



A regenerable process for the removal of SO₂ from flue gases
by James George Pedersen

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

In our pollution-conscious society, the prevention of sulfur oxide emissions to the atmosphere is an area of much concern. Considerable research has been, and is being, done in this area; however, results, to date, have not provided universally applicable methods to achieve that end. This investigation was, therefore, undertaken to determine the potential of calcium sulfide in a water slurry as a reducing agent for the sulfur dioxide evolved in smelting Montana's metal sulfide ores.

A standard mixture of SO₂, nitrogen and oxygen was scrubbed with a CaS-water slurry on a laboratory scale, over a range of concentrations and flow rates and the resulting gas analysed chromatographically. For all cases, SO₂ was reduced by nominally 100% to H₂S. A mechanism was hypothesized to explain this reaction. It is intended that the H₂S thus formed would be converted to elemental sulfur via the Claus process. The reduction of SO₂ resulted in 97% the CaS being converted to CaSO₃.

This CaSO₃ was, in turn, reduced with carbon monoxide using a ferric oxide catalyst with the intent of recycling to the SO₂ scrubber. The optimum conditions, among those tried for this reaction, were 5% Fe₂O₃ at approximately 500° C. The reduction was effective in regenerating CaS which was successfully used in the SO₂ reduction process; however, impurities present in the reagents acted to reduce SO₂ to some unidentified compound, clouding somewhat this portion of the research.

Analysis of these solid products was accomplished by quantitatively converting CaS and CaSO₃ to H₂S and SO₂ respectively, and analysing these gases on a gas chromatograph.

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Dec 22, 1972

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Approved

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TABLE OF CONTENTS

	Page
List of Figures	v
Abstract	vi
Introduction and Background	1
Objective	4
Apparatus and Procedure	5
Results and Discussion	11
Conclusions	20
Recommendations	21
Appendices	22
Analysis for Sulfate	23
Analysis for Sulfite and Sulfide	24
Analysis for Elemental Sulfur	25
Analysis for Calcium	26
Calibration Curves	27
Literature Cited	32

LIST OF FIGURES

	Page
SO ₂ Reduction Apparatus Schematic	6
CaSO ₃ Reduction Reactor	9
CaSO ₃ Reduction Apparatus Schematic	10
Progress of Typical SO ₂ Reduction Run	14-15
SO ₂ Calibration Curve	27
H ₂ S Calibration Curve (low range)	28
H ₂ S Calibration Curve (high range)	29
H ₂ S Calibration Curve (whole range)	30
Rotameter Calibration Plot	31

ABSTRACT

In our pollution-conscious society, the prevention of sulfur oxide emissions to the atmosphere is an area of much concern. Considerable research has been, and is being, done in this area; however, results, to date, have not provided universally applicable methods to achieve that end. This investigation was, therefore, undertaken to determine the potential of calcium sulfide in a water slurry as a reducing agent for the sulfur dioxide evolved in smelting Montana's metal sulfide ores.

A standard mixture of SO_2 , nitrogen and oxygen was scrubbed with a CaS-water slurry on a laboratory scale, over a range of concentrations and flow rates and the resulting gas analysed chromatographically. For all cases, SO_2 was reduced by nominally 100% to H_2S . A mechanism was hypothesized to explain this reaction. It is intended that the H_2S thus formed would be converted to elemental sulfur via the Claus process. The reduction of SO_2 resulted in 97% of the CaS being converted to CaSO_3 .

This CaSO_3 was, in turn, reduced with carbon monoxide using a ferric oxide catalyst with the intent of recycling to the SO_2 scrubber. The optimum conditions, among those tried for this reaction, were 5% Fe_2O_3 at approximately 500°C . The reduction was effective in regenerating CaS which was successfully used in the SO_2 reduction process; however, impurities present in the reagents acted to reduce SO_2 to some unidentified compound, clouding somewhat this portion of the research.

Analysis of these solid products was accomplished by quantitatively converting CaS and CaSO_3 to H_2S and SO_2 respectively, and analysing these gases on a gas chromatograph.

INTRODUCTION AND BACKGROUND

"Sulfur oxides are among the more harmful of the known air pollutants. Studies have related human health effects of varying severities to exposure to this class of compounds. Sulfur oxides have also been shown to be deleterious to plant life, to decrease visibility under certain conditions, and to lead to accelerated corrosion of many common materials. The estimate of cost to society due to air pollution is many billions of dollars annually, with sulfur oxides a major contributor."

This rather rhetorical condemnation begins a recent Environmental Protection Agency report on major research and development programs for the control of sulfur oxide emissions. (Craig, 1972) A more quantitative approach is found in Sax's Dangerous Properties of Industrial Materials. (Sax, 1968) In this source the hazard is characterized as "High": [SO₂] "may cause death or permanent injury after very short exposure to small quantities." Concentrations of this compound from 6-12 ppm cause immediate irritation of the nose and throat...400-500 ppm is immediately dangerous to life and 50-100 ppm is considered to be the maximum permissible concentration for exposures of 30 to 60 minutes. The threshold limit value (TLV), the maximum concentration to which nearly all workers can be exposed, day after day, without ill effect is 5 ppm in air or 13 mg/cubic meter of air as recommended by the American Conference of Governmental and Industrial Hygienists (ACGIH)

Within the state of Montana, 800 tons of sulfur are collectively emitted each day in the form of SO_2 by American Smelting and Refining at East Helena and Anaconda Company at Anaconda. The Environmental Protection Agency has issued proclamations which require that American Smelting and Refining Company reduce sulfur oxide emissions from its East Helena lead smelter by 87% by July 31, 1975, and that the Anaconda Company reduce these emissions from their copper smelter in Anaconda by 89% before August 1, 1977.

Although the technology exists to convert this sulfur dioxide to sulfuric acid, (Craig, 1972) the industrial base of Montana and surrounding states is such that no market exists for 2100 tons per day of sulfuric acid (85% conversion). High inland transportation costs make shipment to distant, potential markets infeasible. The cost and space requirements for storage of this volume of acid production makes this alternative equally impractical. The logical alternative, then, would seem to be the reduction of sulfur oxides, principally sulfur dioxide, to elemental sulfur. In this form the sulfur can be most economically and easily shipped or, if need be, stored due to its minimal volume to weight ratio and its relative chemical stability.

Although a variety of processes exist for removal of SO_2 from flue gases, (Slack, 1971; Craig, 1972) an economic, regenerable process to effect the reduction of SO_2 to elemental sulfur has not been forthcoming. This project was therefore initiated to investigate one

candidate process to fill this gap.

This project was based upon preliminary work in this laboratory using metal sulfides as reducing agents. (McCandless, 1971)

In this endeavor, it was decided that calcium sulfide suspended in a water slurry would be the agent investigated to reduce sulfur dioxide. No direct reference was found in the literature regarding this reaction.

OBJECTIVE

The objectives of this research were to investigate the potential of calcium sulfide in a water slurry as a reducing agent for the SO_2 evolved in the smelting of Montana's metal sulfide ores and to determine whether the products of this process might be regenerated for recycle in the process.

APPARATUS AND PROCEDURE

The sulfur dioxide bearing gas mixture was fed through a rotameter to a 250 or 300 ml gas washing bottle filled with a calcium sulfide-water slurry. The slurry was held in suspension by means of a magnetic stirrer as well as by action of the gas bubbles. The gas mixture, from the slurry, was led to a cold trap, cooled with ice, to remove water vapor from the gas mixture, thereby facilitating chromatographic analysis of the gas. The gas mixture then flowed through a Swagelok fitting equipped with a septum and finally exhausted to a hood. (see figure 1)

Gas flow was controlled with the rotameter and ranged from six standard liters per hour to 30 standard liters per hour. The inlet gas mixture contained 3.5% SO_2 , 77% N_2 , and 19.5% O_2 . Slurry compositions ranged from 25 grams $\text{CaS}/200$ ml water to 5 grams $\text{CaS}/250$ ml water. For most runs 10 grams of calcium sulfide were mixed with 250 ml of distilled water.

Entrance and exit gases were sampled manually with a 0.5 ml gastight syringe and analysed by gas chromatograph with Porapak Q-S column maintained at $119 \pm 1^\circ$ C. The chromatograph was calibrated for SO_2 and H_2S by manually injecting air diluted samples of pure gas at a variety of concentrations and correlating these concentrations to peak heights. Prior to all analyses or calibrations the column was conditioned with 2-4 ml each pure H_2S and SO_2 to negate effects of adsorption by the column packing.

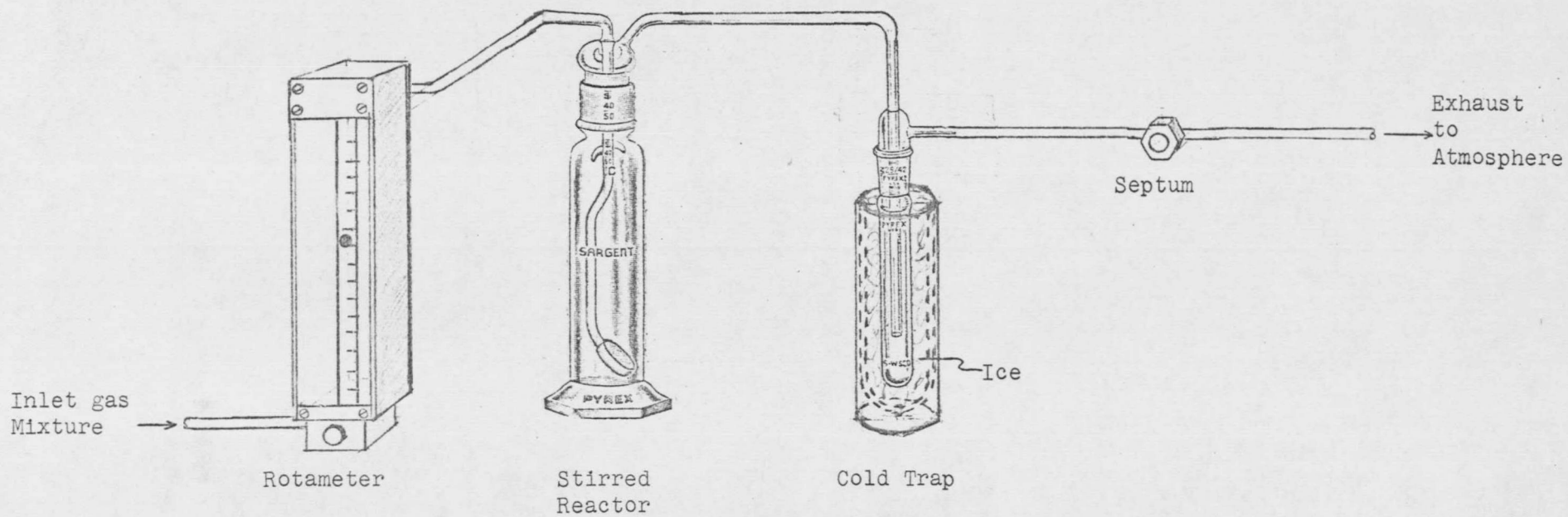


Figure 1: SO₂ Reduction Apparatus Schematic.

Sulfate ion in the solid product was determined gravimetrically as BaSO_4 . (see appendices for detailed procedure)

Sulfite and sulfide ions were determined with a Beckman GC-2A gas chromatograph with Porapak Q-S column using the method published by Birk et al. (Birk, et al; 1970) In this procedure a weighed, pelletized sample was introduced into the reaction vessel. The vessel was evacuated and the sample subsequently acidified. The gases evolved were bled to an evacuated sample loop and introduced into the chromatograph carrier gas stream by means of a six-way valve. A calibration curve was drawn using various amounts of known sulfides and sulfites. Correlation was made between the weights of Xerox copies of chromatograph peaks and known sample weights of sulfite and sulfide compounds. (see appendices for detailed procedure)

Elemental sulfur was analysed by extraction with carbon disulfide in a soxhlet apparatus. (see appendices for detailed procedure)

Calcium ion was determined by EDTA titration with Erichrome Black T indicator. (see appendices for detailed procedure)

CaSO_3 reduction was accomplished by intimately mixing the CaSO_3 with catalyst and charging this mixture to the reactor. This reactor was a one inch nominal stainless steel pipe 15 inches long. The bottom nine inches of pipe were filled with stainless steel rings to increase heat transfer to the entering gas. This volume was separated from the upper portion by a porous stainless steel disc; the upper six

inches serving as the actual reaction site. A second porous stainless steel disc prevented the CaSO_3 from being carried from the reactor with the gas stream. (see figures 2 and 3) The reactor was fitted with three Chromel Alumel thermocouples connected to an eight point temperature recorder. The reactor was situated in two nichrome heating coils controlled by two Powerstat rheostats. After purging the system with nitrogen, carbon monoxide was introduced to the reactor at a rate of approximately 15 standard liters per hour, hopefully sufficient to fluidize the CaSO_3 . The exit gases were led through a water-cooled, shell and tube heat exchanger, past a sample port and through a pair of water scrubbers, before exiting. The exit gases were analysed for CO and CO_2 on a Beckman GC-2A gas chromatograph. Following the run, the reactor was again purged with nitrogen, allowed to cool, and the contents analysed for sulfide and sulfite ion content.

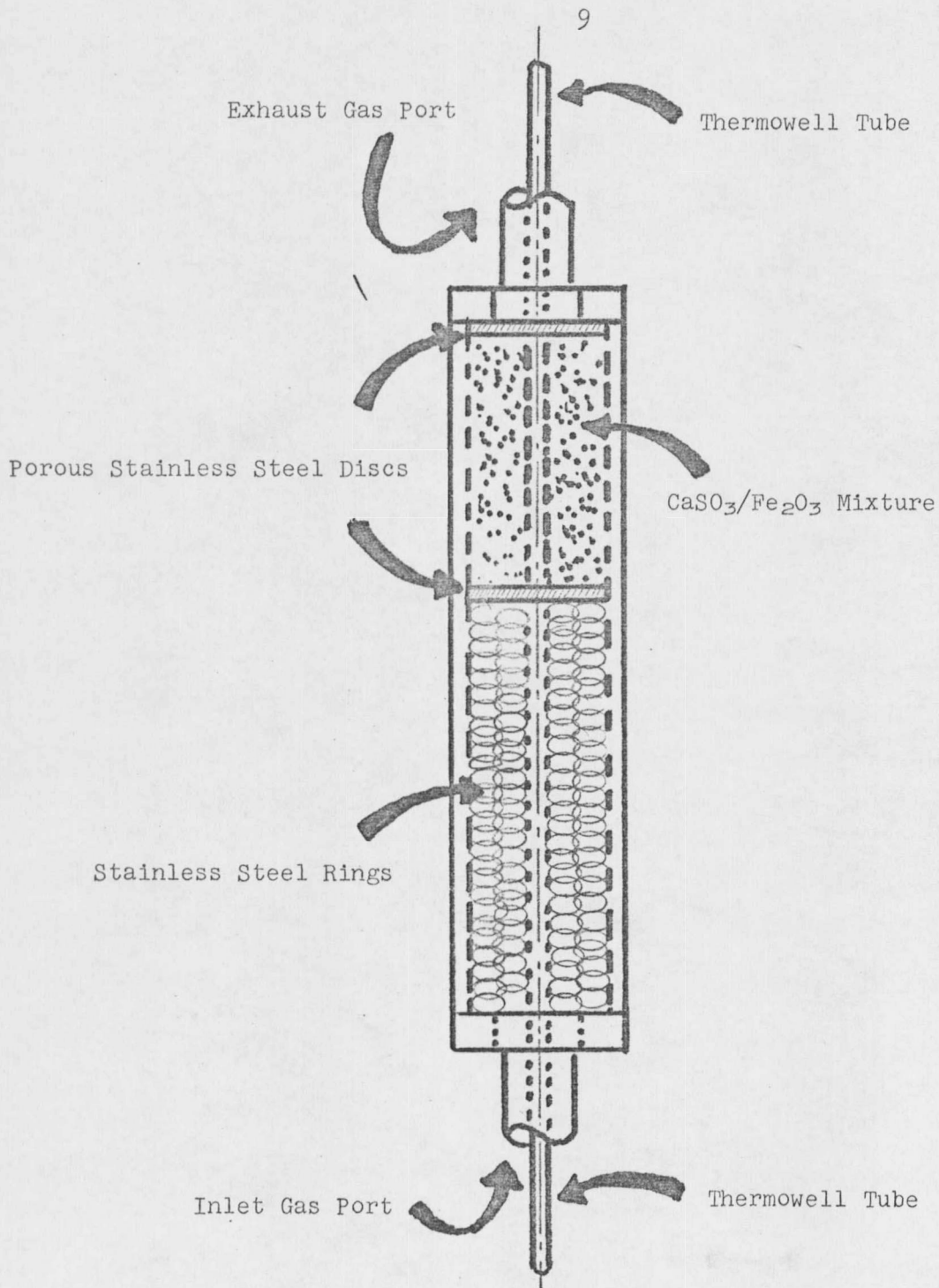


Figure 2: CaSO₃ Reduction Reactor.

