constantly circulated through the liquid saturator, into the overhead feed tank, out the overflow line (during periods of no liquid flow into the reactor), and back into the holding tank.

For 80°C experiments, during periods of no liquid flow, the liquid recirculates between the overhead tank and the saturator column only. In this way no hot dilute sulfuric acid comes into contact with the poly-propylene holding tank. During the period of liquid flow to the reactor, liquid is pumped from the holding tank through the liquid saturator and into the overhead feed tank in order to keep the overhead tank at its maximum level. This method also meant only 23 litres of liquid must be heated, not 73 litres.

3.1.3 Preparation of the Gas Phase

At 20°C the simulated flue gas phase consists of a mixture of 0.25 volume % SO₂, ≈2% water vapour, 5% O₂, 15% CO₂ with the remainder N₂. At 80°C the gas is 0.25 % SO₂, 5% O₂, 10% CO₂, 10% water vapour with the remainder N₂. These compositions were provided by the United States Department of Energy (U.S. D.O.E.) at the Pittsburgh Energy Technology Center (P.E.T.C.) who also provided funding for this research. The 80°C composition is representative of power plant stack gases.

At 20°C the dry gas mixture (without any SO₂) is saturated with water (this is the ≈2% water vapour) in a Plexiglas air-water saturation column of exactly the same dimensions as the liquid phase saturator. This saturator is packed with 80 cm of 12 mm poly-ethylene Rasching rings. The gas from the saturator then flows to a Plexiglas separation column which is 60 cm high. The gas with entrained water from the saturator then passes into the middle of the separator column. Saturated air leaves through a 6 mm port in the top and water flows out a 6 mm port in the bottom. Saturating the gas minimized any mass transfer occurring between the gas and the liquid phase once in the reactor. In this way only the absorption and reaction of SO₂ induced mass transfer. SO₂ is then added to the gas stream and this simulated flue gas is fed to the reactor.

In order to achieve 10% water vapour in the gas mixture for the 80°C experiments, the mixed dry gas (without any SO₂) is heated to approximately 120°C and superheated steam is injected. SO₂ is then added and the gas mixture passes on to the reactor. The gas is heated above 80°C because of heat losses before the reactor. Its temperature has dropped about 80°C by the time it reaches the catalyst bed. The reactor itself is heated with heating tape to maintain a wall temperature of 80°C.

The oxygen content is achieved by using air provided from the compressed air pipeline in the laboratory. All other gases are obtained in a purified bottled form supplied by Linde (Union Carbide of Canada Ltd.). The specifications for each gas is provided in Table 3.1

Table 3.1. Bottled Gas Grade and Quality

Gas	Nitrogen	Carbon Dioxide	Sulfur Dioxide
Grade	High Purity	Coleman Instrument	Anhydrous
Minimum Purity	99.997%	99.99%	99.98%
Maximum Moisture	10 ppm	N.A.	N.A.
Maximum Oxygen	10 ppm	N.A.	N.A.

All the gases (except steam) pass through 20 cm long by 5 cm I.D. Plexiglas tubes containing 8-12 mesh molecular sieves (Type 13X, grade 544, Matheson Coleman and Bell Manufacturing Chemists). Gas flows (except steam) are measured and controlled by a mass flow controller (model UFC-1200A, Unit Instrument Inc.). These mass flow controllers have an accuracy of $\pm 1\%$ of full scale at 273 K and 101.3 KPa. The controllers are capable of temperature compensation and their range of control is 2-100% of full scale. The mass flow controllers require a ± 15 volt power supply (model URS-100-1, Unit Instruments Inc.). The power supply can provide power and monitor or control up to 5 mass flow controllers. Either manual operation or automatic computer control can be selected for the set of mass flow controllers. Computer interfacing was accomplished by wiring the interface (Section 3.1.4) to a 34 pin connector, on the back of the power supply, which accepts a 0-5 volt D.C. setpoint signal, and 0-5 vdc flow signal

per channel (See Unit mass flow controller manual for specifics). The mass flow controllers are calibrated by the manufacturer. The calibration was verified using a wet test meter (model 63126, Precision Scientific) which has a guaranteed accuracy of $\pm 0.5\%$. Assuming that the gases behave ideally, the calibration was converted from volumetric to molar flow.

Steam flow for the high temperature experiments is controlled using a gas rotameter (tube number N102-05ST, Cole Parmer Instrument Company). This was calibrated by passing air through one of the mass flow controllers and then heating the air to 150°C (This is the temperature of the steam entering the system at 128.9 KPa absolute). From the rotameter reading the precise molar flow of steam is obtained.

3.1.4 Computer and Interface System

To monitor and control the system a model 386 SX computer is connected with a Sciometric Instruments Inc., interface system. The Sciometric interface contains enough room for 16 analog inputs, 8 analog outputs, and 8 digital outputs. This system allows us to monitor apparatus temperatures, mass flows and the reactor outlet SO_2 concentration (see Section 3.3.1 on the SO_2 analyzer). It also allows us to manipulate the mass flow controller set-points and switch the solenoids (see Sciometric operating manuals for details of wiring system).

The computer was programmed using Quick BASIC version 4.5 since Sciometric supplied all necessary subroutines for reading inputs and sending outputs in this language. The program consists of a section for displaying information to the computer screen, reading inputs, writing outputs to the mass flow controllers, timers for the solenoids, energizing

and de-energizing the solenoids and saving the inputs in an ASCII file (Programming followed instruction given in the Sciometric software manuals). One scan of all 16 analog inputs takes 4-5 seconds.

3.2 Catalyst

The catalyst is activated carbon, type BPL, produced by the Calgon Corporation, Pittsburgh. Data on the catalyst and the bed are presented in Table 3.2 and 3.3. Prior to use the carbon is boiled in de ionized water for about two hours to eliminate fines. The catalyst particles are then deposited sequentially in layers, compacted and vibrated from the outside of the reactor wall to achieve the bed porosity specified by the manufacturer. The bed is supported by a Teflon screen.

3.3 Equipment Operation Procedures

20°C Startup Procedure is as follows:

1. Open up the air to the liquid phase saturator.
2. Start the peristaltic recirculation pump.
3. Open all gas bottles and set the mass flow controllers to the desired flowrate (except for SO₂).
4. If the overhead feed tank provides sufficient head to feed liquid into the reactor at the desired flow rate, set reactor liquid phase feed rotameter to the desired liquid flow rate. If the overhead feed tank does not provide enough head pressure, fully open the reactor

Table 3.2: Properties of Activated Carbon Catalyst

Type:	BPL Calgon Corporation
Raw Material:	Bituminous Coal
Activation:	High Temperature Steam
Mesh Size:	4X6
average size in inches:	3.6 mm
Surface Area (BET method):	1050-1150 m ² /g
Particle Density (Hg displacement):	0.8 g/cm ²
Real Density (He displacement):	2.1 g/cm ³
Particle Porosity:	0.6
Bed Porosity:	.39

Table 3.3: Dimensions of Catalytic Bed

Cross Sectional Area	19.572 cm ²
Reactor Inside Diameter	4.992 cm
Height of Bed	19 cm
Volume of Bed	371.87 cm ³

liquid phase feed rotameter and set the peristaltic feed pump to the desired liquid flow rate. (Set the liquid flow rate with the gas passing through the reactor, this makes sure the bed is fully wetted)

5. Calibrate the SO₂ Analyzer

6. Open the three way valve such that the reactor gas outlet passes to the analyzer.
7. Set the SO₂ mass flow controllers to the desired flow rates.
8. Turn on the water flow to the air-water saturator.
9. Start the computer timer for the solenoid valve switching.

80°C Startup Procedure was as follows:

1. Open up the air to the liquid phase saturator. The liquid in the overhead feed tank must be heated up to 80°C using a Corning Vycor 1100 Watt immersion heater and the Corning Model 520 stirrer/hot plate. Once the liquid is at temperature the immersion heater is shut off.
2. Start the peristaltic recirculation pump.
3. Open all gas bottles and set the mass flow controllers to the desired flowrate (except for SO₂). Turn on the gas heaters and the steam superheater and set the steam flow using the steam rotameter.
4. If the overhead feed tank provides sufficient head pressure to feed liquid into the reactor at the desired flow rate, set reactor liquid phase feed rotameter to the desired liquid flow rate. If the overhead feed tank does not provide enough head pressure, fully open the reactor liquid phase feed rotameter and set the peristaltic feed pump to the desired liquid flow rate. (Set the liquid flow rate with the gas passing through the reactor, this makes sure the bed is fully wetted)
5. Calibrate the SO₂ Analyzer
6. Open the three way valve such that the reactor gas outlet passes to the analyzer.

7. Set the SO₂ mass flow controllers to the desired flow rates.
8. Start the computer timer for the solenoid valve switching.

The equipment is operated for at least 3 hours before sampling begins to ensure that reproducible cycling has been reached. All the liquid from a liquid flush is collected and shaken to ensure the sample is well mixed. The sample is then analyzed for total acidity and sulfurous acid concentration. When three consecutive samples give the same total acidity result (within ± 0.05 ml of titrant) the system is said to be at a cycling invariant state.

The liquid outlet (liquid product) is collected in a 20 litre capacity Nalgene polyethylene container. The liquid is neutralized with NaOH before disposal. After three hours the liquid product is collected in 1 or 5 litre polyethylene bottles (depending on the quantity of liquid flowing per cycle) which have lids to prevent vapour loss. The liquid product is analyzed immediately to determine the sulfuric and sulfurous acid concentration.

The shutdown procedures differed slightly:

20°C Shutdown Procedure

1. Turn off the solenoid timer.
2. Turn off the SO₂ mass flow controller.
3. Let the system run for an additional 15 minutes in this configuration to purge the system of SO₂.
4. If on, turn off the liquid phase feed pump. Close the liquid rotameter to the reactor.
5. When the bed is drained, turn off all gas flows to the reactor.
6. Turn off the water and air to the two saturators.
7. Turn off the recirculation pump.

80°C Shutdown Procedure

1. Turn off the solenoid timer.
2. Turn off the SO₂ mass flow controller.
3. Let the system run for an additional 15 minutes in this configuration to purge the system of SO₂.
4. If on, turn off the liquid phase feed pump. Close the liquid rotameter to the reactor.
5. When the bed is drained, turn off all gas flows to the reactor. Turn off the gas heaters and the steam superheater.
6. Turn off the water and air to the two saturators. Also shut off the hot plate/stirrer.
7. Turn off the recirculation pump.

3.4 Analysis Methods

Two methods of analysis are used. The first method measures the reactor outlet SO₂ concentration using a U.V. gas analyzer. The second method measures the product liquid sulfuric and sulfurous acid concentrations by wet chemistry methods.

Using the results from these two methods, both the removal and the conversion of SO₂ were calculated. The double measurement also permitted a S balance to be made.

3.4.1 SO₂ Gas Analyzer

In order to more accurately measure SO₂ removal from the gas stream, a Western Research model 721AT Sulfur Dioxide Analyzer was used. This analyzer incorporates a dual cell, split beam measuring and detection method using a single radiation source, and provides a continuous SO₂ reading in ppm. The analyzer also contains a 0-5 vdc output that was wired to the interface and monitored by the computer.

The accuracy and sensitivity is typically $\pm 0.5\%$ of full scale. It requires a gas sample at non-condensing conditions at a rate of 1-2 litres/min. The analyzer also needs to be calibrated every 24 hours of continuous operation or at each start-up, with both a zero and a span gas. Calibrating must occur at the same pressure as the analyzer is very sensitive to changes in pressure. It was these requirements that necessitated the fairly complex gas analysis system (Figure 3.4).

As previously mentioned, the analyzer must be calibrated upon start-up. The zero gas used is nitrogen of the same composition as in Table 3.1. The full scale range of the gas analyzer was 5000 ppm. The span gas specified by the manufacturer of the analyzer was one half of full scale (a special analyzed gas mixture was ordered from Linde to contain 2500 ppm SO_2 in High Purity N_2).

A three-way valve is used to select first the zero and then the span gases. The gas then passes through a needle valve which is used in combination with the needle valve just before the vacuum pump to control the pressure and the gas flow rate in the analyzer. The gas then passes through another three way valve which is used to select either the calibration gases, or the outlet gas from the reactor. After passing through the three way valve the gas flows through the analyzer, through a flow meter and into the vacuum pump. The vacuum pump was necessary as the reactor is essentially at atmospheric pressure and there is not enough driving force to get the required flow through the analyzer. A mercury manometer is used just after the analyzer in order to get accurate pressure measurements. The analyzer is operated precisely at atmospheric pressure. After the instrument was calibrated and if there is gas flow through the reactor, the second three way valve was switched to sample gas from the reactor. On the gas outlet from the

reactor there is another valve, not shown in Figure 3.4, before the three-way valve that is used for pressure and flow control.

For the experiments at 20 °C, it is not necessary to dry the gas before the analyzer. However, for experiments conducted at 80 °C, the gas exiting the reactor appeared to be saturated with water. Water droplets formed inside uninsulated Teflon tubing on the reactor outlet. Therefore in order to prevent water from condensing in the gas analyzer cell, the entire gas stream from the reactor was cooled by passing it through two 25 cm tall 5 cm I.D. glass separation vessels. The gas entered in the middle of these columns through 6 mm connections and exited out the top. Condensed water was collected in the bottom. These separators were placed in an ice bath to reduce the dew point of the gas before it entered the analyzer system.

Figure 3.4. Sampling system for SO₂ analyzer

3.4.2 Wet Chemistry Analysis

The method used to determine the sulfuric acid concentration in the liquid outlet is described by Hartmann and Coughlin (1972). The product contains both sulfuric and sulfurous acid so a simple pH determination is inadequate. The sulfuric acid concentration was determined by subtracting the sulfurous determination from the total acidity.

Titration were duplicated in order to verify the results. All titrations were carried out using a Mettler model DL25 auto-titrator.

3.4.2.1 Total Acidity Determination

This method involves first adding 30% of analytical grade hydrogen peroxide to a liquid product sample. The H_2O_2 oxidizes all the dissolved SO_2 in the sample.

The sample was then titrated with 0.1 or 1 N NaOH, depending on the sulfuric acid strength of the liquid used to flush the reactor, using the autotitrator. Sample sizes varied between 20 and 50 ml. As a blank titration a sample of the feed solution was used. Typical variation of the autotitrator was ± 0.05 ml of titrant. Calculation of variation is given in Appendix A.

2

of

2

3.4.2.2 Sulfurous Acid Determination

For this titration 50 ml of sample were titrated with 0.025 mole/L using starch as an indicator. The reaction occurring was:

Special care was taken to protect the iodine solution from light nevertheless, concentration of the iodine solution was checked daily by titrating a 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution. The typical variation between duplicate titrations was ± 0.3 ml. Sample calculations for the wet chemistry methods are shown in Appendix B.

3.4.3 SO_2 Removal and Conversion Calculations

It is necessary to differentiate between removal and conversion since all the SO_2 removed from the gas stream is not converted to sulfuric acid. Removal is defined as the difference between the number of moles of SO_2 scrubbed from the gas stream, divided by the total number of moles of SO_2 in the reactor inlet gas. Conversion is defined as the number of moles of sulfuric acid created divided by the total number of moles of SO_2 scrubbed from the inlet gas.

3.4.3.1 SO_2 Removal

The removal of SO_2 is based on the total number of moles of SO_2 entering the reactor during a cycle and the amount exiting the reactor as measured by the SO_2 gas analyzer. It

can also be calculated based on the amount of SO₂ entering and the amount leaving in the product liquid as both sulfurous and sulfuric acid.

The % of SO₂ removed can be calculated by:

$$\frac{y_{\text{SO}_2\text{i}} - y_{\text{SO}_2\text{o}}}{y_{\text{SO}_2\text{i}}} \times 100 \quad (3.1)$$

where, $y_{\text{SO}_2\text{i}}$ = the SO₂ reactor inlet gas concentration

$y_{\text{SO}_2\text{o}}$ = the SO₂ reactor outlet gas concentration

or by using the total acidity determination:

$$\frac{C_{\text{TA}} \cdot Q_{\tau}}{F_{\text{SO}_2\text{i}}} \times 100 \quad (3.2)$$

where, C_{TA} = the increase in the product total acidity concentration $\equiv$ (mol / L)

Q_{τ} = the total volumetric flow of liquid per cycle $\equiv$ (L / cycle)

$F_{\text{SO}_2\text{i}}$ = the molar flow of SO₂ into the reactor per cycle $\equiv$ (mol / cycle)

3.4.3.2 SO₂ Conversion

Again there were two possible methods for calculating % conversion. The first method is:

$$\frac{(y_{\text{SO}_2\text{o}} - y_{\text{SO}_2\text{i}}) \cdot F_{\text{g}} - C_{\text{H}_2\text{SO}_3} Q_{\text{l}}}{F_{\text{SO}_2\text{i}}} \times 100 \quad (3.3)$$

where, $C_{\text{H}_2\text{SO}_3}$ = the sulfurous concentration in the liquid product

The second way to calculate the % conversion is:

$$\frac{C_{\text{H}_2\text{SO}_4} \cdot Q_{\tau}}{F_{\text{SO}_2\text{i}}} \times 100 \quad (3.4)$$

3.4.3.3 Sulfur Balance

Sulfur balance is a means of assessing the accuracy of the experimental system. The concentration of SO_2 in the scrubber outlet was measured by the UV gas analyzer. Then using Equation 3.1, the removal was determined. The total acidity determination was used to determine the quantity of sulfur in the liquid product. Using Equation 3.2 the removal could again be determined. Comparing the removal found from these two methods enabled us to close the sulfur mass balance.

4.0 Experimental Design

The purpose of the experiments conducted at 20°C was to determine which manipulated variables affect the following responses, SO₂ removal, conversion of the SO₂ removed and sulfuric and sulfurous acid concentrations. SO₂ conversion as defined in Section 3.4.3 is dependent on removal since only the SO₂ removed from the gas is converted to sulfuric acid. The objective here is to increase the conversion of the SO₂ removed from the gas stream. Also, as part of these experiments, the pressure drop across the reactor and the temperature profile of the reactor were measured.

From past work by Haure et al.(1989), the important manipulated variables are expected to be the acid strength of the flushing liquid, the flushing liquid velocity, the gas velocity, the cycle length and the duration of liquid flushing.

Experiments conducted at 80°C used the same variables and responses but were chosen based on a factorial design.

4.1 Low Temperature Experiments

The experiments at 20°C were conducted in order to determine which of the above five manipulate variables have the greatest effect on the desired responses.

4.1.1 Experimental Layout

Since five manipulated variables are used in this experimental plan, a two-level factorial design was chosen. Each level consists of a high and a low level of each manipulated variable. Table 4.1 shows the range and the variables studied. The factorial design chosen was a 2^{5-1} of resolution V. This results in a total of 16 experiments plus 8 replicates in order to estimate the experimental variance. Resolution V means that single factor interactions are confounded with four factor interactions, and two factor and three factor interactions are confounded. The order in which each experiment was run was randomized. The settings of the five different variables for each of the 24 experiments are illustrated in Table 4.2.

Table 4.1: Levels of Variables studied in Factorial Experiments

Variables	Low Value "-"	High Value "+"
1-Space Velocity (v_g)	1000 cc•cc ⁻¹ •hr ⁻¹	2850 cc•cc ⁻¹ •hr ⁻¹
2-Liquid Velocity (v_l)	0.2 cm•s ⁻¹	1.0 cm•s ⁻¹
3-Period (τ)	5 minutes	30 minutes
4-Flush Duration (D)	0.5 minutes	3 minutes
5-Flush Liquid (A)	De ionized Water	2.0 N H ₂ SO ₄

Due to practical considerations in conducting the experiments, it was not possible to randomize liquid phase composition, since it took a day to clean out the system before changing the reactor inlet liquid sulfuric acid concentration. The experiments were therefore carried out in 2 blocks where each block corresponded to a particular liquid

composition. Each block consisted of 8 runs with 4 replicates. Where a replicate experiment was conducted (in order to estimate the experimental variance), the responses were averaged and are displayed as a single result (shown later in Section 6.0).

Table 4.2: Conditions for each experiment

Run #	Variables				
Block A	v_a	v_l	τ	A	D
A12	-	-	-	-	+
A5, A6	+	-	-	-	-
A4, A8	-	+	-	-	-
A7	+	+	-	-	+
A3, A10	-	-	+	-	-
A9	+	-	+	-	+
A2, A11	-	+	+	-	+
A1	+	+	+	-	-
Block B					
B5	-	-	-	+	-
B9	+	-	-	+	+
B11	-	+	-	+	+
B12	+	+	-	+	-
B6, B8	-	-	+	+	+
B2, B7	+	-	+	+	-
B3, B4	-	+	+	+	-
B1, B10	+	+	+	+	+

4.1.2 Factorial Design Data Interpretation

Within each block of experiments the main effect of each variable can be calculated as the difference between the average of the response at the high value of the variable and the average at the low value of the variable.

$$EFFECT = \overline{y_+} - \overline{y_-}$$

The effect of each variable on a response was determined by using the Yate's algorithm.

The variance of each effect is given by:

$$\text{Var}(EFFECT) = \frac{s^2}{2}$$

The variance of an observation, is estimated from the replicates in the first set of experiments. The significance of an effect was determined by both a 95% confidence interval and a probability plot (Yate's algorithm and significance test calculations are shown in Appendix D).

4.2 High temperature Experiments

The number of manipulated variables were reduced for the 80°C experiments. The liquid superficial velocity was set at 0.2 cm/s and the flush duration was set at 3 minutes when the cycle length was 30 minutes, and 6 minutes when the cycle was 60 minutes long. The

levels of the manipulated variables are shown in table 4.3. The responses were the same as those used at low temperatures. These experiments were not run according to a factorial design but as a test to see if there would be an improvement if the system were run at higher temperatures. A total of 9 experiments were conducted.

Table 4.3 Level of variable studied at high temperature

Variables	Low Value	High Value
1-Space Velocity(v_s)	1000 cc•cc ⁻¹ •hr ⁻¹	2850 cc•cc ⁻¹ •hr ⁻¹
2-Cycle Length (τ)	30 minutes	60 minutes
3-Flush Liquid(A)	De ionized Water	2.0 N H ₂ SO ₄

5.0 Scrubber Model

The mean behaviour of the periodically operated trickle bed can be modeled using a plug flow, adiabatic representation. Although this model will not reproduce the time behaviour for switching liquid flows on and off, it is capable of estimating the SO_2 removal, the conversion to sulfuric acid and the pressure drop.

Two versions of the model are developed below. Both will be used to convert the experimental measurements into the predicted bed height for 95% removal from the simulated stack gas. The classical Ergun model will be used to estimate pressure drop for 95% removal.

5.1 Model Development

Development begins with O_2 and SO_2 transport to the porous, liquid filled active carbon particle.

Figure 5.1. Mass Transfer Around a Catalyst Particle

Figure 5.1 shows mass transport around a particle of carbon catalyst. Within the carbon particle,

Since the particle diameter (d_p) is much larger than the film on the surface (Δz liquid) diffusion of oxygen and sulfur dioxide within the particle is important. However, if it is assumed that there is a large stoichiometric excess of water, diffusion of water can be neglected. The diffusion of sulfuric acid is only important during flushing. Figure 5.2 shows the concentration profiles of oxygen and sulfur dioxide for this system.

Figure 5.2. O_2 and SO_2 concentration profiles around a catalyst particle

We assume that the transport of oxygen and its consumption is rate controlling due to low solubility of oxygen in water and sulfuric acid. This is probably a valid assumption at high sulfur dioxide conversion or high sulfur dioxide concentration in the feed gas. Figure 5.3 shows the expected concentration profile of sulfuric acid within a carbon catalyst particle.

Figure 5.3. Sulfuric Acid Concentration in a Catalyst Particle

Assuming that Henry's Law applies for both oxygen and sulfur dioxide, then

$H_{SO_2} \gg H_{O_2}$, where H_i is the Henry's Law constant for substance i , consequently, $x_{SO_2} \gg x_{O_2}$, where x_i the mole fraction of substance i in the liquid phase, even though $P_{O_2} \gg P_{SO_2}$, where P_i is the partial pressure of substance i in the gas phase.

Assuming the oxidation of sulfur dioxide is first order in oxygen and sulfur dioxide (when mass transfer interference is absent)

$$-r = k_m \rho_p x_{SO_2} x_{O_2} \quad 5.1$$

Since $x_{SO_2} \gg x_{O_2}$ it is possible to neglect variations of x_{SO_2} in the particle, therefore using the cylindrical pore model as a basis

$$D_{O_2} \frac{d^2 x_{O_2}}{dz^2} = r \quad 5.2$$

$$\text{B.C.1 } z = 0; x_{O_2} = x_{O_2,0} \quad 5.3$$

$$\text{B.C.2 } z = L; \frac{dc}{dz} = 0 \quad 5.4$$

$$D_{O_2} \frac{d^2 x_{O_2}}{dz^2} = (k_m \rho_p x_{SO_2}) x_{O_2} \quad 5.5$$

This is a conventional first-order case

$$\Phi_L = \frac{d_p}{2} \left(\frac{k_m \rho_P x_{SO_2}}{D_{O_2}} \right)^{1/2} \quad 5.6$$

$$\eta = \frac{\tanh \Phi_L}{\Phi_L} \approx \frac{1}{\Phi_L} \quad 5.7$$

$$\therefore r = k_m \rho_P \eta x_{SO_2} x_{O_2} \quad 5.8$$

$$r = \frac{(k_m \rho_P D_{O_2} x_{SO_2})^{1/2} x_{O_2}}{d_p / 2} \quad 5.9$$

Now allowing for a gas phase and a liquid film resistance to oxygen transport

$$\begin{aligned} N_{O_2} &= \text{flux of oxygen into particle / unit bed volume} \\ &= (k_g a)_{O_2} (P_{O_2} - H_{O_2} (x_{O_2})_1) \quad 5.10 \end{aligned}$$

$$= (k_l a)_{O_2} ((x_{O_2})_1 - (x_{O_2})_P^0) \quad 5.11$$

$$= r(1 - \epsilon) \quad 5.12$$

Eliminating $(x_{O_2})_P^0$, $(x_{O_2})_1$ and substituting $P_{O_2}/H_{O_2} = x_{O_2}$

$$N_{O_2} = \frac{P_{O_2}}{\frac{1}{(k_g a)_{O_2}} + \frac{H_{O_2}}{(k_l a)_{O_2}} + \frac{H_{O_2}}{(k_m \rho_P D_{O_2})^{1/2} (1 - \epsilon) x_{SO_2}^{1/2}}} \quad 5.13$$

Considering the co-current flow of liquid and gas in a trickle bed (Figure 5.4), but neglecting draining and filling behaviour

Figure 5.4. Flow of Gas and Liquid Co-currently Through Reactor

Assuming that the variation of P_{O_2} is small and can be neglected such that

$$M_{SO_2} = y_{SO_2} \frac{P v_g A_x}{RT} \quad 5.14$$

where M_{SO_2} = molar rate of SO_2 through the column

v_g = gas superficial velocity

A_x = column cross sectional area

P = total pressure

R = gas constant

therefore,

$$-\frac{P v_g}{RT} \frac{\partial y_{SO_2}}{\partial w} - N_{SO_2} = 0 \quad 5.15$$

By stoichiometry $N_{SO_2} = 2N_{O_2}$

It is possible to simplify the analysis by looking at two limiting cases;

- 1) Resistance for O_2 transport » Resistance for reaction in carbon particle and
- 2) Surface catalytic reaction controls

5.2 Quantitative Development for Oxygen Transport Controlling

The molar flux of oxygen is equal to

$$N_{O_2} = k_{app} P_{O_2}$$

where, k_{app} = the overall resistance to mass transfer and is equal to

$$k_{app} = \frac{1}{\frac{1}{(k_g a)_{O_2}} + \frac{H_{O_2}}{(k_l a)_{O_2}} + \frac{H_{O_2}}{(k_m \rho D_{O_2} x_{SO_2})^{1/2} (1 - \epsilon)}} \quad 5.13$$

negligible since mass
transfer controls

Substituting and letting $P_{O_2} = P y_{O_2}$

$$-\frac{\partial y_{SO_2}}{\partial w} = \frac{RT}{P v_g} (2 k_{app} P y_{O_2}) \quad 5.16$$

Integrating from $w=0$ to $w=z$

$$(y_{SO_2})_o - (y_{SO_2})_i = -\frac{2RTk_{app}y_{O_2}z}{v_g} \quad 5.17$$

$$k_{app} = \frac{\Delta y_{SO_2} v_g}{2RT y_{O_2} z} \quad 5.18$$

where, y_{SO_2} is measured from experiments

rearranging for bed height

$$z = \frac{0.95(y_{SO_2})_i v_g}{2RTk_{app}y_{O_2}} \quad \text{for 95\% removal} \quad 5.19$$

a sulfuric acid balance leads to the equation

$$(x_{\text{H}_2\text{SO}_4})_o = (x_{\text{H}_2\text{SO}_4})_i + \frac{0.95(y_{\text{SO}_2})_i v_g}{v_l} b \quad 5.20$$

$$\text{where, } b = \frac{P}{RT} X_{\text{SO}_2}$$

X_{SO_2} = conversion of sulfur dioxide to sulfuric acid

v_l = mean liquid velocity(time averaged)

5.3 Quantitative Development for when Surface Reaction Controls

In this case,

$$(x_{\text{SO}_2})^{1/2} = \left(\frac{y_{\text{SO}_2} P_T}{H_{\text{SO}_2}} \right)^{1/2} \quad 5.21$$

$$N_{\text{O}_2} = \frac{\frac{P^{3/2}}{(H_{\text{SO}_2})^{1/2}} y_{\text{SO}_2}^{1/2} y_{\text{O}_2}}{\frac{\left(\frac{P}{H_{\text{SO}_2}} \right)^{1/2} y_{\text{SO}_2}^{1/2}}{(k_g a)_{\text{O}_2}} + \frac{H_{\text{O}_2} \left(\frac{P}{H_{\text{SO}_2}} \right)^{1/2} y_{\text{SO}_2}^{1/2}}{(k_l a)_{\text{O}_2}} + \frac{H_{\text{O}_2}}{(k_m \rho_P D_{\text{O}_2})^{1/2} (1 - \epsilon)}} \quad 5.22$$

negligible since oxidation

resistance controls

$$N_{\text{O}_2} = k'_{\text{app}} y_{\text{SO}_2}^{1/2} P_{\text{O}_2} \left(\frac{P}{H_{\text{SO}_2}} \right)^{1/2} \quad 5.23$$

$$-\frac{\partial y_{\text{SO}_2}}{\partial w} = \frac{2RT}{P v_g} \frac{P^{3/2}}{(H_{\text{SO}_2})^{1/2}} k'_{\text{app}} y_{\text{O}_2} y_{\text{SO}_2}^{1/2} \quad 5.24$$

or

$$\frac{\partial (y_{\text{SO}_2}^{1/2})}{\partial w} = -\frac{RT}{v_g} \left(\frac{P}{H_{\text{SO}_2}} \right)^{1/2} k'_{\text{app}} y_{\text{O}_2}$$

Integrating yields

$$(y_{SO_2})_o^{1/2} - (y_{SO_2})_i^{1/2} = -\frac{RT}{v_g} \left(\frac{P}{H_{SO_2}} \right)^{1/2} k'_{app} y_{O_2} z \quad 5.25$$

$$k'_{app} = \frac{(y_{SO_2})_o^{1/2} - (y_{SO_2})_i^{1/2} v_g}{RT \left(\frac{P}{H_{SO_2}} \right)^{1/2} y_{O_2} z} \quad 5.26$$

Rearranging for z in Equation 5.26 can be used to estimate the bed height for 95% removal. For both of these limiting equations they are used by first calculating k'_{app} from the experimental data and then using this to estimate the bed height (Appendix B: Sample Calculations).

5.4 Pressure Drop Model

Pressure drop was estimated by using the Ergun equation

$$\frac{\Delta P}{L} = A \frac{\epsilon_{bed}^2}{(1 - \epsilon_{bed})^3} \frac{\mu_g v_g}{d_p^2} + B \frac{\epsilon_{bed}}{1 - \epsilon_{bed}} \rho_g \frac{v_g^2}{d_p} \quad 5.27$$

where, A and B are constants that can be estimated from experimental data

ϵ_{bed} = bed porosity

d_p = mean particle size

L = bed depth

In this report, ΔP is estimated at 95% removal for conditions identical to those used for the measurements. Thus, the right hand side of equation 5.27 is consistent.

5.5 Comments

The effect of space velocity on performance can be predicted from Equations 5.19, 5.25 and 5.27. All these expressions contain v_g . Note that bed height for 95% SO_2 removal is directly proportional to space velocity (v_g^{-1}), but P/L is a function of v_g where $1 < \alpha < 2$.

The model in principle can predict the effect of temperature on bed height through the H_{O_2} , $k_g a$, $k_l a$ terms in Equation 5.13 or through k_{app} , H_{SO_2} , H_{O_2} , D_{O_2} terms in Equations 5.22 and 5.26. The d_p and ϵ dependence is also given through Equations 5.22. There are also d_p and ϵ dependencies embedded in expressions for $k_g a$ and $k_l a$. Thus scale-up can be examined. Such extrapolation is probably not warranted until further data are collected permitting evaluation of the k_{app} , $k_g a$ and $k_l a$ terms.

6.0 Results and Discussions

A sample calculation is contained in Appendix B with the raw data from the experiments conducted for this study contained in Appendix C. The discussion of the results consists of 5 sections. The first section compares the results of periodic and steady state experiments. The steady state experiments were conducted by Wahyu Hasokowati and the results presented here are provided with her permission (Hasokowati M.A.Sc Thesis 1992). Steady state measurements were not part of our subcontract with RTI, and were funded from Canadian sources. Both steady state and periodic experiments were conducted using the same equipment. The second section deals with the interpretation of the 20°C factorial design experiments. The third section looks at the few 80°C experiments while the fourth section considers the predicted pressure drop and bed height required for 95% removal of SO₂ to be achieved. The final section looks at the temperature profiles measured within the reactor bed and the outlet concentration of SO₂ for both the low and high temperature experiments.

6.1 Comparing Periodic and Steady State

The difference between periodic and steady state operation is the fact that under steady state operation the liquid flow over the reactor bed is continuous while in periodic operation the liquid flow is periodic. The comparisons are between data collected when the liquid to flush the reactor was de ionized water.

Figure 6.1 and 6.2 compares the percent removal of SO₂ versus superficial liquid velocity. For periodic operation the superficial liquid velocity is a time averaged value. Figure 6.1 is at a gas space velocity of 1000 scc/cc·hr and Figure 6.2 at 2850 scc/cc·hr.

The steady state and periodic data appear to form a single data population. Both these figures show an increase in removal with an increase in liquid flow. It is evident that steady state operation achieves much higher removals. This is because normal liquid flow is much greater than for periodic operation. The spread in removal for the periodic operation data, at a superficial liquid velocity of 1 mm/s at the low gas velocity, is due to different combinations of period, flush duration and liquid flow per cycle which result in the same time average superficial liquid velocity. From this it is concluded that the combination of period, flush duration and liquid flow used in the experiments were not optimal. Where the data overlap at a superficial liquid velocity of 1 mm/s at the low gas velocity, and at roughly 7 mm/s at the high gas velocity the, % removal under periodic operation is below that achieved at steady state.

The comparison the conversion of SO_2 removed from the gas stream shows that periodic operation results in higher conversion to sulfuric acid of the SO_2 removed at very low time averaged liquid superficial velocities. This was expected since continuous liquid flow decreases interference to the transport of O_2 to the catalyst resulting in higher conversions for periodic operation. Figure 6.3 and 6.4 are for the low and high gas flow rates respectively. Once again steady state and periodic data are compared. At the low gas velocity, a minimum in conversion with liquid superficial velocity is seen for the steady state data (Figure 6.3). In fact both the periodic and steady state data appear to be continuous.

The minimum has been explained by Haure (1989) as follows, at low liquid velocities the catalyst is not completely wetted, therefore there is reduced mass transfer interference to O_2 transport. As the liquid flow increases, there is increased mass transfer interference as more and more of the catalyst surface becomes liquid covered. At a certain point

Figure 6.1: Periodic and Steady State SO₂ Removal at Various Superficial Liquid Velocities ($v_g = 1000$ scc/cc-hr)

Figure 6.2: Periodic and Steady State SO₂ Removal at Various Superficial Liquid Velocities ($v_g = 2850$ scc/cc·hr)

Figure 6.3: Periodic and Steady State SO_2 Conversion at Various Superficial Liquid Velocities ($v_g = 1000$ scc/cc-hr)

Figure 6.4: Periodic and Steady State SO₂ Conversion at Various Superficial Liquid Velocities ($v_g = 2850$ scc/cc-hr)

however, the mass transfer interference is reduced due to increasing liquid turbulence. At the low gas velocity, conversion for periodic operation is higher than for steady state at very low time averaged liquid flow.

It can be seen from Figure 6.3 that the minimum is not pronounced. The difference between this data and that collected by Haure (1989) is that Haure's measurements were made at between 0.8 and 2.2% by volume SO_2 in air (most were at 1.3%) and whereas SO_2 concentrations were almost ten fold less in our present studies. On the other hand oxygen concentrations were only one quarter that used by Haure. We speculate that the less pronounced minima may have been the result of a shift in rate controlling step from oxygen transport to reaction rate between the dissolved species.

In Figure 6.4 there is no minima in the steady state data; instead it appears that increasing the liquid flow rate increases conversion. The periodic and steady state data appear to be consistent, however, the combined data does exhibit a minimum. It should be noted that when the time averaged liquid velocity in periodic operation was increased above 6, a higher conversion was achieved which is in line with the steady state data points. Again at very low time averaged liquid flow rates the conversion of the SO_2 removed during periodic operation is much higher than can be achieved with steady state operation.

Figure 6.5 and 6.6 show the decrease in sulfuric acid concentration with increased liquid flow at low and high gas space velocities respectively. Both periodic and steady state data are shown and form a continuous curve. In these Figures, an advantage of periodic operation is evident. Much higher sulfuric acid concentrations can be achieved with periodic rather than steady state operation. In steady state operation, it is not possible to reduce the liquid flow below a certain point without the liquid flow becoming

maldistributed and therefore reducing removal. With periodic operation a higher liquid flow can be used, but since it is only for a short portion of the cycle, the time average liquid flow can be much lower than can be achieved with steady state.

Finally, Figure 6.7 and 6.8 are plots of sulfurous acid concentration versus liquid superficial velocity at low and high gas space velocities respectively. The steady state data seem to indicate that with increased liquid flow the concentration of sulfurous acid is reduced. The periodic operation data show no clear trend. The lower sulfurous acid concentrations for periodic operation are consistent with lower SO₂ removals as seen in Figure 6.1 and 6.2. The reasons for this are explained above.

6.2 Factorial Design Interpretation

As was mentioned in the section 4 of this appendix, the effects of the variables and their interactions were calculated using the Yate's Algorithm. The main effect is the average of the response at the high value of the variable and the average at the low value of the variable. The significance of an effect was then determined by using a statistical significance test after calculating the estimated standard error of an effect from the replicates. Both a confidence interval and a probability plot were used to determine the significance of an effect. The calculations using the Yate's algorithm and the significance tests are shown in Appendix D. A 95 % confidence interval was chosen to determine the effect on the responses of conversion and product sulfuric acid strength, while a 99% confidence interval was chosen to determine the effect on the responses of removal and

Figure 6.5: Periodic and Steady State Product Sulfuric Acid Concentraions
at Various Superficial Liquid Velocities ($v_g = 1000$ scc/cc-hr)

Figure 6.6: Periodic and Steady State Product Sulfuric Acid Concentraions at Various Superficial Liquid Velocities ($v_g = 2850$ scc/cc·hr)

Figure 6.7: Periodic and Steady State Product Sulfurous Acid Concentraions at Various Superficial Liquid Velocities ($v_g = 1000$ scc/cc·hr)

Figure 6.8: Periodic and Steady State Product Sulfurous Acid Concentraion
at Various Superficial Liquid Velocities ($v_g = 2850$ scc/cc-hr)

product sulfurous acid strength. A different confidence interval was chosen so that the two significance tests (confidence interval and probability plot) would be in closer agreement.

Table 6.1 shows the position of the manipulated variables ("-1" means low value, "1" means high value of that variable as given in Table 4.1) and the measured responses for each experiment in the factorial design.

6.2.1 SO₂ Removal

The average removal for all the factorial experiments was 26.7%. The significant variables affecting SO₂ removal are:

Single Factor Effects

The cycle period (τ): the period had the most significant effect. The average effect was to decrease the removal by 24.4% between the 5 and the 30 minute cycle lengths.

Increasing the period therefore reduces the removal. This would seem to indicate that with longer exposure to the flue gas, the catalyst is becoming loaded with SO₂ and that all the SO₂ is not removed during the liquid flushing part of the cycle.

The flushing liquid sulfuric acid concentration (A): increasing the flushing liquid acid concentration from 0 to 1 Molar had the average effect of decreasing the removal by 16.2%. Removal is therefore best when the liquid phase acid concentration is low.

The gas space velocity (v_g): in moving from the low to the high gas velocity the average effect was to decrease the removal by 15.6%. Increasing the gas velocity therefore had a detrimental effect on the removal.

Table 6.1: Results of Factorial Experiments

Block A - Flushing Liquid is Pure Deionized Water

Experiment #	v_a	v_i	τ	A	D	Removal	Conversion of SO ₂ Removed	Sulfurous Acid Concentration mol/L	Sulfuric Acid Concentration mol/L
12	-	-	-	-	+	75.35	30.44	2.480×10^{-3}	1.090×10^{-3}
5, 6	+	-	-	-	-	9.18 ± 0.52	44.28 ± 3.86	$4.600 \pm 0.05 \times 10^{-3}$	$3.655 \pm 0.565 \times 10^{-3}$
4, 8	-	+	-	-	-	50.33 ± 0.09	41.15 ± 5.77	$1.685 \pm 0.175 \times 10^{-3}$	$1.175 \pm 0.155 \times 10^{-3}$
7	+	+	-	-	+	73.34	31.09	1.390×10^{-3}	6.30×10^{-4}
3, 10	-	-	+	-	-	12.96 ± 1.52	90.67 ± 1.25	$2.095 \pm 0.45 \times 10^{-3}$	$2.0375 \pm 0.286 \times 10^{-2}$
9	+	-	+	-	+	10.10	78.60	1.780×10^{-3}	6.530×10^{-3}
2, 11	-	+	+	-	+	37.96 ± 3.51	57.62 ± 5.61	$9.05 \pm 0.55 \times 10^{-4}$	$1.225 \pm 0.225 \times 10^{-3}$
1	+	+	+	-	-	3.67	38.59	2.320×10^{-3}	1.460×10^{-3}

Block B - Flushing Liquid is 1 mole/L Sulfuric Acid

5	-	-	-	+	-	14.49	69.91	1.260×10^{-3}	2.920×10^{-3}
9	+	-	-	+	+	15.90	45.28	1.340×10^{-3}	1.110×10^{-3}
11	-	+	-	+	+	53.70	48.32	2.50×10^{-4}	2.30×10^{-4}
12	+	+	-	+	-	13.53	72.65	5.40×10^{-4}	1.450×10^{-3}
6, 8	-	-	+	+	+	16.29 ± 0.15	77.06 ± 2.09	$1.100 \pm 0.06 \times 10^{-3}$	$3.715 \pm 0.225 \times 10^{-3}$
2, 7	+	-	+	+	-	4.92 ± 0.17	94.40 ± 0.10	$1.285 \pm 0.105 \times 10^{-3}$	$2.213 \pm 0.176 \times 10^{-2}$
3, 4	-	+	+	+	-	13.76 ± 2.34	88.11 ± 1.70	$5.85 \pm 0.05 \times 10^{-4}$	$4.335 \pm 0.835 \times 10^{-3}$
1, 10	+	+	+	+	+	10.80 ± 0.79	61.05 ± 2.70	$7.05 \pm 0.05 \times 10^{-4}$	$1.100 \pm 0.12 \times 10^{-3}$

The flush duration (D): the average effect was to increase in the removal by 15.2% between 0.5 and 3 minute flush duration. Therefore, in order to increase removal, the flush duration should be increased.

The liquid velocity (v_l): moving from the low to the high liquid flow the average increase in the removal was 12.2%. Therefore, increasing the superficial liquid velocity increases removal.

The effects of v_l and D indicate an increase in contact between the liquid and gas phases result in higher removals

Two Factor Effects

τ and D together indicate that optimum removal is obtained by using a short period with a long flush duration. This suggests that steady state operation is better than periodic operation for SO_2 removal at 20°C and confirms the discussion in section 6.1.

The interaction between τ and A seems to show that the optimum removal is obtained with a short period and a low acid concentration of the liquid phase. However as the liquid phase acid strength increases the period should be increased in order to maintain the removal.

6.2.2 Conversion of SO_2 Removed

The average of the conversion of SO_2 removed from the gas stream, for all the factorial experiments was 60.58%. The only variable affecting conversion was τ . In moving from the short to the long period the average effect on conversion was an increase of 25.37%.

It is therefore indicated that increasing the period increases the conversion of the SO_2 removed from the gas stream to sulfuric acid.

6.2.3 Product Increase in Sulfuric Acid Concentration

In the case of the product sulfuric acid concentration the average increase for all factorial experiments was 5.2×10^{-3} molar and the main affects are:

Single Factor Effects

The liquid superficial velocity (v_l): increasing v_l has the average effect of reducing the product sulfuric acid concentration by 0.00624 molar. The reduction of the sulfuric acid concentration with increased liquid flow is the result of increased dilution.

The period (τ): The average effect of increasing the period is to increase the sulfuric acid concentration of the product by 0.00607 molar. This follows from the result that increasing the period increases the conversion of SO_2 removed.

6.2.4 Product Sulfurous Acid Concentration

In the case of the sulfurous acid concentration in the product the average increase in concentration was 1.5×10^{-3} . The significant variables were determined to be:

Single Factor Effects

Inlet liquid sulfuric acid concentration (A): the average effect of increasing A between 0 and 1 molar is to decrease the product sulfurous acid concentration by 1.2×10^{-3} molar. This appears to be the result of decreased SO_2 removal.

The liquid velocity (v_l): has a small effect on the sulfurous acid concentration decreasing it on average by 9.5×10^{-4} molar when v_l increased between the low and the high value.

The reduction in the sulfurous acid concentration in the product is due to increased dilution.

Two Factor Effects

There are three two factor interactions. The most significant is v_g and D which show that the minimum sulfurous acid concentration occurs when the gas velocity is low but the flush duration is long.

The second two factor interaction is v_l and τ in which the sulfurous acid concentration is minimized by using the high liquid velocity and the longer period.

The interaction between τ and A is that in order to minimize sulfurous acid concentration a long period with high liquid phase acid strength is favoured.

6.2.5 Conclusions from Factorial Design

From the above results, it appears that in order to maximize removal, a low gas velocity, short period, long flush duration, high liquid superficial velocity and low inlet liquid sulfuric acid concentrations are desirable. This indicates that steady state operation would be superior to periodic. However, this would lead to low conversion of the SO_2 removed, a liquid product with a low sulfuric acid concentration and a high sulfurous acid concentration. Since marketability of the sulfuric acid product is paramount to the

usefulness of this process, it appears that the long period with the low liquid superficial velocity and the longer flush duration should be used. This means however that in order to achieve 95% removal, a deeper reactor bed will be necessary.

The fact that steady state operation is superior to periodic operation may suggest that at these experimental conditions of temperature and gas composition the system is at least partially reaction rate limited. With liquid constantly flowing over the catalyst during steady state operation, there must be greater O_2 transfer interference. Allowing the reactor to drain during times of no liquid flow for periodic operation must reduce O_2 transfer interference. It is for these reasons that we believe the system could be reaction rate limited.

It should be noted that the variables chosen are not necessarily the at the optimum operating conditions. The factorial design was used only to determine which variables have the most significant effect on the desired responses. Further experimentation is needed in order to determine where the optimum conditions for this process lie.

Since we can increase the product acid strength over the 2N sulfuric acid used to flush the catalyst we conclude that at least 2N acid strengths can be achieved using this process.

6.3 80°C Experiments

It was expected that increased temperatures would lead to increased removal and conversion early on in the experiments. Nevertheless, the low temperature experiments were conducted to demonstrate that this process could work at low temperatures and to

provide an estimate of the effect of temperature on process performance. The extensive factorial design at low temperature (20°C) was part of the work statement for the project. A total of nine experiments were run at 80°C with several duplicates. For experiments R1, R2 and R4, the responses are averages of the results of replicates. Table 6.2 shows the level of the variables (as defined in Table 4.3) and the measured responses for each experiment.

As is quickly apparent, removal and conversion are remarkably higher at 80°C. In contrast to the 20°C data in which the conversion of SO₂ removed from the gas stream was 60%, 99% of the SO₂ removed from the gas is converted to sulfuric acid. With the exception of the one run at the high gas velocity, SO₂ removals ranged from 67 to 80% with the same 19 cm deep catalyst bed. At the high gas velocity, the removal is about 5 times greater than the removal at 20°C.

Another effects is that increasing the cycle length from 30 to 60 minutes increased removal and conversion by about 10%. This is in line with Haure's results obtained at 25°C but with much higher SO₂ concentrations. This is an indication that SO₂ removal is controlled by mass transfer of oxygen to the catalyst surface so that reducing the liquid holdup increases the rate of oxygen transfer. At high gas velocities the removal and conversion were greatly reduced. This is the expected space velocity effect.

It also appears that increasing the flushing liquid sulfuric acid concentration reduces the removal and conversion (Compare R2 and R4 in Table 6.2). These results show that scrubber performance is affected by the acid concentration of the flushing liquid. The effect was also found at 20°C

Table 6.2: Results of high temperature experiments

Exp. #	v_p	τ	A	% Removal	% Conversion	$[\text{SO}_3]^{2-}$ (mol/L)	$[\text{SO}_4]^{2-}$ (mol/L)
R1	-	-	-	67.07 ± 1.91	66.79 ± 1.90	8×10^{-5}	$1.99 \pm 0.061 \times 10^{-2}$
R2	-	+	-	80.36 ± 3.32	79.92 ± 3.16	$1.25 \pm 0.45 \times 10^{-5}$	$2.25 \pm 0.047 \times 10^{-2}$
R3	+	-	-	25.71	25.52	1.7×10^{-4}	2.29×10^{-2}
R4	-	+	+	69.91 ± 4.07	69.62 ± 4.07	8×10^{-5}	$1.99 \pm 0.115 \times 10^{-2}$

These experiments demonstrate that this scrubbing process should be operated at 80°C or more. In order to quantify the temperature behaviour and the effect of the flushing liquid sulfuric acid concentration further study is required. To optimize this process, further experiments will be necessary.

6.4 Pressure Drop and Required Bed Depth for 95% SO₂ Removal

Calculations have been completed to predict the required bed height and the pressure drop across the reactor bed (ΔP) for 95% SO₂ removal and are based on a model developed in Section 5. The model assumes that either oxygen mass transfer or the SO₂ oxidation reaction is rate controlling. The experimental results are used to calculate k_{app} . Using this value and assuming plug flow and an isothermal system, the bed height for 95% SO₂ removal can be calculated by the model.

Table 6.3 and 6.4 show the predicted bed height and pressure drop for each experiment in the factorial design. However, Table 6.3 assumes that oxygen transport controls and Table 6.4 assumes that the oxidation rate controls. The average bed height for 95% SO₂ removal in all the experiments at 20°C in the factorial design were a bed height of between 146 cm and 231 cm for oxygen transport and oxidation rate controlling respectively (hence forth the first number assumes oxygen transport and the second oxidation rate controlled). To achieve 95% SO₂ removal at a gas velocity of 2850 scc•cc⁻¹•hr⁻¹, period of 30 minutes, flush liquid acid strength of 1M, superficial liquid velocity of 0.2 cm•s⁻¹ and a flush duration of 0.5 minutes the reactor bed would be 491 - 796 cm high. This was done to calculate the maximum bed height for this process. The shortest calculated bed height was 23.95 - 29.3 cm and occurred when all the variables except the flush duration were at their lower values.

Table 6.3: Estimated Bed Height and Pressure Drop for 95% SO₂ Removal Assuming Oxygen Transport Controls

Block A - Flushing Liquid is Pure Deionized Water

Experiment #	v_g	v_l	τ	A	D	Bed Height (cm)	ΔP (Pa)
12	-	-	-	-	+	23.95	7.76
5, 6	+	-	-	-	-	197.26	224.17
4, 8	-	+	-	-	-	35.86	17.44
7	+	+	-	-	+	24.61	36.60
3, 10	-	-	+	-	-	141.29	45.60
9	+	-	+	-	+	178.71	202.22
2, 11	-	+	+	-	+	47.95	23.29
1	+	+	+	-	-	491.82	774.44

Block B - Flushing Liquid is 1 mole/L Sulfuric Acid

5	-	-	-	+	-	124.57	40.76
9	+	-	-	+	+	113.52	130.72
11	-	+	-	+	+	33.61	16.58
12	+	+	-	+	-	133.41	208.56
6, 8	-	-	+	+	+	110.84	36.45
2, 7	+	-	+	+	-	367.70	417.74
3, 4	-	+	+	+	-	135.15	66.34
1, 10	+	+	+	+	+	168.10	262.36

Table 6.4: Estimated Bed Height and Pressure Drop for 95% SO₂ Removal Assuming Oxidation Rate Controls

Block A - Flushing Liquid is Pure Deionized Water

Experiment #	v_g	v_l	τ	A	D	Bed Height (cm)	ΔP (Pa)
12	-	-	-	-	+	29.30	9.49
5, 6	+	-	-	-	-	314.87	357.82
4, 8	-	+	-	-	-	49.96	24.30
7	+	+	-	-	+	30.50	45.36
3, 10	-	-	+	-	-	223.30	72.06
9	+	-	+	-	+	284.54	321.96
2, 11	-	+	+	-	+	70.12	34.06
1	+	+	+	-	-	796.11	1254.11

Block B - Flushing Liquid is 1 mole/L Sulfuric Acid

5	-	-	-	+	-	195.11	64.11
9	+	-	-	+	+	177.85	204.80
11	-	+	-	+	+	46.16	22.77
12	+	+	-	+	-	210.41	328.94
6, 8	-	-	+	+	+	173.48	57.04
2, 7	+	-	+	+	-	593.55	674.33
3, 4	-	+	+	+	-	213.26	104.69
1, 10	+	+	+	+	+	267.16	416.99

Table 6.5 and 6.6 show the predicted bed height and pressure drop for the high temperature experiments. When the gas velocity was low the average calculated bed height was 25.06 - 31.26 cm. For the higher gas velocity the bed height rose to 70.21 - 106.83 cm. It should be noted that with the higher temperatures higher conversions were also observed indicating that 99% of the SO_2 removed was converted to sulfuric acid. Since much shallower beds are required to remove 95% of the SO_2 from the gas as compared to the 20°C data, this scrubbing process should be operated at 80°C or greater.

The pressure drop per meter of bed depth is reported in Table 6.7 and 6.8 as a summary of the findings for experiments conducted at 20°C with the corresponding gas space velocity and the liquid superficial velocity. Table 6.7 shows the pressure drop for one meter of packing when there is no liquid flowing. For periodic operation the bed has no liquid flow for the majority of the cycle and therefore, has a very low ΔP . Table 6.8 shows the pressure drop when liquid is flowing through one meter of packing. It is obvious that under steady state operation the pressure drop is significantly higher than for periodic operation.

There were not enough experiments conducted at 80°C in order to estimate the pressure drop for these experiments. In Tables 6.5 and 6.6 the low temperature data was used to estimate the pressure drop. However, it is certain that with shorter catalyst beds required to achieve 95% SO_2 removal, the overall pressure drop for a reactor operating at 80°C would be significantly lower. The pressure drop reported in units of Pa/m of bed.

Table 6.5: Estimated Bed Height and Pressure Drop for 95% SO₂ Removal at 80 °C Assuming Oxygen Transport Controls

Experiment #	v_g	τ	A	Bed Height (cm)	ΔP (Pa)
R1	-	-	-	26.91	10.48
R2	-	+	-	22.46	8.87
R3	+	-	-	70.21	102.80
R4	-	+	+	25.81	10.34

Table 6.6: Estimated Bed Height and Pressure Drop for 95% SO₂ Removal at 80 °C Assuming Oxidation Rate Controls

Experiment #	v_g	τ	A	Bed Height (cm)	ΔP (Pa)
R1	-	-	-	34.62	13.62
R2	-	+	-	26.49	10.46
R3	+	-	-	106.83	156.43
R4	-	+	+	32.68	13.09

Table 6.7: Pressure drop / m depth of reactor bed for periodic operation

v_a	v_l	ΔP
-	-	32.88
-	+	49.33
+	-	115.10
+	+	156.20

Table 6.8: Pressure drop / m depth of reactor bed for steady state operation

v_a	v_l	ΔP
-	-	65.77
-	+	164.43
+	-	180.87
+	+	690.59

6.5 Temperature within the Reactor Bed

Three rows of thermocouples, each row containing three thermocouples were placed at different depths within the reactor bed. Figure 6.9 shows readings made during experiments conducted at 20°C. These measurements indicate that the trickle bed is essentially isothermal. This diagram shows only the axial temperature variation in the bed as no radial variation was detected.

In the course of the 80°C experiments, a substantial temperature variation in the scrubber was observed. Initially, it was thought that this was caused by thermal losses from the bed. To prevent these losses two heating tapes were wrapped around the reactor

Figure 6.9: Typical Axial Reactor Temperature Profile for 20 °C Experiments

bed between the glass walls of the reactor and the insulation. Thermocouples were mounted on the reactor walls and the current through the tapes were adjusted to maintain a wall temperature of 80°C. Despite this precaution, the temperature drop between the top and bottom of the bed persisted (Figure 6.10). The difference for some runs was 15°C. The temperature of the gas entering the reactor was very close to the design value of 80°C. It was also observed that there was a radial variation of 3°C at each axial position. The temperature closest to the wall was higher than that measured at the middle of the reactor. Furthermore, during flushing, the temperature in the bed quickly rose to the design temperature. It should be noted from Figure 6.10 that the middle of the reactor is cooler than the bottom. All these observations demonstrate that the temperature drop results from evaporation of water retained in the bed after flushing is discontinued. This is a beneficial effect because it increases acid concentration and the water content of the flue gas is therefore increased providing buoyancy for stack discharge.

When the flushing liquid is introduced, the temperature rises immediately. The top of the reactor often reached a temperature of 100°C. Haure also observed the temperature exceeding the liquid temperature in her experiments at 20°C with 1.3% SO₂ in air. It was not seen in our 20°C experiments. In those runs the gas feed was saturated with water so evaporation did not occur. This temperature rise can be explained only by heat release from the exothermic dilution of concentrated acid at the top of the reactor with fresh de ionized water. This is consistent with other evidence which suggest high concentration of sulfuric acid develop in the porous carbon during the zero liquid flow portion of the cycle.

Figure 6.10: Typical Axial Reactor Temperature Profile for 80 °C Experiments

6.6 SO₂ Removal Profiles

Using the UV SO₂ gas analyzer made it possible to trace the outlet sulfur dioxide concentration during an experiment. Figure 6.11 shows a typical outlet SO₂ profile for experiments conducted at 20°C. This figure illustrates that most of the removal occurs during a liquid flush. There is a sharp drop in the outlet concentration when flushing starts and it rises fairly quickly to a steady value once flushing stops.

Figure 6.12 shows the typical outlet SO₂ profile for an experiment conducted at 80°C. In this case most of the removal occurs when a liquid flush is not occurring. At the start of a liquid flush the outlet concentration rises rapidly and maintains a steady but high value for approximately 10 minutes. After this time the outlet concentration drops steadily until the next flush occurs. The reason that the concentration remains steady for the first 10 minutes after flushing has occurred could be a result of water evaporation. Once most of the liquid film around the catalyst has evaporated SO₂ and O₂ transfer to the surface becomes more rapid increasing removal and conversion. This is the dropping portion of the response.

The decrease at 20°C and the increase at 80°C in the outlet concentration during liquid flushing could be the result of changing O₂ and SO₂ solubilities. Increasing the temperature by 60°C decreases the solubility of both SO₂ and O₂ by approximately half. This results in most of the SO₂ removal at low temperatures occurring during a liquid flush and less of the removal at high temperature occurring during a liquid flush.

Comparison of Figures 6.11 and 6.12 show that the maximum SO₂ levels in the outlet at 80°C are less than the minimum levels at 20°C. This indicates the temperature effect on

Figure 6.11: Typical SO₂ Outlet Concentration Profile for 20 °C Experiments

Figure 6.12: Typical SO₂ Outlet Concentration Profile for 80 °C Experiments

the rate coefficient which increases the driving force for O_2 absorption and on the mass transfer coefficient which accelerates O_2 transport to the catalyst. It is the fundamental explanation of why increasing temperature increases SO_2 removal and conversion to sulfuric acid.

6.7 Liquid Maldistribution

For experiments conducted at $20^\circ C$ there was no clear evidence that there was any liquid maldistribution occurring. However, for the $80^\circ C$ experiments, the total acidity which was used to determine when a cycling invariant state was reached, was very erratic from cycle to cycle. Figure 6.13 shows the variation in the total acidity determination for a single experiment. For this experiment in particular, the average removal based on the SO_2 gas analyzer was 65.5%. This translates into an expected total acidity concentration of 0.01887 mole/L. Recall that the experimental error of the autotitrator is ± 0.05 mL of titrant. Based on the total acidity predicted by the gas analyzer, the confidence interval is between 0.01882 and 0.01892 mole/L, which is too small to be shown on the graph. All the measured values for the total acidity fall outside this region.

All the high temperature experiments exhibited these large fluctuations from cycle to cycle in the total acidity concentration. It was concluded that these fluctuations are the result of liquid maldistribution during flushing in the reactor. Unfortunately, D and v_l were not varied in the $80^\circ C$ experiments so the effect of flushing duration and the liquid loading were not examined. Liquid loading, that is v_l , should have a large effect of maldistribution. Experiments were performed at the low v_l level of 0.2 cm/s.

Figure 6.13: Typical Variation in Product Total Acidity Concentration for 80 °C Experiments

7.0 Conclusions and Recommendations

7.1 Conclusions

The results of this study of the application of a periodically operated trickle bed reactor for SO₂ removal from stack gases suggest:

1. 95% removal can be easily achieved with carbon bed heights between 1-2 m deep with pressure drops generally less than 0.5 kPa at 2850 h⁻¹ space velocity operating the bed at 20°C.
2. Operating at 80°C, 95% removal is readily obtained with a bed depth less than 1 m and a pressure drop of less than 0.15 kPa at 2850 h⁻¹ space velocity.
3. This process should be operated at 80°C or better, as experimental removal, conversion and sulfuric acid concentrations are significantly higher. The higher temperature essentially eliminates sulfurous acid in the liquid product. The bed height and therefore the pressure drop required for 95% SO₂ removal would be much lower if the system were operated at 80°C.
4. At 20°C it appears that steady state operation obtains higher removal at superficial liquid velocities between 0 and 9 mm/s, than does periodic operation for the periodic variables studied. It is likely that for removal purposes periodic operation is not advantageous. However, with steady state operation, sulfurous acid concentration in the liquid product are high.

5. Periodic operation is superior to steady state in producing a higher concentration of acid product at 20°C and in converting SO₂ to sulfuric acid.
6. Pressure drop for the periodic operation at 95% is much less than for steady state and the same removal.
7. The factorial design experiments indicate that maximum SO₂ removal would be achieved at low gas velocities, high liquid superficial velocities, a short period, a long flush duration and pure water as the flushing medium. This supports the above conclusion that periodic operation does not offer an advantage over steady state operation with respect to SO₂ removal at 20°C.
8. Since periodic operation (at 20°C and a gas stream composition of 0.25% SO₂, 5% O₂ 10 % CO₂ and the balance N₂), is not better than steady state for SO₂ removal, it appears that the system is at least partially reaction rate limited at this low temperature.
9. The reactor operates isothermally at 20°C. However, at 80°C there is evidence that evaporation is occurring within the reactor. This is advantageous because it raises acid strength and increases the water content of the flue gas thereby increasing the buoyancy for stack discharge.
10. During operation at 20°C most of the removal of SO₂ was occurring during the liquid flushing. For 80°C operation most of the removal occurred when there was no liquid flowing through the reactor. This appears to be a result of higher mass transfer

and reaction rate and decreased SO_2 and O_2 solubility and evaporation of the liquid film on the catalyst.

11. Total acidity titrations for experiments conducted at 80°C indicate that there are problems with liquid maldistribution in the reactor at a liquid loading of 0.2 cm/s.

7.2 Recommendations

The objective of the research program was demonstration of 95% SO removal at low pressure drop thus no attempt was made optimize this process. Optimization is now appropriate.

This periodic scrubbing process performed exceptionally well with a simulated flue gas stream, but it is unknown how it would perform under the conditions of an actual flue gas from a coal fired generating station. This is the next demonstration in order.

Appendix A

Calculating the Experimental Variation Between Titrated Samples

Upon the approach of the system to a cycling invariant state the liquid collected during a flush is analyzed twice to ensure reproducibility. However, to determine when a cycling invariant state has been reached, the standard variation between pairs within a sample is used in order to estimate the least significant difference(LSD) between samples. The LSD is then used to compare the difference between liquid samples from successive cycles and if the difference is less than the LSD for two successive cycles it can then be assumed that a cycling invariant state has been achieved.

In order to calculate the LSD the Sum of Squares within a sample pair is calculated using

$$S_R = \sum_{t=1}^k \sum_{i=1}^{n_t} (y_{ti} - \bar{y}_t)^2$$

where, $k = 16$, or the number of samples(treatments)

$n_t = 2$, or the number of tests of each sample

y_{ti} = the value of a test i in sample t

$\bar{y}_t$ = the average of test 1 and 2 in sample t

Then the within-treatment mean square can be calculated by

$$s_R^2 = \frac{S_R}{v_R} = \frac{S_R}{N - k}$$

where, N = the total number of tests

The least significant difference can then be calculated by a standard confidence interval

$$\text{Confidence interval} = (\bar{y}_1 - \bar{y}_2) \pm t_{\alpha/2} s_R \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}$$

where, $t_{\alpha/2}$ = critical value of the t distribution

Table A.1 is a random series of experimental total acidity samples tested before the factorial design experiments were conducted.

Table A.1: Random Total Acidity Samples

Sample #	Test #1	Test #2	Average of test 1 & 2
1	11.152	11.209	11.1805
2	12.697	12.709	12.703
3	13.667	13.65	13.6585
4	17.665	17.642	17.6535
5	2.9475	2.9521	2.9498
6	2.9861	2.9759	2.981
7	2.9111	2.905	2.90805
8	3.6974	3.6977	3.69755
9	3.4989	3.5361	3.5175
10	2.2454	2.2561	2.25075
11	2.0937	2.0882	2.09095
12	1.9951	1.9866	1.99085
13	4.15	4.1661	4.15805
14	4.0103	4.0325	4.0214
15	3.9882	3.9698	3.979
16	4.0334	3.9932	4.0133

Using the above formulas the total acidity sum of squares is 0.00434 and the within-treatment mean square is 0.000543. Now at cycling invariant state the average of the total acidity between two successive samples should be 0. Therefore with 95% confidence the LSD is ± 0.0537 .

Table A.2 shows a random sampling of sulfurous acid titrations. Again following the same procedure as outlined above the LSD for the sulfurous acid titration is ± 0.3132 .

Table A.2: Random Sulfurous Acid Titration Samples

Sample #	Test #1	Test #2	Average of test 1 & 2
1	1.91	2.03	1.97
2	1.81	1.8175	1.81375
3	1.5825	1.7175	1.65
4	4.1974	4.2431	4.22025
5	3.8719	3.7041	3.788
6	4.3699	4.2432	4.30655
7	3.0089	3.2995	3.1542
8	3.286	3.4517	3.36885
9	4.0364	3.9883	4.01235
10	1.8609	2.0298	1.94535
11	2.2434	2.0491	2.14625
12	5.0962	5.2625	5.17935
13	2.3619	2.415	2.38845
14	1.716	1.7287	1.72235
15	1.7898	1.8174	1.8036
16	1.257	1.322	1.2895

Appendix B Sample Calculations

Table B.1 Sample Data from Experiment R1-3

Experimental Conditions	
v_g Gas Space Velocity (scc/cc h)	1000
y_{SO_2} Inlet SO_2 Concentration (ppm)	2500
v_l Actual Superficial Liquid Velocity (cm/s)	0.2037
v_l Time Averaged Superficial Liquid Velocity (cm/s)	0.0204
A Flush Liquid Sulfuric Acid Concentration (mole/L)	0
τ Cycle Time (min)	30
D Flush Duration (min)	3
T_g Gas Temperature ($^{\circ}C$)	80
P_a Atmospheric Pressure (mmHg)	730
P_r Reactor Pressure, above atmospheric (mmHg)	35
M_{cat} Mass Catalyst (g)	178.02
Experimental Measurements	
Q_{τ} Average Amount of Liquid Collected (mL/cycle)	720
V_{TA} Total Acidity (TA) and Blank Sample Size (mL)	50
V_{SA} Sulfurous Acid Determination (SA) Sample Size (mL)	50
amount of Peroxide added to TA Sample and Blank (mL)	3
TA_0 Blank TA of flushing liquid (mL of NaOH)	0
Na_2SO_3 (0.1 mole/L) for Sulfurous Blank (mL)	3
SA_0 Blank Sulfurous (mL of I_2)	7.2396
NaOH Strength (mole/L)	0.0988
TA_m Average required NaOH for TA (mL)	15.6
SA_m Average required I_2 for Sulfurous (mL)	0.2

The cross sectional area of the column is:

$$\phi = 4.992 \text{ cm}$$

$$A_x = \pi(2.496)^2 = 19.5722 \text{ cm}^2$$

actual bed height (h) was 19 cm

$$V_B = A_x \times \phi = 19.5722 \text{ cm}^2 \times 19 \text{ cm} = 371.8713 \text{ cm}^3$$

The volumetric flow of gas at STP (0 °C, and 1 atm)

$$Q_g = v_g \times V_B$$

$$1000 \frac{\text{cm}^3}{\text{cm}^3 \cdot \text{h}} \times 371.8713 \text{ cm}^3 \times \frac{h}{60 \text{ min}} = 6197.85 \frac{\text{cm}^3}{\text{min}}$$

The volumetric flow of SO₂ entering the reactor is at 20 °C and 765 mmHg:

$$Q_{\text{SO}_2} = y_{\text{SO}_2} \times Q_g \times \frac{T_{\text{SO}_2}}{T_s} \times \frac{P_s}{P_s + P_r}$$

$$\frac{0.0025 \times 6197.85 \text{ cm}^3}{\text{min}} \times \frac{293.15 \text{ K}}{273.15 \text{ K}} \times \frac{760 \text{ mmHg}}{765 \text{ mmHg}} = 16.52 \frac{\text{cm}^3}{\text{min}}$$

This calculation was done for each of the experiment from F1BB1 to R4-2 in order to measure the volumetric flow of SO₂ and thereby verify that the inlet concentration was 2500 ppm.

Using the Ideal Gas Law the moles of SO₂ flowing through the reactor in one cycle is then

$$F_{\text{SO}_2} = \frac{0.01652 \text{ l}}{\text{min}} \times \frac{765 \text{ mmHg}}{293.15 \text{ K}} \times \frac{\text{gmol} \cdot \text{K}}{62.3656 \text{ l} \cdot \text{mmHg}} \times \frac{30 \text{ min}}{\text{cycle}} = 0.02074 \frac{\text{gmols}}{\text{cycle}}$$

The actual superficial liquid velocity is

$$v_1 = \frac{Q_1}{D \times A_x} = \frac{720 \text{ cm}^3}{3 \text{ min} \times 19.5722 \text{ cm}^2} \times \frac{\text{min}}{60 \text{ s}} = 0.20437 \frac{\text{cm}}{\text{s}}$$

The time averaged superficial liquid velocity is

$$v_1 = v_1 \times \frac{D}{\tau} = 0.2037 \frac{\text{cm}}{\text{s}} \times \frac{3 \text{ min}}{30 \text{ min}} = 0.020437 \frac{\text{cm}}{\text{s}}$$

Wet Chemistry Calculations

The total increase in acid concentration of the product liquid (C_{TA})

$$C_{TA} = (TA_m - TA_0) \times \frac{\text{NaOH}}{2} \times \frac{1}{V_{TA}} = (15.6 - 0) \text{ ml} \times \frac{0.0988 \text{ mol}}{2 \text{ L}} \times \frac{1}{50 \text{ mL}} = 0.01541 \frac{\text{mol}}{\text{L}}$$

The removal is the calculated using equation 3-2

$$\frac{0.01542 \text{ mol}}{\text{L}} \times \frac{0.72 \text{ L}}{\text{cycle}} \times \frac{1}{0.02074 \text{ mol}} \times 100 = 53.506\%$$

to determine the sulfurous acid concentration ($C_{H_2SO_3}$), first the iodine strength must be calculated

$$I_2 = 0.003 \text{ L} \times \frac{0.1 \text{ mol}}{\text{L}} \times \frac{1}{0.0072396 \text{ L}} = 0.04144 \frac{\text{mol}}{\text{L}}$$

Then

$$C_{H_2SO_3} = \frac{SA_m \times I_2}{V_{TA}} = 0.0002 \text{ L} \times \frac{0.04144 \text{ mol}}{2 \text{ L}} \times \frac{1}{0.05 \text{ L}} = 0.00008 \frac{\text{mol}}{\text{L}}$$

The concentration of sulfuric acid ($C_{H_2SO_4}$) can then be found

$$C_{H_2SO_4} = C_{TA} - C_{H_2SO_3} = 0.01542 \frac{\text{mol}}{\text{L}} - 0.00008 \frac{\text{mol}}{\text{L}} = 0.01533 \frac{\text{mol}}{\text{L}}$$

The conversion is then calculated using equation 3-4

$$\frac{0.01534 \text{ mol}}{\text{L}} \times \frac{0.720 \text{ L}}{\text{cycle}} \times \frac{\text{cycle}}{0.02074 \text{ mol}} \times 100 = 53.22\%$$

Calculations based on UV gas analyzer

Data was collected from the gas analyzer through the computer interface system and saved as an ASCII file. This file was then imported into a spreadsheet program. A plot of the SO₂ outlet concentration with the experimental run time is shown in Figure B.1. The SO₂ outlet concentration is averaged over a cycle (y_{SO_2}). The system is thought to be at a cycling invariant state when the y_{SO_2} is relatively constant ($\pm 2\%$) for three consecutive cycles.

For Figure 5.12 $y_{\text{SO}_2} = 862.675 \text{ ppm} = 0.000862675$

The removal is then calculated using equation 3.1

$$\frac{(2500 - 862.675) \text{ ppm}}{2500 \text{ ppm}} \times 100 = 65.49 \%$$

Before the conversion can be determined using equation 3.3 the total molar flow of gas into the reactor (F_g) is needed

$$F_g = \frac{F_{\text{SO}_2}}{y_{\text{SO}_2}} = \frac{0.02074 \text{ mol}}{\text{cycle}} \times \frac{1}{0.0025} = 8.296 \frac{\text{mol}}{\text{cycle}}$$

then conversion is

$$\frac{(0.0025 - 0.000862)8.296 \frac{\text{mol}}{\text{cycle}} - 0.00008 \frac{\text{mol}}{\text{L}} \times 0.72 \frac{\text{L}}{\text{cycle}}}{0.02074 \frac{\text{mol}}{\text{cycle}}} \times 100 = 65.24\%$$

for factorial design experiments, the conversion of the SO₂ removed was calculated by

$$\frac{\% \text{ SO}_2 \text{ Conversion}}{\% \text{ SO}_2 \text{ Removal}} = \frac{65.24\%}{65.49\%} = 99.6\%$$

Therefore 99.6% of the SO_2 removed is actually converted to sulfuric acid.

During the first block of experiments in the factorial design, the difference between the wet chemistry and gas analysis removal and conversion calculations was not even $\pm 5\%$. However, when the concentration of the flushing liquid increased to 1 molar sulfuric acid the discrepancy could be as high as 200%. This was due to the sulfuric acid in the flushing liquid decreasing the accuracy of the total acidity titrations (there seemed to be no effect of sulfurous acid determinations). It was therefore decided that all data would be reported based on the gas analysis results. The sulfurous acid determination is still necessary because it determines the amount of SO_2 removed that is not converted to sulfuric acid.

Bed Height and ΔP Calculations for 95% Removal

These calculations are based on the model developed in Appendix E. For these calculations the average values of experiments conducted at conditions R1 are used.

$$(y_{\text{SO}_2})_f = 0.000823$$

$$(y_{\text{SO}_2})_0 = 0.0025$$

$$v_g = 6.75 \text{ cm / s}$$

$$T = 353.15\text{K}$$

$$P = 734 \text{ mmHg}$$

Assuming the gas phase resistance is controlling k_{app} is determined using the above experimental results and equation 5.18.

$$k_{\text{app}} = \frac{(0.0025 - 0.000823) \times 6.75 \text{ cm / s}}{2 \times 353.15\text{K} \times 0.05 \times 19 \text{ cm} \times 8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{gmol} \cdot \text{K}}} = 2.03 \times 10^{-6} \frac{\text{gmol}}{\text{Pa} \cdot \text{m}^3 \cdot \text{s}}$$

Now using equation 5.19

$$z = \frac{0.95 \times (0.0025) \times 6.75 \text{ cm / s}}{2 \times 353.15 \text{ K} \times 0.05 \times 8.314 \frac{\text{Pa} \cdot \text{m}^3}{\text{gmol} \cdot \text{K}} \times 2.03 \times 10^{-6} \frac{\text{gmol}}{\text{Pa} \cdot \text{m}^3 \cdot \text{s}}} = 26.9 \text{ cm}$$

If oxidation resistance controls Equation 5.26 is used. However, for this equation an estimate of the Henry's law constant for SO_2 in water is required. Assuming Henry's Law of the form

$$x_{\text{SO}_2} = H P_{\text{SO}_2}$$

where P_{SO_2} = the partial pressure of SO_2 in the gas

H = the Henry's Law constant

x_{SO_2} = the mole fraction of SO_2 in the liquid

From Perry's Handbook of Chemical Engineering (50th edition) H was estimated as 8584.659 mole fraction/mmHg. Using equation 5.26 and the above data k_{app} is calculated to be $8.82 \times 10^{-5} \text{ gmol/Pa} \cdot \text{m}^3 \cdot \text{s}$. Rearranging Equation 5.26 to estimate the bed height for 95% removal results in a height of 34.6 cm.

The pressure drop was estimated using the Ergun equation 5.27. The constant A and B were estimated using experimental values of v_g (cm/s) and $\Delta P/L$ (Pa/cm). The results of this calculation are shown in Table 5.3.

Appendix C
Measured and Calculated Results

	Experiment #			
	FIBA1	FIBA2	FIBA3	FIBA4
SO2 Volumetric Flow (cc/min)	48.15	16.65	16.65	16.65
SO2 Concentration (ppm)	2601	2439	2462	2460
Actual Superficial Liquid Flow (cm/s)	1.0152	1.0327	0.1986	1.0101
Flush Liquid Acidity (mol/L)	0	0	0	0
Cycle Time (min)	30	30	30	5
Flush Duration (min)	0.5	3	0.5	0.5
Gas Temperature (C)	18.80	23.00	20.00	20.00
Atmospheric Pressure (mmHg)	730.70	736.85	736.98	733.37
Reactor Pressure (Top) (mmHg)	44.00	11.00	10.00	13.00
Mass Catalyst (g)	178.02	178.02	178.02	178.02
Pressure Drop (mmHg)				
Liquid Flow	4	2	2	2
No Liquid Flow	1	1	1	1
Collected Sample Size (ml/cycle)	598	3650	117	595
Total Acidity Sample Size (ml)	20	50	20	50
Sulfurous Sample Size (ml)	20	50	20	50
ml Peroxide added to TA	3	3	3	3
ml Peroxide added to blank TA	10	10	10	10
Blank TA	0	0	0	0
ml Na2SO3 for blank	3	3	3	3
ml H2O for Sulphurous blank	20	20	20	20
Blank Sulfurous	6.38	6.43	6.04	6.80
NaOH Strength (N)	0.10	0.10	0.10	0.10
Average mls NaOH for TA	4.00	1.99	12.48	2.86
Average mls I2 for Sulfurous	1.97	1.81	1.65	4.22

RESULTS

Superficial Gas Flow (cm/s)	15.72135	5.79652	5.74448	5.74918
Mols SO2 in gas per cycle	0.06149	0.02024	0.02042	0.00340
Total Acidity (mol/L)	0.00988	0.00196	0.03079	0.00282
% SO2 Removal(wet chem.)	9.60620	35.41046	17.63994	49.32408
% SO2 Removal(gas analysis)	3.667286	41.46976	14.48382	50.4173
sulfurous Acid (mol/L)	0.00232	0.00085	0.00205	0.00186
Sulfuric Acid (wet chem) (mol/L)	0.00756	0.00112	0.02873	0.00096
Sulfuric Acid (gas analysis) (mol/L)	0.00146	0.00145	0.02323	0.00102
Apparent Reaction Rate (wet chem.)	5.081E-02	4.581E-02	3.777E-02	3.838E-02
Apparent Reaction Rate (gas anal.)	9.777E-03	5.959E-02	3.053E-02	4.088E-02
SO2 Conversion (wet chem.)	7.35410	20.15243	16.46498	16.74285
SO2 Conversion (gas analysis)	1.41519	26.21173	13.30886	17.83607

	Experiment #			
	F1BA5	F1BA6	F1BA7	F1BA8
SO ₂ Volumetric Flow (cc/min)	48.15	48.15	48.15	16.65
SO ₂ Concentration (ppm)	2637	2610	2722	2421
Actual Superficial Liquid Flow (cm/s)	0.1952	0.1952	1.1035	1.0050
Flush Liquid Acidity (mol/L)	0	0	0	0
Cycle Time (min)	5	5	5	5
Flush Duration (min)	0.5	0.5	3	0.5
Gas Temperature (C)	19.00	21.00	21.00	24.20
Atmospheric Pressure (mmHg)	735.84	736.35	734.00	732.24
Reactor Pressure (Top) (mmHg)	50.00	47.00	82.80	13.00
Mass Catalyst (g)	178.02	178.02	178.02	178.02
Pressure Drop (mmHg)				
Liquid Flow	4	3	9	2
No Liquid Flow	2	2	2	1
Collected Sample Size (ml/cycle)	115	115	3900	592
Total Acidity Sample Size (ml)	20	20	50	50
Sulfurous Sample Size (ml)	20	20	50	50
ml Peroxide added to TA	3	3	3	3
ml Peroxide added to blank TA	10	10	10	10
Blank TA	0	0	0	0
ml Na ₂ SO ₃ for blank	3	3	3	3
ml H ₂ O for Sulphurous blank	20	20	20	20
Blank Sulfurous	6.51	6.76	6.80	6.71
NaOH Strength (N)	0.10	0.10	0.10	0.10
Average mls NaOH for TA	4.11	4.20	2.02	2.79
Average mls I ₂ for Sulfurous	3.95	4.19	3.15	3.37

RESULTS

Superficial Gas Flow (cm/s)	15.50914	15.66499	15.02340	5.84039
Mols SO ₂ in gas per cycle	0.01039	0.01029	0.01072	0.00335
Total Acidity (mol/L)	0.01013	0.01037	0.00199	0.00275
% SO ₂ Removal(wet chem.)	11.21481	11.59096	72.44350	48.63589
% SO ₂ Removal(gas analysis)	9.704483	8.6592	73.3377	50.2365
sulfurous Acid (mol/L)	0.00455	0.00465	0.00139	0.00151
Sulfuric Acid (wet chem) (mol/L)	0.00558	0.00572	0.00060	0.00124
Sulfuric Acid (gas analysis) (mol/L)	0.00422	0.00309	0.00063	0.00133
Apparent Reaction Rate (wet chem.)	4.328E-02	4.431E-02	1.584E-01	4.960E-02
Apparent Reaction Rate (gas anal.)	3.270E-02	2.399E-02	1.648E-01	5.321E-02
SO ₂ Conversion (wet chem.)	6.18036	6.39125	21.90784	21.98333
SO ₂ Conversion (gas analysis)	4.67004	3.45949	22.80204	23.58394

	Experiment #			
	F1BA9	F1BA10	F1BA11	F1BA12
SO2 Volumetric Flow (cc/min)	48.15	16.65	16.65	16.65
SO2 Concentration (ppm)	2631	2446	2448	2446
Actual Superficial Liquid Flow (cm/s)	0.2139	0.2003	1.0118	0.2020
Flush Liquid Acidity (mol/L)	0	0	0	0
Cycle Time (min)	30	30	30	5
Flush Duration (min)	3	0.5	3	3
Gas Temperature (C)	22.00	20.00	20.50	21.50
Atmospheric Pressure (mmHg)	732.02	732.24	732.62	734.12
Reactor Pressure (Top) (mmHg)	60.15	10.00	11.50	12.00
Mass Catalyst (g)	178.02	178.02	178.02	178.02
Pressure Drop (mmHg)				
Liquid Flow	2	2	2	2
No Liquid Flow	1	1	1	1
Collected Sample Size (ml/cycle)	756	118	3576	714
Total Acidity Sample Size (ml)	20	20	50	50
Sulfurous Sample Size (ml)	50	20	50	50
ml Peroxide added to TA	3	3	3	3
ml Peroxide added to blank TA	10	10	10	10
Blank TA	0	0	0	0
ml Na2SO3 for blank	3	3	3	3
ml H2O for Sulphurous blank	20	20	20	20
Blank Sulfurous	6.77	6.82	6.40	6.26
NaOH Strength (N)	0.10	0.10	0.10	0.10
Average mls NaOH for TA	3.69	9.60	2.12	3.47
Average mls I2 for Sulfurous	4.01	1.95	2.05	5.18

RESULTS

Superficial Gas Flow (cm/s)	15.54316	5.78117	5.77640	5.78053
Mols SO2 in gas per cycle	0.06220	0.02029	0.02031	0.00338
Total Acidity (mol/L)	0.00910	0.02369	0.00209	0.00342
% SO2 Removal(wet chem.)	11.06315	13.77815	36.77944	72.20731
% SO2 Removal(gas analysis)	10.0994	11.4342	34.45803	75.35459
sulfurous Acid (mol/L)	0.00178	0.00214	0.00096	0.00248
Sulfuric Acid (wet chem) (mol/L)	0.00732	0.02155	0.00113	0.00094
Sulfuric Acid (gas analysis) (mol/L)	0.00653	0.01752	0.00100	0.00109
Apparent Reaction Rate (wet chem.)	6.220E-02	2.857E-02	4.530E-02	4.513E-02
Apparent Reaction Rate (gas anal.)	5.547E-02	2.323E-02	4.001E-02	5.230E-02
SO2 Conversion (wet chem.)	8.90189	0.00000	19.85764	19.79489
SO2 Conversion (gas analysis)	7.93814	10.18980	17.53624	22.94217

	Experiment #			
	F1BB1	F1BB2	F1BB3	F1BB4
SO ₂ Concentration (ppm)	2500	2500	2500	2500
Actual Superficial Liquid Flow (cm/s)	0.9988	0.2020	0.9846	0.9846
Flush Liquid Acidity (mol/L)	1.00	1.00	1.00	1.00
Cycle Time (min)	30	30	30	30
Flush Duration (min)	3	0.5	0.5	0.5
Gas Temperature (C)	26.00	22.00	27.50	25.00
Atmospheric Pressure (mmHg)	732.03	736.85	736.80	738.63
Reactor Pressure (Top) (mmHg)	67.20	61.00	11.00	11.00
Mass Catalyst (g)	178.02	178.02	178.02	178.02
Pressure Drop (mmHg)				
Liquid Flow	10	2	3	3
No Liquid Flow	3	1	1	1
Collected Sample Size (ml/cycle)	3530	119	580	580
Total Acidity Sample Size (ml)	20	20	20	20
Sulfurous Sample Size (ml)	50	50	50	50
ml Peroxide added to TA	3	3	3	3
ml Peroxide added to blank TA	3	3	3	3
Blank TA	42.46	42.22	39.18	38.80
ml Na ₂ SO ₃ for blank	3	3	3	3
ml H ₂ O for Sulphurous blank	20	20	20	20
Blank Sulfurous	5.54	5.42	5.49	5.53
NaOH Strength (N)	1.05	1.05	1.04	1.04
Average mls NaOH for TA	42.67	43.94	39.58	39.14
Average mls I ₂ for Sulfurous	1.29	2.51	1.07	1.08

RESULTS

Superficial Gas Flow (cm/s)	15.61465	15.43243	5.88499	5.82179
Mols SO ₂ in gas per cycle	0.05910	0.05910	0.02074	0.02074
Total Acidity (mol/L)	0.00568	0.04507	0.01049	0.00881
% SO ₂ Removal(wet chem.)	33.91411	9.07503	29.33781	24.64753
% SO ₂ Removal(gas analysis)	10.01	5.09	16.1	11.41
sulfurous Acid (mol/L)	0.00070	0.00139	0.00059	0.00058
Sulfuric Acid (wet chem) (mol/L)	0.00498	0.04368	0.00990	0.00823
Sulfuric Acid (gas analysis) (mol/L)	0.00098	0.02389	0.00517	0.00350
Apparent Reaction Rate (wet chem.)	1.975E-01	5.840E-02	6.454E-02	5.362E-02
Apparent Reaction Rate (gas anal.)	3.879E-02	3.194E-02	3.370E-02	2.277E-02
SO ₂ Conversion (wet chem.)	29.74539	8.79548	27.70035	23.01277
SO ₂ Conversion (gas analysis)	5.84128	4.81045	14.46254	9.77524

	Experiment #			
	F1BB5	F1BB6	F1BB7	F1BB8
SO2 Concentration (ppm)	2500	2500	2500	2500
Actual Superficial Liquid Flow (cm/s)	0.2037	0.2037	0.2207	0.1938
Flush Liquid Acidity (mol/L)	1.00	1.00	1.00	1.00
Cycle Time (min)	5	5	30	30
Flush Duration (min)	0.5	0.5	0.5	3
Gas Temperature (C)	25.00	25.00	24.00	24.00
Atmospheric Pressure (mmHg)	738.00	735.00	731.10	732.00
Reactor Pressure (Top) (mmHg)	11.00	11.00	57.00	10.00
Mass Catalyst (g)	178.02	178.02	178.02	178.02
Pressure Drop (inches H2O)				
Liquid Flow	2	0.5"	1.375"	.5"
No Liquid Flow	1	.25"	.875"	.375"
Collected Sample Size (ml/cycle)	120	120	130	685
Total Acidity Sample Size (ml)	10	20	20	20
Sulfurous Sample Size (ml)	50	50	50	50
ml Peroxide added to TA	3	3	3	3
ml Peroxide added to blank TA	3	3	3	3
Blank TA	19.76	38.61	37.46	38.78
ml Na2SO3 for blank	3	3	3	3
ml H2O for Sulphurous blank	20	20	20	20
Blank Sulfurous	5.53	5.56	7.25	5.98
NaOH Strength (N)	1.01	1.04	1.04	1.04
Average mls NaOH for TA	19.87	38.91	39.42	39.02
Average mls I2 for Sulfurous	2.32	2.16	2.86	2.07

RESULTS

Superficial Gas Flow (cm/s)	5.82671	5.85014	15.72930	5.86195
Mols SO2 in gas per cycle	0.00346	0.00346	0.05910	0.02074
Total Acidity (mol/L)	0.00543	0.00769	0.05094	0.00609
% SO2 Removal(wet chem.)	18.86567	26.69906	11.20342	20.12934
% SO2 Removal(gas analysis)	14.49	16.14	4.74	16.43
sulfurous Acid (mol/L)	0.00126	0.00116	0.00118	0.00104
Sulfuric Acid (wet chem) (mol/L)	0.00418	0.00653	0.04975	0.00506
Sulfuric Acid (gas analysis) (mol/L)	0.00292	0.00349	0.02037	0.00394
Apparent Reaction Rate (wet chem.)	3.380E-02	5.280E-02	7.266E-02	3.893E-02
Apparent Reaction Rate (gas anal.)	2.360E-02	2.820E-02	2.974E-02	3.031E-02
SO2 Conversion (wet chem.)	14.50718	22.66258	10.94278	16.70762
SO2 Conversion (gas analysis)	10.13151	12.10353	4.47936	13.00828

	Experiment #			
	F1BB9	F1BB10	F1BB11	F1BB12
SO ₂ Concentration (ppm)	2500	2500	2500	2500
Actual Superficial Liquid Flow (cm/s)	0.1811	1.0044	1.0893	1.1374
Flush Liquid Acidity (mol/L)	1.00	1.00	1.00	1.00
Cycle Time (min)	5	30	5	5
Flush Duration (min)	3	3	3	0.5
Gas Temperature (C)	25.50	24.00	25.50	24.00
Atmospheric Pressure (mmHg)	734.60	735.90	734.40	735.00
Reactor Pressure (Top) (mmHg)	57.00	58.00	10.00	58.00
Mass Catalyst (g)	178.02	178.02	178.02	178.02
Pressure Drop (inches H ₂ O)				
Liquid Flow	1.375"	5.25"	1.25"	5.25"
No Liquid Flow	.875"	1.1875"	.375"	1.1875"
Collected Sample Size (ml/cycle)	640	3550	3850	670
Total Acidity Sample Size (ml)	20	20	20	20
Sulfurous Sample Size (ml)	50	50	50	50
ml Peroxide added to TA	3	3	3	3
ml Peroxide added to blank TA	3	3	3	3
Blank TA	39.07	38.66	38.55	37.39
ml Na ₂ SO ₃ for blank	3	3	3	3
ml H ₂ O for Sulphurous blank	20	20	20	20
Blank Sulfurous	5.87	7.17	5.84	7.17
NaOH Strength (N)	1.04	1.04	1.04	1.04
Average mls NaOH for TA	39.29	38.94	38.65	37.56
Average mls I ₂ for Sulfurous	2.61	1.69	0.49	1.30

RESULTS

Superficial Gas Flow (cm/s)	15.73880	15.61439	5.87254	15.63211
Mols SO ₂ in gas per cycle	0.00985	0.05910	0.00346	0.00985
Total Acidity (mol/L)	0.00563	0.00717	0.00250	0.00455
% SO ₂ Removal(wet chem.)	36.55446	43.08128	278.76249	30.93252
% SO ₂ Removal(gas analysis)	15.9	11.58	53.7	13.53
sulfurous Acid (mol/L)	0.00134	0.00071	0.00025	0.00054
Sulfuric Acid (wet chem) (mol/L)	0.00429	0.00647	0.00225	0.00400
Sulfuric Acid (gas analysis) (mol/L)	0.00111	0.00122	0.00023	0.00145
Apparent Reaction Rate (wet chem.)	1.851E-01	2.579E-01	5.848E-01	1.808E-01
Apparent Reaction Rate (gas anal.)	4.791E-02	4.872E-02	6.046E-02	6.528E-02
SO ₂ Conversion (wet chem.)	27.86938	38.83891	251.01193	27.23313
SO ₂ Conversion (gas analysis)	7.21492	7.33762	25.94944	9.83061

	Experiment #			
	R1-2	R1-3	R1-5	R1-6
SO ₂ Concentration (ppm)	2500	2500	2500	2500
Actual Superficial Liquid Flow (cm/s)	0.1839	0.2037	0.1924	0.2094
Flush Liquid Acidity (mol/L)	0	0	0	0
Cycle Time (min)	30	30	30	30
Flush Duration (min)	3	3	3	3
Gas Temperature (C)	80.00	80.00	80.00	80.00
Atmospheric Pressure (mmHg)	735.99	729.99	735.99	733.74
Reactor Pressure (Top) (mmHg)	35	35	35	35
Mass Catalyst (g)	178.02	178.02	178.02	178.02
Pressure Drop (inches H ₂ O)				
Liquid Flow	0.6875	0.6875	0.75"	0.625"
No Liquid Flow	0.125"	0.125"	0.125"	0.125"
Collected Sample Size (ml/cycle)	650	720	680	740
Total Acidity Sample Size (ml)	50	50	50	50
Sulfurous Sample Size (ml)	50	50	50	50
ml Peroxide added to TA	3	3	3	3
ml Peroxide added to blank TA	3	3	3	3
Blank TA	0	0	0	0
ml Na ₂ SO ₃ for blank	3	3	3	3
ml H ₂ O for Sulphurous blank	20	20	20	20
Blank Sulfurous	7.2396	7.2396	7.2396	7.2396
NaOH Strength (N)	0.10	0.10	0.10	0.10
Average mls NaOH for TA	18.7	15.6	18.7	22.5
Average mls I ₂ for Sulfurous	0.2	0.2	0.2	0.2

RESULTS

Superficial Gas Flow (cm/s)	6.70472	6.75731	6.70472	6.72434
Mols SO ₂ in gas per cycle	0.02074	0.02074	0.02074	0.02074
Total Acidity (mol/L)	0.01848	0.01542	0.01848	0.02224
% SO ₂ Removal(wet chem.)	57.93210	53.53298	60.60589	79.35577
% SO ₂ Removal(gas analysis)	65.968	65.493	65.9465	70.884
sulfurous Acid (mol/L)	0.00008	0.00008	0.00008	0.00008
Sulfuric Acid (wet chem) (mol/L)	0.01840	0.01534	0.01840	0.02216
Sulfuric Acid (gas analysis) (mol/L)	0.02096	0.01878	0.02003	0.01978
Apparent Reaction Rate (wet chem.)	1.344E-01	1.241E-01	1.406E-01	1.842E-01
Apparent Reaction Rate (gas anal.)	1.531E-01	1.519E-01	1.530E-01	1.645E-01
SO ₂ Conversion (wet chem.)	57.67233	53.24524	60.33413	79.06004
SO ₂ Conversion (gas analysis)	65.70823	65.20526	65.67475	70.58827

	Experiment #		
	R2-1	R2-2	R3-1
SO2 Concentration (ppm)	2500	2500	2500
Actual Superficial Liquid Flow (cm/s)	0.2122	0.2051	0.1867
Flush Liquid Acidity (mol/L)	0	0	0
Cycle Time (min)	60	60	30
Flush Duration (min)	6	6	3
Gas Temperature (C)	80.00	80.00	80.00
Atmospheric Pressure (mmHg)	741.99	737.50	732.24
Reactor Pressure (Top) (mmHg)	17	17	55
Mass Catalyst (g)	178.02	178.02	178.02
Pressure Drop (inches H2O)			
Liquid Flow	0.625"	0.625"	1.125"
No Liquid Flow	0.125"	0.125"	0.125"
Collected Sample Size (ml/cycle)	1500	1450	660
Total Acidity Sample Size (ml)	50	50	50
Sulfurous Sample Size (ml)	50	50	50
ml Peroxide added to TA	3	3	3
ml Peroxide added to blank TA	3	3	3
Blank TA	0	0	0
ml Na2SO3 for blank	3	3	3
ml H2O for Sulphurous blank	20	20	20
Blank Sulfurous	7.2396	7.2396	7.2396
NaOH Strength (N)	0.10	0.10	0.10
Average mls NaOH for TA	17.9	21.9	30.8
Average mls I2 for Sulfurous	0.4	0.2	0.4

RESULTS

Superficial Gas Flow (cm/s)	6.81072	6.85125	18.71402
Mols SO2 in gas per cycle	0.04148	0.04148	0.05910
Total Acidity (mol/L)	0.01769	0.02165	0.03044
% SO2 Removal(wet chem.)	63.98506	75.67395	33.99493
% SO2 Removal(gas analysis)	83.683	77.048	25.711
sulfurous Acid (mol/L)	0.00017	0.00008	0.00017
Sulfuric Acid (wet chem) (mol/L)	0.01753	0.02156	0.03028
Sulfuric Acid (gas analysis) (mol/L)	0.02297	0.02196	0.02286
Apparent Reaction Rate (wet chem.)	1.477E-01	1.756E-01	2.245E-01
Apparent Reaction Rate (gas anal.)	1.936E-01	1.788E-01	1.695E-01
SO2 Conversion (wet chem.)	63.38560	75.38421	33.80983
SO2 Conversion (gas analysis)	83.08354	76.75826	25.52590

	Experiment #	
	R4-1	R4-2
SO2 Concentration (ppm)	2500	2500
Actual Superficial Liquid Flow (cm/s)	0.2051	0.2051
Flush Liquid Acidity (mol/L)	1	1
Cycle Time (min)	60	60
Flush Duration (min)	6	6
Gas Temperature (C)	80.00	80.00
Atmospheric Pressure (mmHg)	734.50	723.99
Reactor Pressure (Top) (mmHg)	20	18
Mass Catalyst (g)	178.02	178.02
Pressure Drop (inches H2O)		
Liquid Flow	0.625"	0.625"
No Liquid Flow	0.125"	0.125"
Collected Sample Size (ml/cycle)	1450	1450
Total Acidity Sample Size (ml)	50	50
Sulfurous Sample Size (ml)	50	50
ml Peroxide added to TA	3	3
ml Peroxide added to blank TA	3	3
Blank TA	29.327	29.327
ml Na2SO3 for blank	3	3
ml H2O for Sulphurous blank	20	20
Blank Sulfurous	7.2396	7.2396
NaOH Strength (N)	0.10	0.10
Average mls NaOH for TA	31	31.8
Average mls I2 for Sulfurous	0.2	0.2

RESULTS

Superficial Gas Flow (cm/s)	6.85125	6.96681
Mols SO2 in gas per cycle	0.04148	0.04148
Total Acidity (mol/L)	0.01268	0.01874
% SO2 Removal(wet chem.)	44.32052	65.51383
% SO2 Removal(gas analysis)	73.976	65.841
sulfurous Acid (mol/L)	0.00008	0.00008
Sulfuric Acid (wet chem) (mol/L)	0.01259	0.01866
Sulfuric Acid (gas analysis) (mol/L)	0.02108	0.01875
Apparent Reaction Rate (wet chem.)	1.026E-01	1.520E-01
Apparent Reaction Rate (gas anal.)	1.717E-01	1.527E-01
SO2 Conversion (wet chem.)	44.03078	65.22409
SO2 Conversion (gas analysis)	73.68626	65.55126

Appendix D

Factorial Design Interpretation

Conversion of the SQ Removed Interpretation Using Yates Algorithm

Experimental
Value

Avg.
Affect

0.99
(Confidence Interval)

30.44459	74.72019	146.9631	412.4361	969.2367
44.2756	72.24294	265.473	556.8005	-59.0991
41.15128	169.2679	236.1707	-27.3231	-92.0654
31.09166	96.20514	320.6299	-31.776	-47.9151
90.66602	115.1933	3.771383	-75.54	202.969
78.60184	120.9774	-31.0945	-16.5254	-66.046
57.61774	171.4697	-0.29792	-30.8568	-98.679
38.5874	149.1602	-31.4781	-17.0583	-26.671
69.91028	13.83101	-2.47725	118.5099	144.3644
45.28302	-10.0596	-73.0627	84.45917	-4.45284
48.32402	-12.0642	5.784083	-34.8659	59.01458
72.65336	-19.0303	-22.3095	-31.1801	13.79851
77.06478	-24.6273	-23.8906	-70.5855	-34.0507
94.40488	24.32934	-6.96617	-28.0936	3.685772
88.11341	-4.41142	5.596922	1.581159	39.40534
61.04678	-27.0666	-22.6552	-28.2521	-29.8333

16	60.57729271			avg
8	-7.38738904	-25.7705422	10.99576411	Vg
8	-11.5081695	-29.8913227	6.874983656	VI
8	-5.98938581	-24.372539	12.39376735	Vg,VI
8	25.37113091	6.987977754	43.75428406	period
8	-8.25575389	-26.638907	10.12739927	Vg,Period
8	-12.3348776	-30.7180307	6.048275575	VI,Period
8	-3.33387183	-21.717025	15.04928132	Acid,Flush
8	18.04555155	-0.33760161	36.4287047	Acid
8	-0.5566051	-18.9397583	17.82654806	Vg,Acid
8	7.37682227	-11.0063309	25.75997542	VI,Acid
8	1.724813398	-16.6583398	20.10796655	Period,Flush (split)
8	-4.25633748	-22.6394906	14.12681567	Period,Acid or Vg,VI,Flush
8	0.460721511	-17.9224316	18.84387466	VI,Flush
8	4.925666921	-13.4574862	23.30882007	Vg,Flush
8	-3.72916163	-22.1123148	14.65399152	Flush

Variance estimate from duplicates

48.14433	39.94226	33.63695
35.37675	46.94595	66.92319
91.8876	89.12017	3.82934
63.20714	50.89094	75.84437
74.98761	79.18442	8.806608
94.49902	94.51477	0.000124
89.81366	85.71429	8.402454
58.34166	63.38515	12.71839
	$s^2 =$	30.02306
	$s =$	5.47933

Normal Probability Plot of Conversion

Removal Interpretation

Experimental
Value

Avg.
Affect

0.99
(Confidence Interval)

75.35	84.53	208.1945	272.8836	416.2536
9.18	123.6645	64.6891	143.37	-124.791
50.3265	23.0581	97.62	-80.3156	97.8974
73.338	41.631	45.75	-44.475	21.8326
12.9591	30.39	-43.1585	57.7074	-195.375
10.099	67.23	-37.1571	40.19	39.0464
37.964	21.2	-38.76	57.7446	-54.0516
3.667	24.55	-5.715	-35.912	-50.3295
14.49	-66.17	39.1345	-143.505	-129.514
15.9	23.0115	18.5729	-51.87	35.8406
53.7	-2.8601	36.84	6.0014	-17.5174
13.53	-34.297	3.35	33.045	-93.6566
16.285	1.41	89.1815	-20.5616	91.6354
4.915	-40.17	-31.4369	-33.49	27.0436
13.755	-2.755	-35.707	-85.8315	53.6066
10.795	-2.96	-0.205	35.502	121.3335

16	26.01585			avg
8	-15.598825	-24.1344696	-7.06318042	Vg
8	12.237175	3.701530419	20.77281958	VI
8	2.729075	-5.80656958	11.26471958	Vg, VI
8	-24.421925	-32.9575696	-15.8862804	period
8	4.8808	-3.65484458	13.41644458	Vg, Period
8	-6.75645	-15.2920946	1.779194581	VI, Period
8	-6.2911875	-14.8268321	2.244457081	Acid, Flush
8	-16.1892	-24.7248446	-7.65355542	Acid
8	4.480075	-4.05556958	13.01571958	Vg, Acid
8	-2.189675	-10.7253196	6.345969581	VI, Acid
8	-11.707075	-20.2427196	-3.17143042	Period, Flush (split)
8	11.454425	2.918780419	19.99006958	Period, Acid or Vg, VI, Flush
8	3.38045	-5.15519458	11.91609458	VI, Flush
8	6.700825	-1.83481958	15.23646958	Vg, Flush
8	15.1666875	6.631042919	23.70233208	Flush

Variance Estimates From Duplicates

9.704	8.659	0.546013
50.417	50.236	0.016381
14.484	11.4342	4.65064
26.212	34.458	33.99826
5.84128	7.33762	1.119517
4.81045	4.47936	0.05481
14.46254	9.77524	10.98539
12.10353	13.01	0.410844
	$s^2 =$	6.472732
	$s =$	2.544156

Multi-Variable Effects

Multi-variable effects are determined using a two way table of means. It is assumed that only two factor interactions are significant. **Removal:** there are two significant multi-variable effects. The first interaction is period (τ) and flush duration (D) and the second interaction is τ and flushing liquid acid concentration (A).

τ and D					
$\tau-, D-$			$\tau+, D-$		
9.18			12.96		
50.33	Average = 21.88		3.67	Average = 8.83	
14.49			4.92		
13.53			13.76		
$\tau-, D+$			$\tau+, D+$		
75.35			10.10		
73.34	Average = 54.57		37.96	Average = 18.79	
15.90			16.29		
53.70			10.80		
	+	8.83		18.79	
	τ				
	-	21.88		54.57	
		-	D	+	
τ and A					
$\tau-, A-$			$\tau+, A-$		
75.35			12.96		
9.18	Average = 52.05		10.10	Average = 16.17	
50.33			37.96		
73.34			3.67		
$\tau-, A+$			$\tau+, A+$		
14.49			16.29		
15.90	Average = 24.40		4.92	Average = 45.77	
53.70			13.76		
13.53			10.80		
	+	16.17		45.77	
	τ				
	-	52.05		24.40	
		-	A	+	

[SO4] interpretation

Experimental
Value

0.00109	0.004745	0.00655	0.03614	0.07313
0.003655	0.001805	0.02959	0.03699	-0.01768
0.001175	0.026905	0.00571	-0.01159	-0.04992
0.00063	0.002685	0.03128	-0.00609	0.012045
0.020375	0.00403	0.00202	-0.02716	0.04861
0.00653	0.00168	-0.01361	-0.02276	-0.02054
0.001225	0.025845	-0.00059	0.01097	-0.03934
0.00146	0.005435	-0.0055	0.001075	-0.02032
0.00292	0.002565	-0.00294	0.02304	0.00085
0.00111	-0.00055	-0.02422	0.02557	0.0055
0.00023	-0.01385	-0.00235	-0.01563	0.0044
0.00145	0.000235	-0.02041	-0.00491	-0.0099
0.003715	-0.00181	-0.00311	-0.02128	0.00253
0.02213	0.00122	0.01408	-0.01806	0.01072
0.004335	-0.00227	0.002045	-0.0173	0.01637
0.0011	-0.00324	-0.00097	-0.00302	0.014285

Variance estimate from duplicates

0.00422	0.00309	6.38E-07
0.00102	0.00133	4.8E-08
0.02323	0.01752	1.63E-05
0.00145	0.001	1.01E-07
0.00098	0.00122	2.88E-08
0.02389	0.02037	6.2E-06
0.00517	0.0035	1.39E-06
0.00349	0.00394	1.01E-07
	$s^2 =$	3.1E-06
	$s =$	0.001761

Avg.
Affect0.95
(Confidence Interval)

16	0.004570625			avg
8	-0.00221	-0.00730991	0.002889911	Vg
8	-0.00624	-0.01133991	-0.00114009	VI
8	0.001505625	-0.00359429	0.006605536	Vg, VI
8	0.00607625	0.000976339	0.011176161	period
8	-0.0025675	-0.00766741	0.002532411	Vg, Period
8	-0.0049175	-0.01001741	0.000182411	VI, Period
8	-0.00253938	-0.00763929	0.002560536	Acid, Flush
8	0.00010625	-0.00499366	0.005206161	Acid
8	0.0006875	-0.00441241	0.005787411	Vg, Acid
8	0.00055	-0.00454991	0.005649911	VI, Acid
8	-0.00123688	-0.00633679	0.003863036	Period, Flush (split)
8	0.00031625	-0.00478366	0.005416161	Period, Acid or Vg, VI, Flush
8	0.00134	-0.00375991	0.006439911	VI, Flush
8	0.00204625	-0.00305366	0.007146161	Vg, Flush
8	0.001785625	-0.00331429	0.006885536	Flush

Normal Probability Plot of [SO₄]

[SO3] Interpretation

Experimental
Value

Avg.
Affect (Confidence Interval)

0.00248	0.00708	0.010155	0.017255	0.02432
0.0046	0.003075	0.0071	0.007065	0.002855
0.001685	0.003875	0.00339	0.002925	-0.00756
0.00139	0.003225	0.003675	-7E-05	0.00133
0.002095	0.0026	0.001825	-0.00466	-0.00277
0.00178	0.00079	0.0011	-0.00291	-0.00154
0.000905	0.002385	0.00037	-0.00068	0.00407
0.00232	0.00129	-0.00044	0.002015	0.000665
0.00126	0.00212	-0.00401	-0.00305	-0.01019
0.00134	-0.0003	-0.00065	0.000285	-0.003
0.00025	-0.00032	-0.00181	-0.00073	0.00175
0.00054	0.001415	-0.0011	-0.00081	0.0027
0.0011	8E-05	-0.00242	0.003355	0.00334
0.001285	0.00029	0.00173	0.000715	-8.5E-05
0.000585	-0.00056	0.001335	0.00132	-0.00417
0.000705	0.00012	0.00068	-0.00066	-0.00198

16	0.00152			avg
8	0.000356875	-2.8768E-05	0.000742518	Vg
8	-0.000945	-0.00133064	-0.00055936	VI
8	0.00016625	-0.00021939	0.000551893	Vg,VI
8	-0.00034625	-0.00073189	3.93926E-05	period
8	-0.00019188	-0.00057752	0.000193768	Vg,Period
8	0.00050875	0.000123107	0.000894393	VI,Period
8	8.3125E-05	-0.00030252	0.000468768	Acid,Flush
8	-0.00127375	-0.00165939	-0.00088811	Acid
8	-0.00037438	-0.00076002	1.12676E-05	Vg,Acid
8	0.00021875	-0.00016689	0.000604393	VI,Acid
8	0.0003375	-4.8143E-05	0.000723143	Period,Flush (split)
8	0.0004175	3.18574E-05	0.000803143	Period,Acid or Vg,VI,Flush
8	-1.0625E-05	-0.00039627	0.000375018	VI,Flush
8	-0.00052063	-0.00090627	-0.00013498	Vg,Flush
8	-0.00024688	-0.00063252	0.000138768	Flush

Variance estimate from duplicates

0.00085	0.00096	6.05E-09
0.00205	0.00214	4.05E-09
0.00186	0.00151	6.13E-08
0.00455	0.00465	5E-09
0.0007	0.00071	5E-11
0.00139	0.00118	2.2E-08
0.00059	0.00058	5E-11
0.00116	0.00104	7.2E-09
	$s^2 =$	1.32E-08
	$s =$	0.000115

Normal Probability Plot of [SO₃]

Increase in sulfurous acid concentration in the product: there are three significant multi-variable effects. The first is the liquid superficial velocity (v_l) and the period (τ), the second is gas space velocity (v_g) and flush duration (D) and the third multi-variable effect is τ and flushing liquid sulfuric acid concentration (A).

v_i and τ			
$v_i-, \tau-$		$v_i+, \tau-$	
0.00248	Average = 0.00242	0.001685	Average = 0.000966
0.00460		0.001390	
0.00126		0.000250	
0.00134		0.000540	
$v_i-, \tau+$		$v_i+, \tau+$	
0.002095	Average = 0.001565	0.000905	Average = 0.001128
0.001780		0.002320	
0.001100		0.000585	
0.001285		0.000705	
		+	0.000966 MINIMUM 0.001128
v_i	-	0.00242	0.001565
	-	τ	+

v_g and D			
$v_g-, D-$		$v_g+, D-$	
0.00169	Average = 0.00141	0.00460	Average = 0.00219
0.00210		0.00232	
0.00126		0.00054	
0.00059		0.00129	
$v_g-, D+$		$v_g+, D+$	
0.00248	Average = 0.00119	0.00139	Average = 0.00131
0.00091		0.00178	
0.00025		0.00134	
0.00110		0.00071	
	+	0.00219	0.00131
	v_g		
	-	0.00141	<u>0.00119</u> MINIMUM
		-	D +

τ and A			
$\tau-, A-$		$\tau+, A-$	
0.00248	} Average = 0.00254	0.00210	} Average = 0.00178
0.00460		0.00178	
0.00169		0.00091	
0.00139		0.00232	
$\tau-, A+$		$\tau+, A+$	
0.00126	} Average = 0.00085	0.00110	} Average = 0.00092
0.00134		0.00129	
0.00025		0.00059	
0.00054		0.00071	
	+	0.00178	(0.00085) MINIMIZE
	τ		
	-	0.00254	0.00092
	-	A	
			+

References

- Bellut, M., University of Waterloo Report (1985).
- Berruti, F., Hudgins, R.R., Rhodes, E., and Sicardi, S., *Can. J. Chem.*, **62**, 644-650 (1984).
- Charpentier, J.C. and Favier, M., *AIChE J.*, **21**, 1213 (1975).
- Chou, T.S., Worley, F.L. and Luss, D., *IEC Proc. Des. Dev.*, **16**, 424 (1977).
- Dacey, D.W. and Cope, D.R., Flue Gas Desulfurisation - system performance, IEC Coal Research, London, December 1986.
- Davtyan, O.K. and Ovchinnikova, E.N., *Doklady Akad. Nauk. SSSR*, **104**, 857 (1955).
- Fukushima, S. and Kusaka, K., *J. Chem. Eng., Jap.*, **10**, 461 (1977).
- Gianetto, A. and Silveston, P.L., *Multiphase Chemical Reactors*. Hemisphere Publishing Corp. (1986).
- Goto, S. and Smith, J.M., *AIChE J.*, **21**, 706 (1975).
- Goto, S. and Smith, J.M., *IEC Proc. Des. Dev.*, **14**, 4 (1975).
- Goto, S. and Smith, J.M., *AIChE J.*, **24**, 286 (1978).
- Hartman, M., Polek, J. and Coughlin, R., *Chem. Eng. Symp. Ser.*, **115**, 67, 7 (1971).
- Hartman, M. and Coughlin, R., *Chem. Eng. Sci.*, **27**, 867-880 (1972).
- Hasokowati, W., MA.Sc. Thesis, Department of Chemical Engineering, University of Waterloo (1993).
- Haure, P., Ph.D. Thesis, Department of Chemical Engineering, University of Waterloo (1989).
- Haure, P., Hudgins, R.R. and Silveston, P.L., *AIChE J.*, **35**, 1437-1444 (1989).
- Haure, P., Hudgins, R.R. and Silveston, P.L., *Chem. Eng. J.*, **43**, 121-125 (1990).

- Haure, P., Hudgins, R.R. and Silveston, P.L., *Can. J. Chem. Eng.*, **70**, 600-603 (1992).
- Herskowitz, M., *Chem. Eng. J.*, **22**, 167-175 (1981).
- Herskowitz, M., Carbonell, R.G. and Smith, J.M., *AIChE J.*, **25**, 272 (1979).
- Herskowitz, M., and Smith, J.M., *AIChE J.*, **24**, 439 (1978).
- Herskowitz, M., and Smith, J.M., *AIChE J.*, **29**, 1 (1983).
- Herskowitz, M., and Mosseri, S., *Ind. Eng. Chem. Fundam.* **22**, 1 (1983).
- Klingspor, J.S. and Cope, D.R., *FGD Handbook*, IEA Coal Research, London, May 1987.
- Komiyama, H., and Smith, J.M., *AIChE J.*, **21**, 664-676 (1975).
- Mata, A.R., and Smith, J.M., *Chem. Eng. J.*, **22**, 229-235 (1981).
- Metzinger, J., Hudgins, R.R., Silveston, P.L. and Gangwal, S., *Chem. Eng. Sci.*, **47**, 13/14, 3723-3727 (1992).
- Mills, P.L. and Dudukovic, M.P., *AIChE J.*, **27**, 893 (1981).
- Morita, S. and Smith, J.M., *Ind. Eng. Chem. Fundam.*, **17**, 113 (1978).
- Otake, T., Tone, S., Yokota, Y. and Yoshimura, K., *J. Chem. Eng. Japan*, **4**, 155 (1971).
- Satterfield, C.N., *AIChE J.*, **21**, 209-227 (1975).
- Satterfield, C.N. and Ozel, F., *AIChE J.*, **19**, 1259 (1973).
- Satterfield, C.N. and Way, P.F., *AIChE J.*, **18**, 305 (1972).
- Seaburn, J.T., and Engel, A.J., *AIChE Symp. Ser.* 134,69,71 (1973).
- Sicardi, S., Baldi, C.N., Specchia, V., Mazzarino, J. and Gianetto, A., *Chem. Eng. Sci.*, **36**, 226 (1981).
- Sicardi, S., Gerhard, H. and Hofmann, H., *Chem. Eng. J.*, **18**, 173 (1979).
- Siedlewski, Y.U., *Int. Chem. Eng.*, **5**, 608 (1965).

Specchia, V. and Baldi, G., Chem. Eng. Sci., **32**, 515 (1977).

Specchia, V. and Baldi, G., Ind. Eng. Chem. Pro. Des. Dev., **17**, 362 (1978).

Talmor, E., AIChE J., **23**, 874 (1977).

DATE

FILMED

2 / 14 / 94

END