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 MASTER OF SCIENCE in Chemical Engineering
Montana State University

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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March, 1973

ACKNOWLEDGMENT

The author wishes to thank the entire staff of the Chemical Engineering Department of Montana State University, and in particular Dr. F. P. McCandless who directed this research, for their help and suggestions in this project. Thanks is also due James Tillery and Silas Huso who helped in building and repairing the equipment.

Finally the author would like to thank his wife, June, and his family for their sacrifices, support, and encouragement.

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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 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 contributer."

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": [SO_2] "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 recomended by the American Conference of Governmental and Industrial Hygenists (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 CaS/200 ml water to 5 grams 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±1° 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.

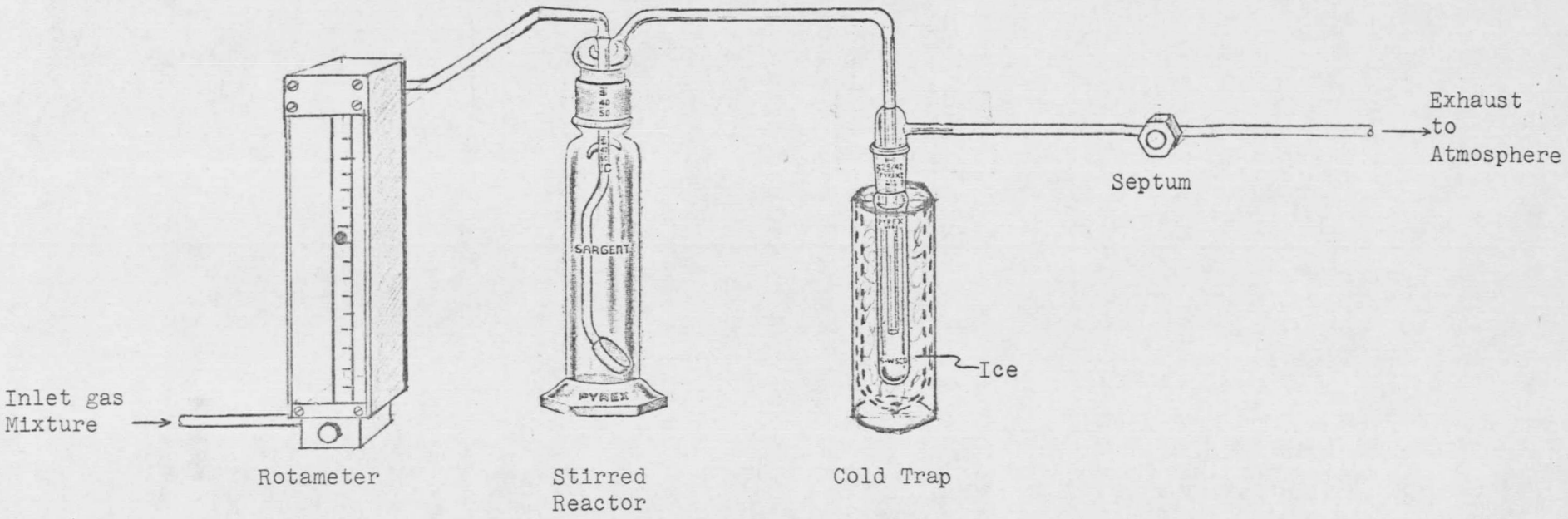

Figure 1: SO_2 Reduction Apparatus Schematic.

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 etal. (Birk, etal; 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.

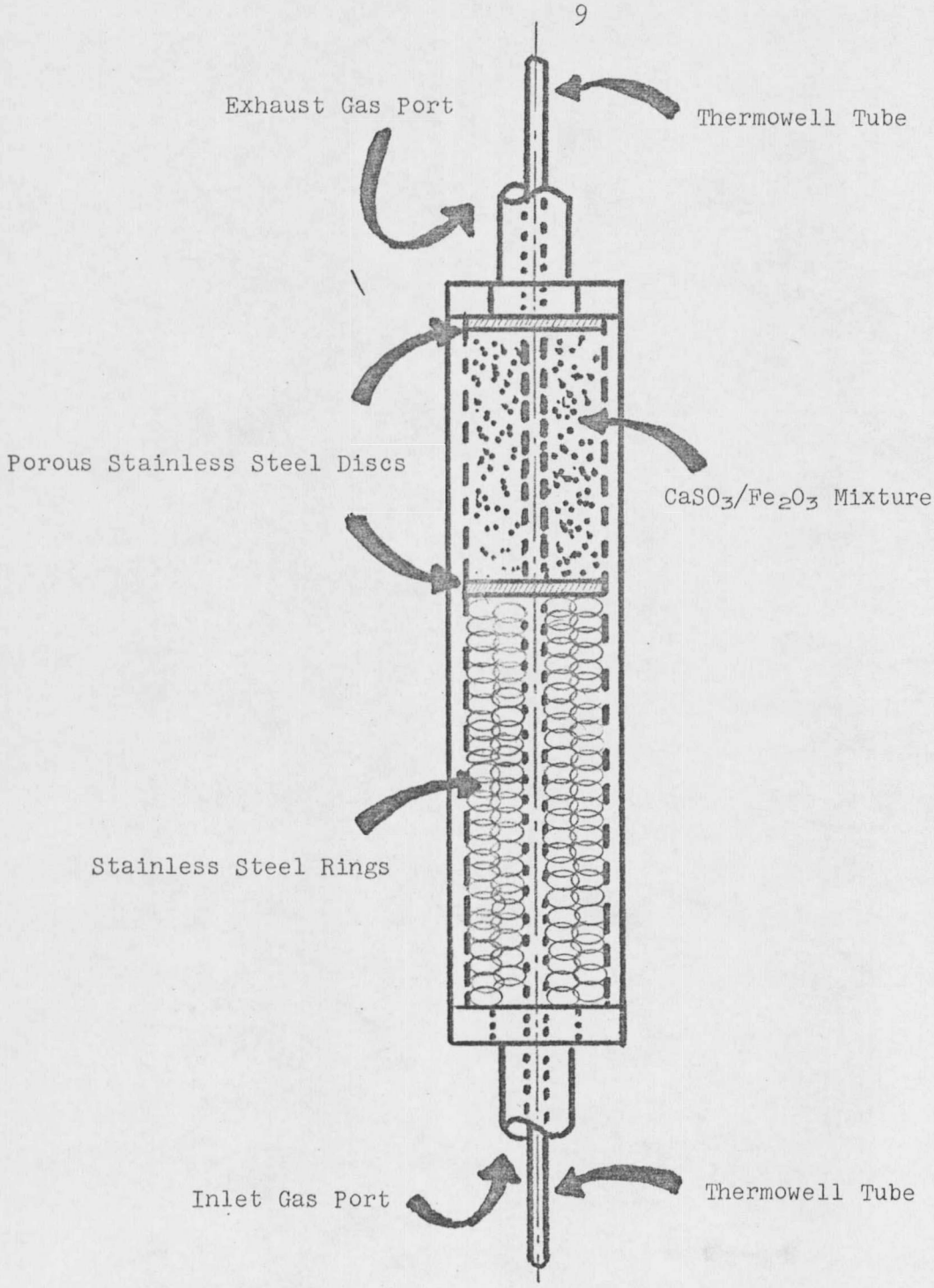

Figure 2: $CaSO_3$ Reduction Reactor.

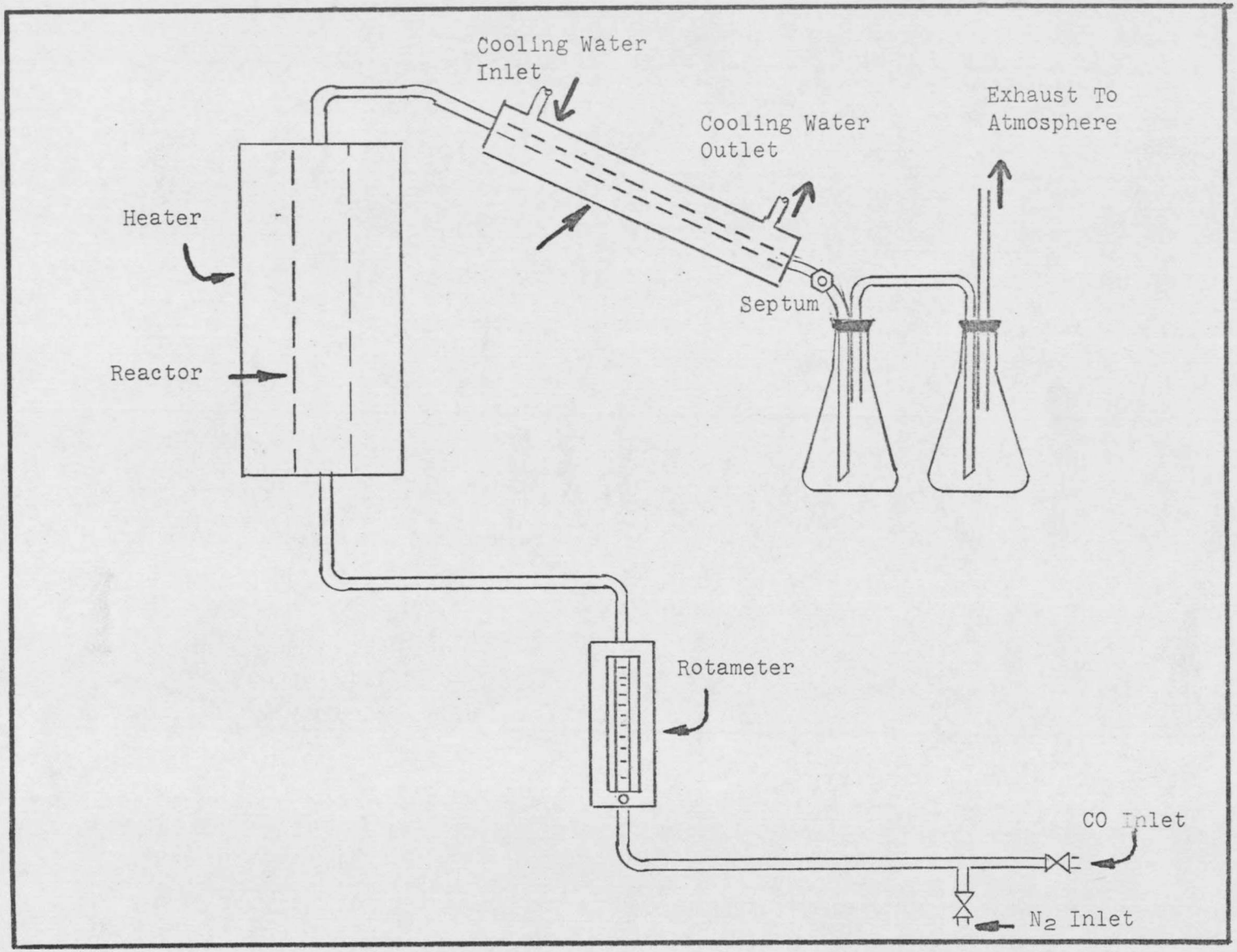

Figure 3: $CaSO_3$ Reduction Apparatus Schematic.

RESULTS AND DISCUSSION

The reduction of SO_2 effected in this investigation is represented by the equation

$$CaS + H_2O + SO_2 \longrightarrow H_2S + CaSO_3. \qquad (1)$$

Thermodynamic data is available for calcium sulfite only as the dihydrate, thus requiring that the reaction be written:

$$CaS + 3H_2O + SO_2 \longrightarrow H_2S + CaSO_3.2H_2O. \qquad (2)$$

For this reaction

$$\Delta F_{298} = -26{,}031 \text{ cal/mole.}$$

Although the reaction is exothermic the temperature did not rise significantly above 300° Kelvin. The temperature of neutral equilibrium was approximated by $T_{NE} = \Delta H_{298}/\Delta S_{298}$, neglecting the terms $\int \Delta C_p dT - T \int (\Delta C_p/T) dT$, with the result that

$$T_{NE} = 911° \text{ C.}$$

At T = 298°K. $K_{eq} = 1.23 \times 10^{19}$.

These calculations indicate that the reaction is thermodynamically most favorable. This finding is borne out by the experimental results. Investigation was made over a CaS concentration range of 20-125 grams per liter and a concurrent gas flow range of 6-30 standard liters/hour.

In each instance, SO_2 was removed to a level below the sensitivity of the analytical instrument, nominally 100%, and converted to hydrogen sulfide. The H_2S thus produced could be readily reduced to elemental sulfur via the Claus process. This was indeed the end sought in this investigation because of elemental sulfur's optimal shipping and storage characteristics. It appears, then, that this reaction might be applicable to the SO_2 emission problems already alluded to which are encountered in the smelting of Montana's metal sulfide ores.

The following mechanism is hypothesized to explain, in part, the reaction which takes place:

$$2CaS + H_2O \longrightarrow Ca(SH)_2 + CaO \qquad (3)$$

$$CaS + H_2S \longrightarrow Ca(SH)_2 \qquad (4)$$

$$Ca(SH)_2 + SO_2 + H_2O \longrightarrow 2H_2S + CaSO_3 \qquad (5)$$

$$CaO + SO_2 \longrightarrow CaSO_3 \qquad (6)$$

This mechanism derives primarily by analogy between equation 5 and equation 7 following:

$$Ca(HS)_2 + CO_2 + H_2O \longrightarrow 2H_2S + CaCO_3 \qquad (7)$$

The reaction represented by equation 7 has been investigated by Ganz, Revzin, and Oratovskii. (Ganz, etal: 1966) They observed that under

"conditions of high turbulance Ca^{++} is practically completely precipitated (.993-.996). Under optimum conditions the reaction rate is high and is quite complete." Ganz and Revzin further observed that "at Ca^{++} concentrations of greater than 40 g/l the reaction rate was constant." (Revzin, Ganz; 1966)

During the course of the reaction, hydrogen sulfide production rapidly attains a relatively stable rate which it maintains for some time before steeply ascending to some maximum value and abruptly falling to zero. Sulfur dioxide then begins to reappear, building slowly to the inlet concentration as the water becomes saturated with SO_2. Figures 4 and 5 illustrate the reaction proceeding for two representative runs. The slurry was observed to take on a deepening green hue as the H_2S level was building but disappeared at the moment that H_2S production dropped to zero.

These phenonena might be explained by interactions between reactions 3,4, and 5. H_2S production might be held relatively constant as reaction 4 competes for the H_2S evolved in reaction 5. Here perhaps, at higher Ca^{++} concentrations, the rate of reaction 5 may be constant as was observed for reaction 7 by Ganz and Revzin. (Ganz, Revzin; 1966) It might then be postulated that as the calcium sulfide concentration drops below a certain level the reaction rates shift, allowing reaction 5 to control and H_2S concentration to rise to a maximum, dropping to zero as all the $Ca(SH)_2$ is consumed.

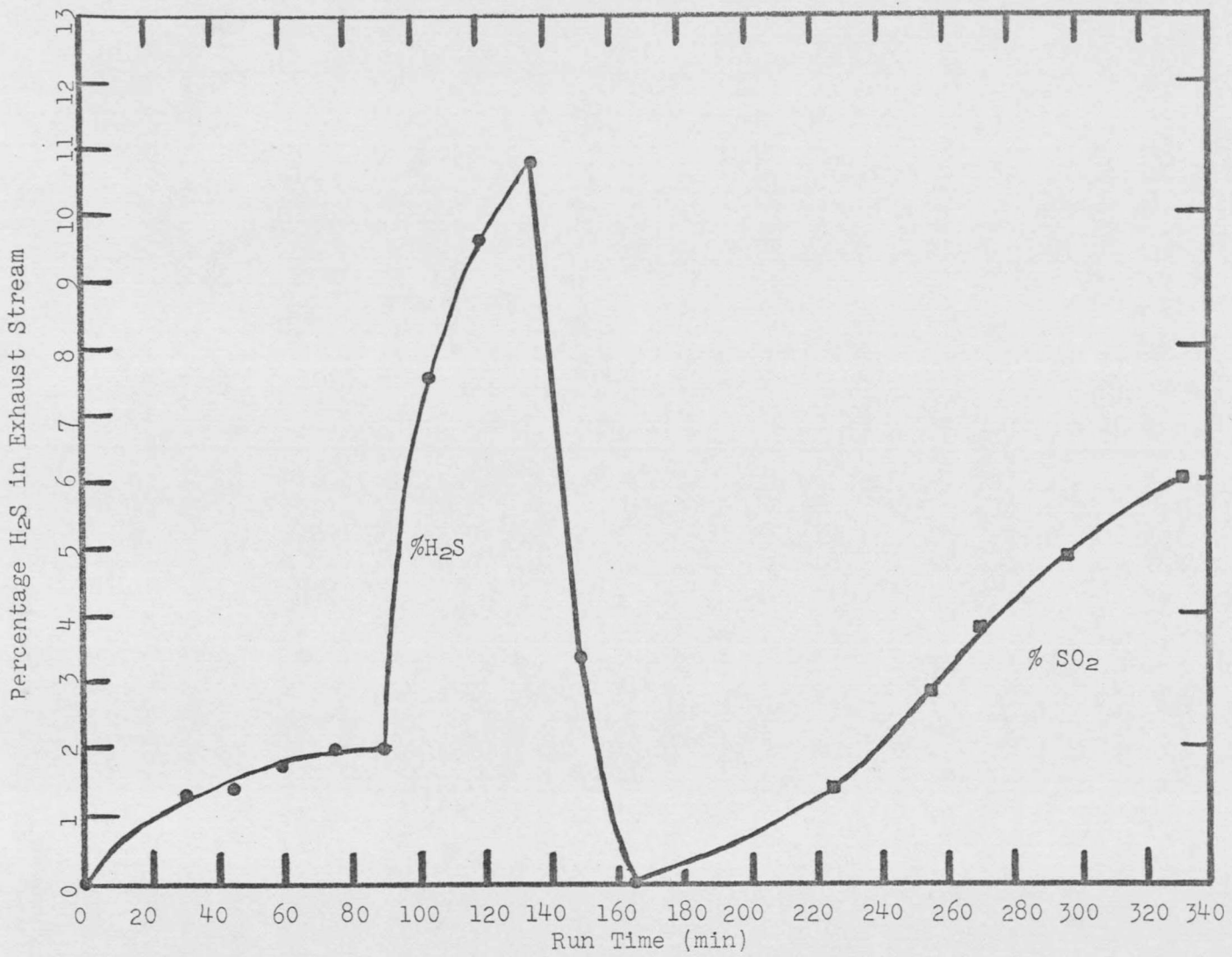

Figure 4: Run Progress for Typical SO_2 Reduction Run.

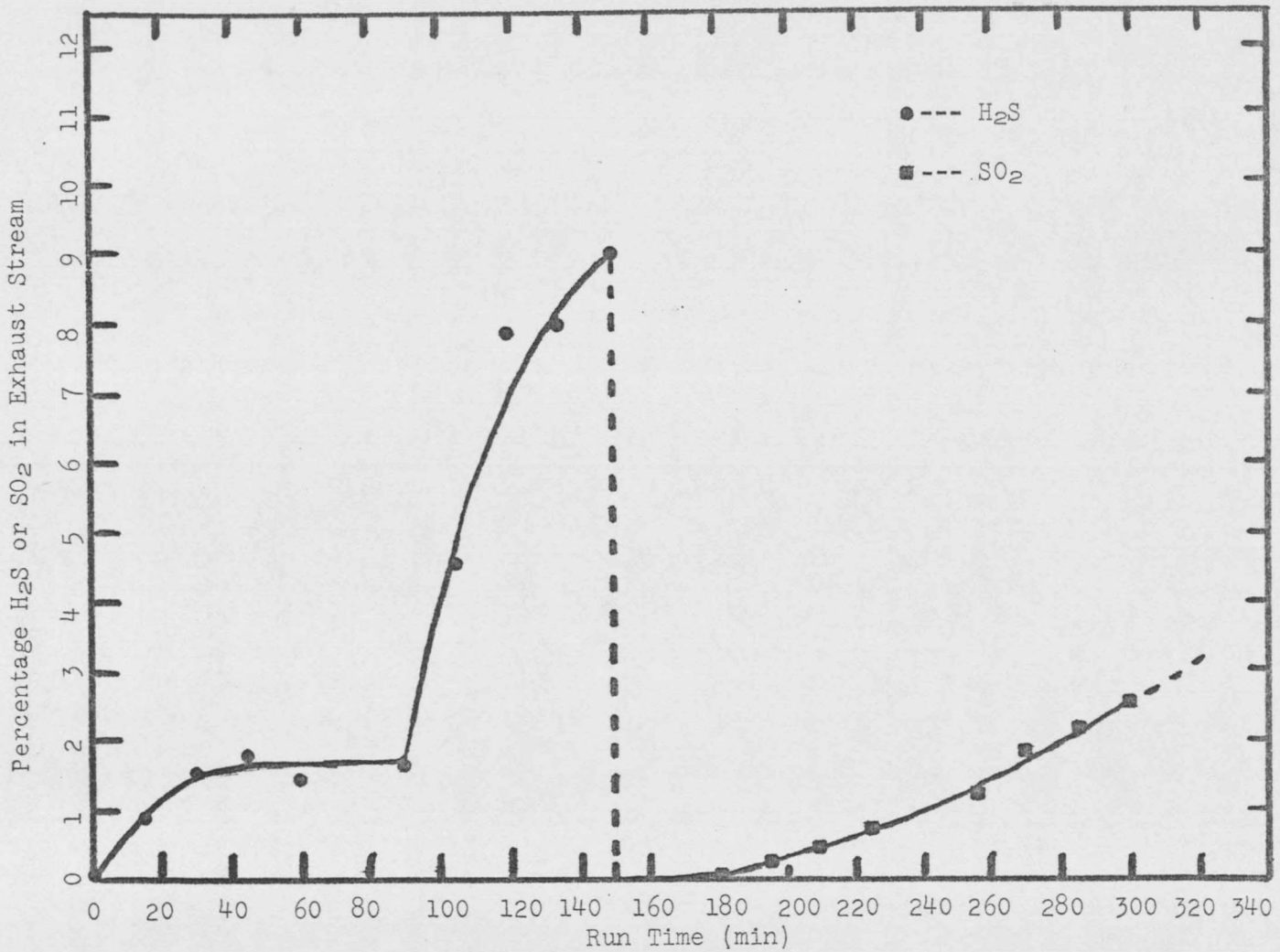

Figure 5: Run Progress for Typical SO_2 Reduction Run.

In so far as thermodynamic data is unavailable for the species calcium sulfhydrate, we must be content with such verbal argument in support of the proposed mechanism.

The dried, insoluble product resulting from reaction 1 was analysed to be approximately 97% $CaSO_3.2H_2O$, 0.7% S, 2% $CaSO_4$, with traces of such compounds as the thiosulfate and dithionate probably formed.

Those solids soluble in the sulfurous acid solution, which resulted from dissolution of SO_2 in the slurry water, were analysed to be nominally 100% $CaSO_3.2H_2O$.

Hydrogen sulfide evolved from the process is intended to be converted to elemental sulfur by the Claus process. The technology of this process is complicated with numerous modifications, but is highly developed and should present no problems. In view of the well developed technology involved, this portion of the total reduction process will not be treated further here.

During the early stages of this investigation, a porous, glass sparger was used to disperse the SO_2 into the slurry. Due to severe plugging problems involved with the spargers, they were abandoned in favor of straight, open tubes; however, for the short period that porous spargers could run before plugging, no sulfurous gases were evolved. Whether this was the result of some different reaction or whether the greater diffusion of SO_2 favored reaction 4, consuming all

the H_2S formed, has not been determined; however, the latter possibility seems more credible.

In an effort to reduce the sulfur dioxide directly to elemental sulfur, one run was made replacing water with a mixture of ethylene glycol monoethyl ether, water, and dibutylamine as in a modified Claus process. (Diah, etal; 1972) This attempt proved unsuccessful, failing to increase sulfur yields appreciably. In view of the separation problem which would arise, should sulfur be formed in the sulfite slurry, this approach was discontinued in favor of a two-step process which would not require such a separation.

Attempts were made to reduce the $CaSO_3$, recovered from the SO_2 reduction process, to CaS, for recycle to the SO_2 scrubber, using a process similar to that published by Zadick for the reduction of $CaSO_4$. (Zadick, 1971) In this endeavor, carbon monoxide was employed as the reducing agent with a ferric oxide catalyst. Runs were made using 0,1,5, and 10 percent catalyst for a total reaction mixture weight of either 20 or 25 grams. When no catalyst was used, the CO was never completely oxidized to CO_2, even at temperatures approaching 1000° C., ergo the $CaSO_3$ was never readily reduced to CaS. Analysis of the product of this run indeed indicated a substantial amount of $CaSO_3$ remaining unreacted. Using 10% catalyst, the reduced product showed only CaS with no $CaSO_3$. This reduced mixture was again utilized in the reduction of SO_2 with 100% conversion to H_2S apparent; however,

the slurry was exhausted after approximately 45 minutes as opposed to the 150 minute run times repeatedly obtained with the same mass of fresh CaS at the same gas flow rate. With 1% catalyst, CO_2 appeared in the exit gas stream as the reactor reached 436° C. Complete conversion of CO to CO_2 occurred at a reactor temperature of 717° C. The temperature was held near this level and CO_2 remained as the sole gaseous product for one hour and 10 minutes. CO then reappeared as the major product and the run was terminated shortly thereafter due to plugging of the reactor. For the 1% catalyst run, as well as the run with 5% Fe_2O_3, purchased $CaSO_3$ was used instead of CaS oxidized in the primary reaction. The purchased $CaSO_3$ subsequently proved to be quite impure. The product from reduction with 1% catalyst was found to be effective in removing SO_2 when used to scrub an SO_2-air mixture, but by some different mechanism than that observed with virgin CaS. A gaseous product other than H_2S was evolved which could not be identified with available procedures or equipment.

A 5% Fe_2O_3 in $CaSO_3$ mixture proved optimum among the conditions tried. Here CO_2 first showed in the exit gas at 100° C., occurred in preponderance at a reactor temperature of 408° C. and was the sole gaseous product at 449° C. CO_2 remained the sole product gas for several hours at temperatures of approximately 550° C.. After a period of approximately 5 hours, at which time presumably all the $CaSO_3$ particles were coated with CaS and rate became dependant upon diffusion of CO and

CO_2 through the CaS, both CO and CO_2 were evolved. Elevating the reactor temperature to 600° C. successfully increased the proportion of CO_2 as might be expected. The run was terminated after six hours due to plugging in the reactor.

The reduced product was used in the primary reaction to reduce SO_2. Again sulfur dioxide was removed from the gas stream to a level below the sensitivity of the chromatograph, nominally 100%. For the first 40 minutes of that run, with a gas feed rate of 15 standard liters/hour, hydrogen sulfide was evolved. At that point in time, although the sulfur dioxide removal was complete, the gaseous product which had been encountered with the one-percent-catalyst product appeared as the only sulfurous gas evolved.

Because of inability to identify this gas, its source can only be postulated. However, because this gas appeared only when the product obtained by reduction of the purchased $CaSO_3$ was used, it can be assumed that this gas is evolved from reaction between SO_2 and some impurity present in the purchased $CaSO_3$.

This anomaly not withstanding, these results point toward the fact that CaS, which is oxidized in the SO_2 reduction process, can be recovered under relatively moderate conditions by utilizing carbon monoxide as the reducing agent with 5% ferric oxide catalyst.

CONCLUSIONS

1. A water slurry of calcium sulfide reduced all detectable traces of SO_2 to H_2S.

2. The above result was observed for SO_2 flow rates varying from 6-30 standard liters per hour through slurry compositions ranging from 20-125 grams per liter CaS in water.

3. The resulting insoluble product was approximately 97% $CaSO_3.2H_2O$ with 2% $CaSO_4$, 0.7% Sulfur, and traces of more complex sulfur compounds.

4. The soluble solid product constituted 2-3% of the solution by weight and was essentially 100% $CaSO_3$.

5. The $CaSO_3$ resulting can be reduced under relatively moderate conditions utilizing carbon monoxide as a reducing agent and ferric oxide as a catalyst in concentrations of approximately five percent.

RECOMMENDATIONS

In so far as this process appears potentially promising, further work may be desirable in certain areas.

Further study into the regenerability of calcium sulfide is needed. A source of high-purity calcium sulfide must be found and the regeneration step carried out on this. Such analysis would serve not only to further knowledge of the reduction of $CaSO_3$ but also affirm or dispell the hypothesis that impurities in the $CaSO_3$ used in the present investigation reduced SO_2 by some other mechanism.

Identification of the impurities in the $CaSO_3$ should likewise prove instructive, perhaps leading to some other research-worthy reduction scheme.

Should the apparatus of Wang, for analysis of sulfurous emissions, be operating in the future, it would be instructive to determine the actual concentration to which SO_2 is reduced by the CaS reaction. (Wang, 1972)

It might be desirable to investigate further the use of organic solvents in place of water in the CaS slurry in an effort to obtain elemental sulfur in a one-step process.

Finally, assuming that these processes, at that stage, appear technically feasible, an economic analysis should be made comparing a one-stage and two-stage process as applicable to the American Smelting and Refining plant at East Helena or the Anaconda smelter at Anaconda.

APPENDICES

ANALYSIS FOR SULFATE

Sulfate ion was determined quantitatively according to the method described in Walton on pages 72-77 (Walton, 1963) utilizing Whatman No. 42 filter paper in a long stemmed funnel in place of a Gooch crucible for filtering the precipitated barium sulfate.

ANALYSIS FOR SULFITE AND SULFIDE

Sulfite and sulfide ions were determined quantitatively using the method described by Brink, etal, (Brink, etal; 1970) with the following modifications:

Standards used for calibration for these ions were Purified Calcium Sulfide obtained from Fisher Scientific Company and Baker reagent grade Sodium Sulfite obtained from J. T. Baker Chemical Company, both without further purification. All samples were pelletized in a mechanical press rather than heat fusing into pellets. A one-milliliter gas sample was analysed in lieu of the 5 ml sample chosen by Brink, etal. Finally a Porapak Q-S column was used in a Beckman GC-2A gas chromatograph for the gas analysis.

ANALYSIS FOR ELEMENTAL SULFUR

Sulfur analysis was accomplished by extraction with carbon disulfide as follows: A boiling flask was charged with 110-130 ml CS_2 and one or two Teflon boiling chips added to prevent bumping. The flask was fitted with a soxhlet apparatus and water-cooled reflux condenser. A tared, 33x80 mm paper extraction thimble containing a weighed sample of the unknown to be analysed was inserted in the soxhlet apparatus. The boiling flask was heated by means of a Glas-Col heating mantle and the CS_2 refluxed for one hour. At the end of the reflux period, the flask was removed from the heating mantle and the extraction thimble removed from the soxhlet. The CS_2 remaining in the flask was decanted and the flask rinsed with fresh CS_2. The CS_2 in the thimble and decanted from the boiling flask were carefully evaporated to dryness at room temperature to prevent combustion of the CS_2. The thimble and CS_2 residue was then dried overnight in an oven at 105° C.. The residue was then weighed on an analytical balance and the weight loss by the thimble contents was likewise determined as a check. This weight or weight loss was recorded as the mass of sulfur present in the analysed sample and expressed as a percentage by weight.

ANALYSIS FOR CALCIUM

Calcium ion was determined quantitatively following Standard Method 122 B., EDTA Titrimetric Method, in Standard Methods for the Examination of Water and Wastewater. (Taras, etal, ed.; 1971)

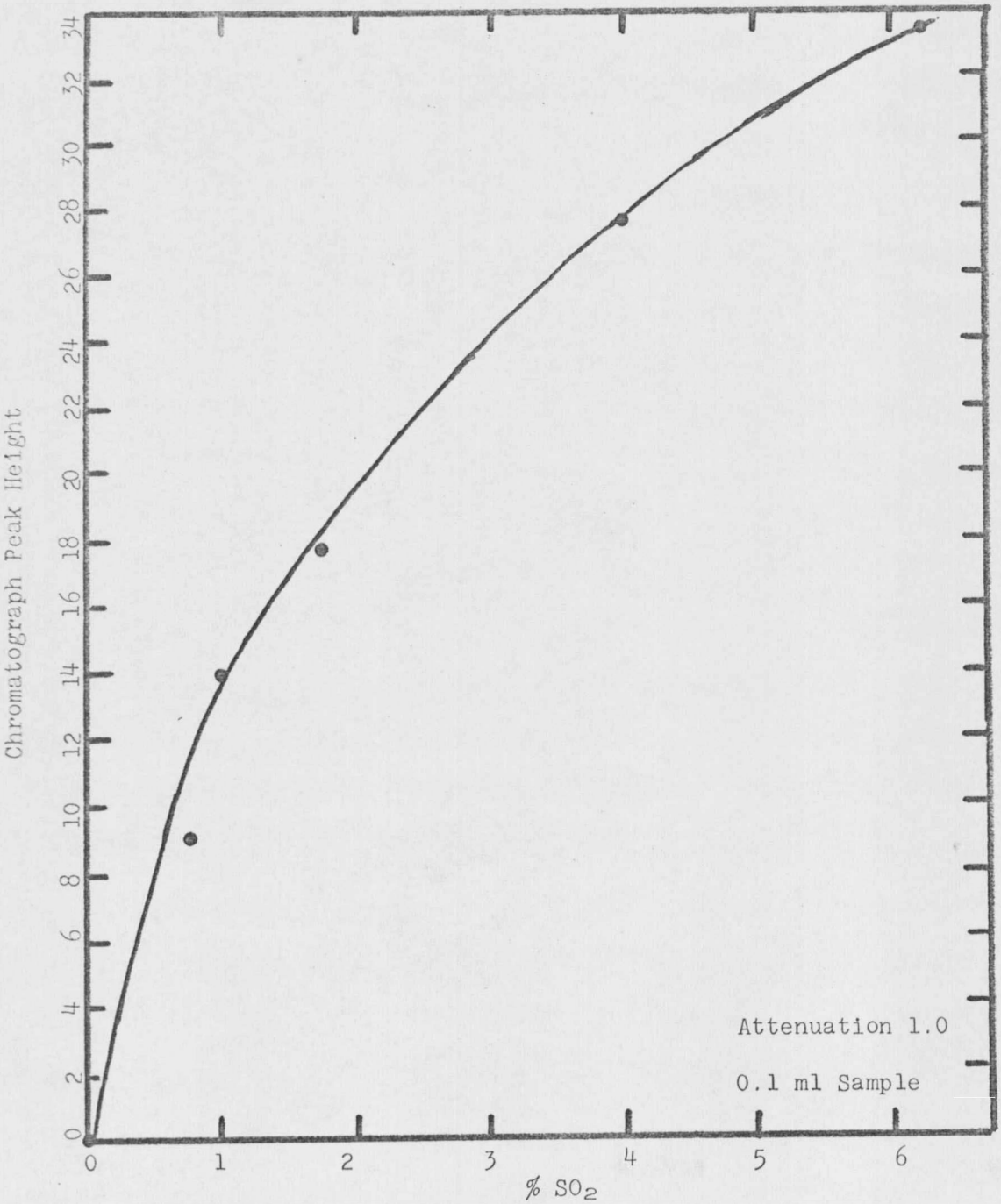

Figure 6: SO_2 Calibration Curve.

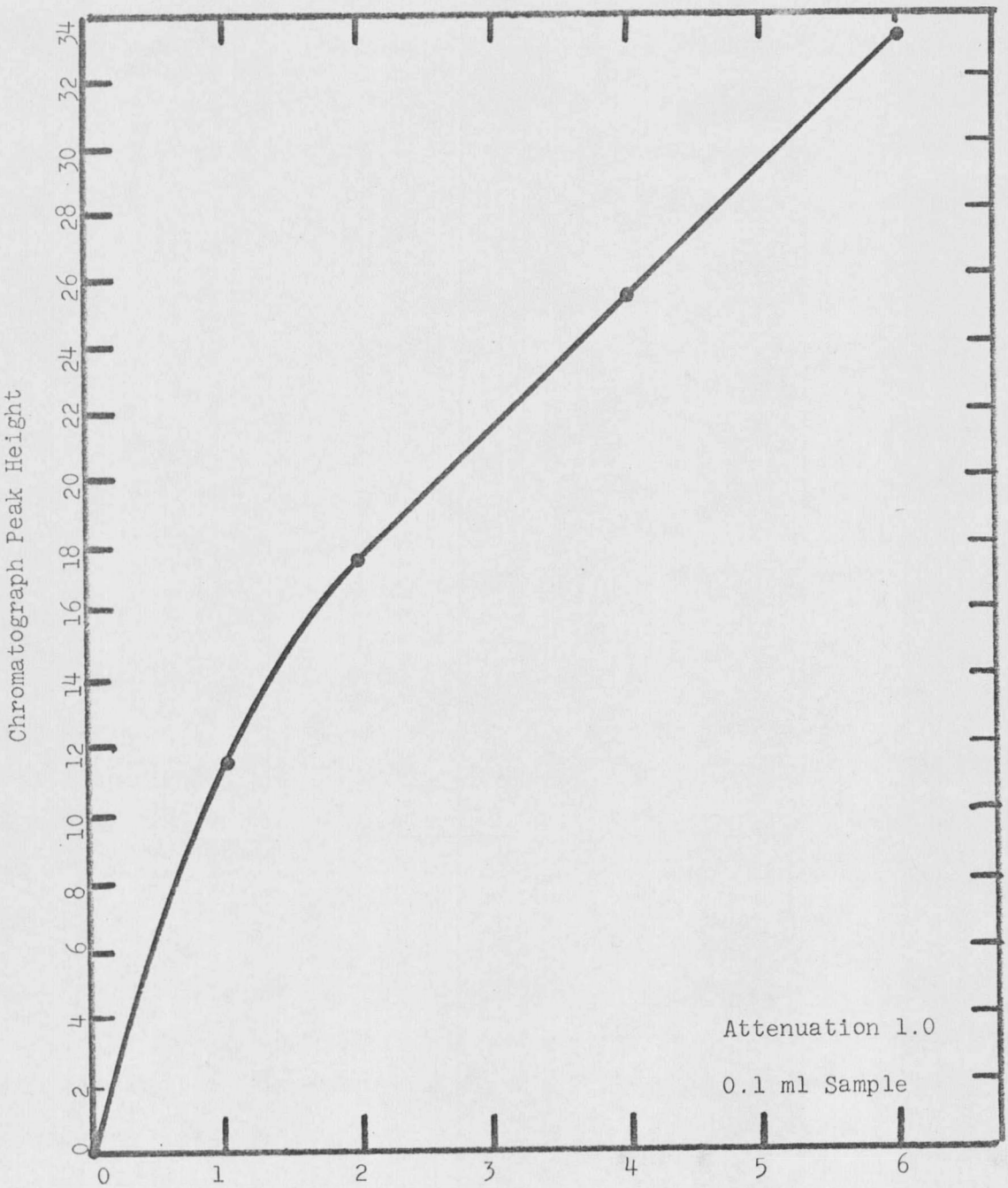

Figure 7: H_2S Calibration Curve. (low range)

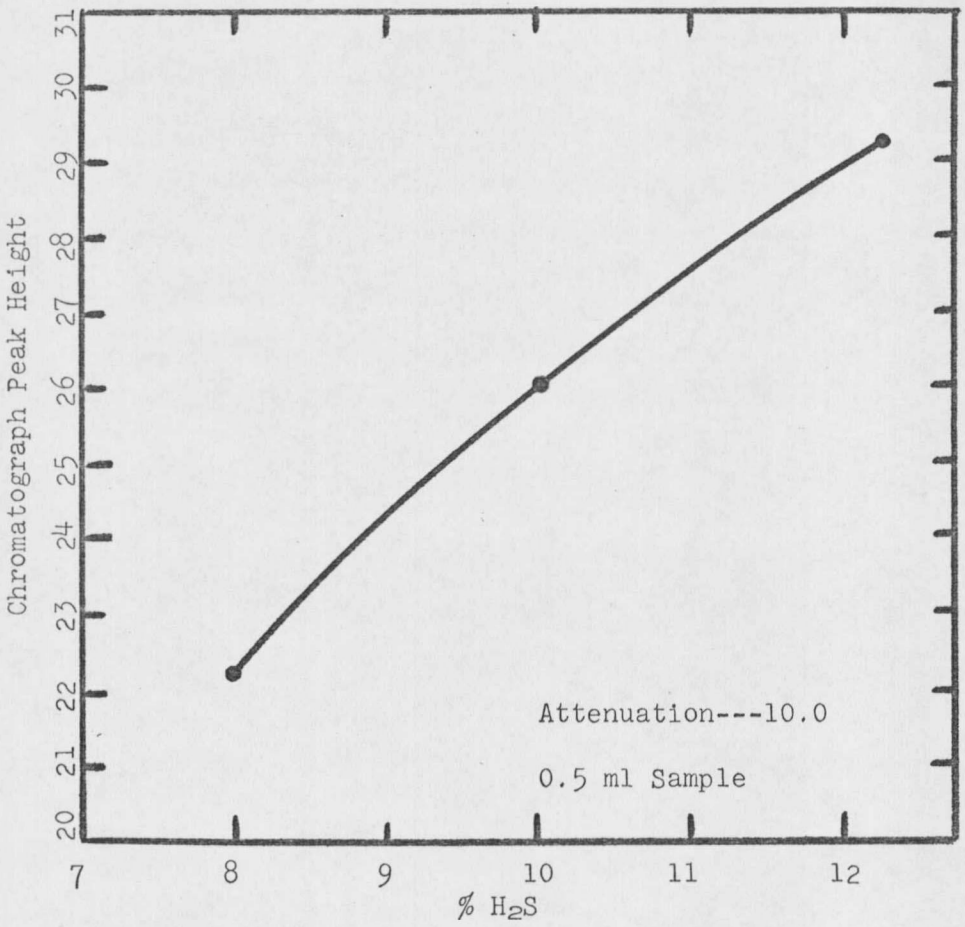

Figure 8: H_2S Calibration Curve (high range)

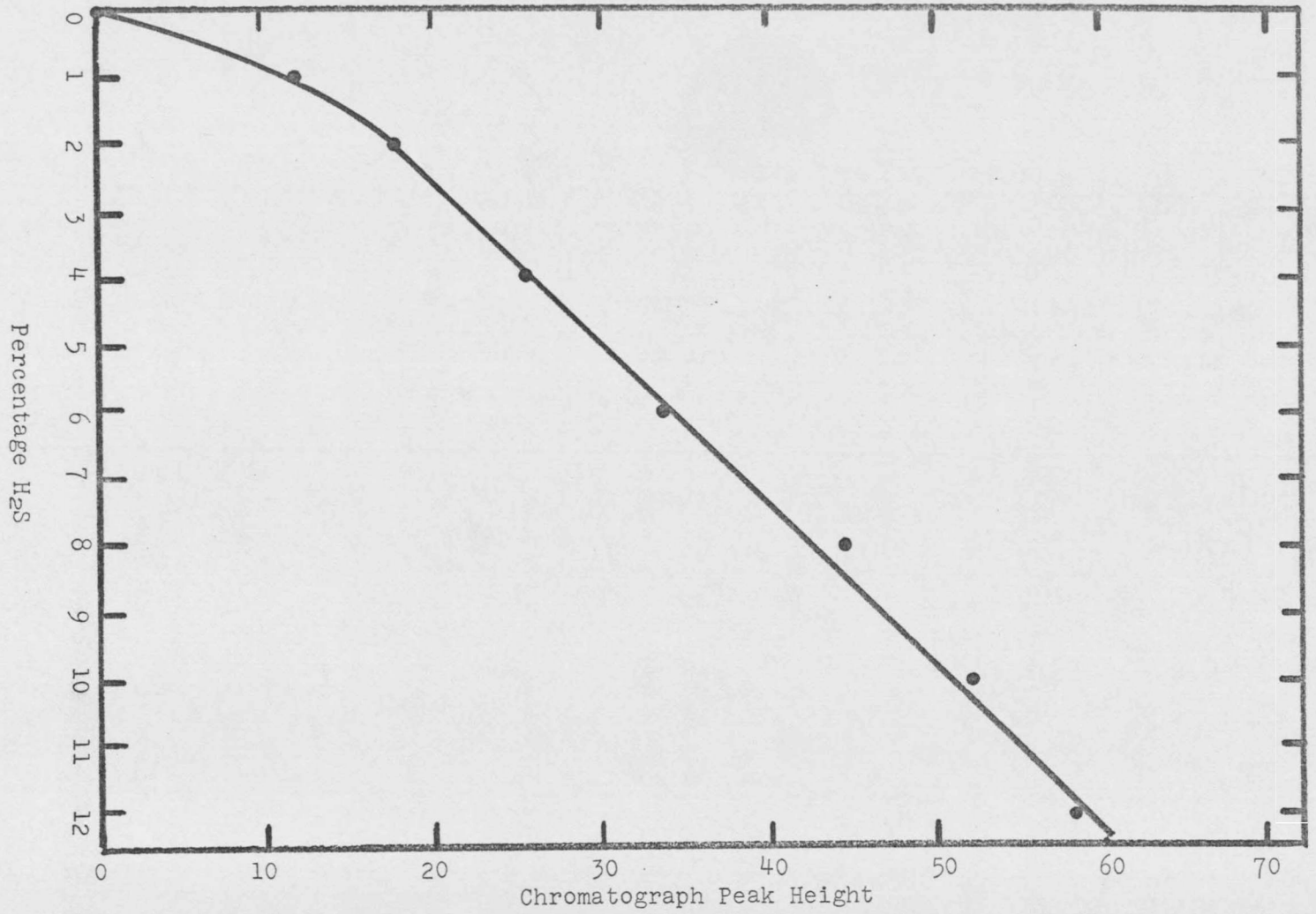

Figure 9: H_2S Calibration Curve Combining Figures 7 and 8 and Adjusted for 0.1 ml Sample at 1.0 Attenuation.

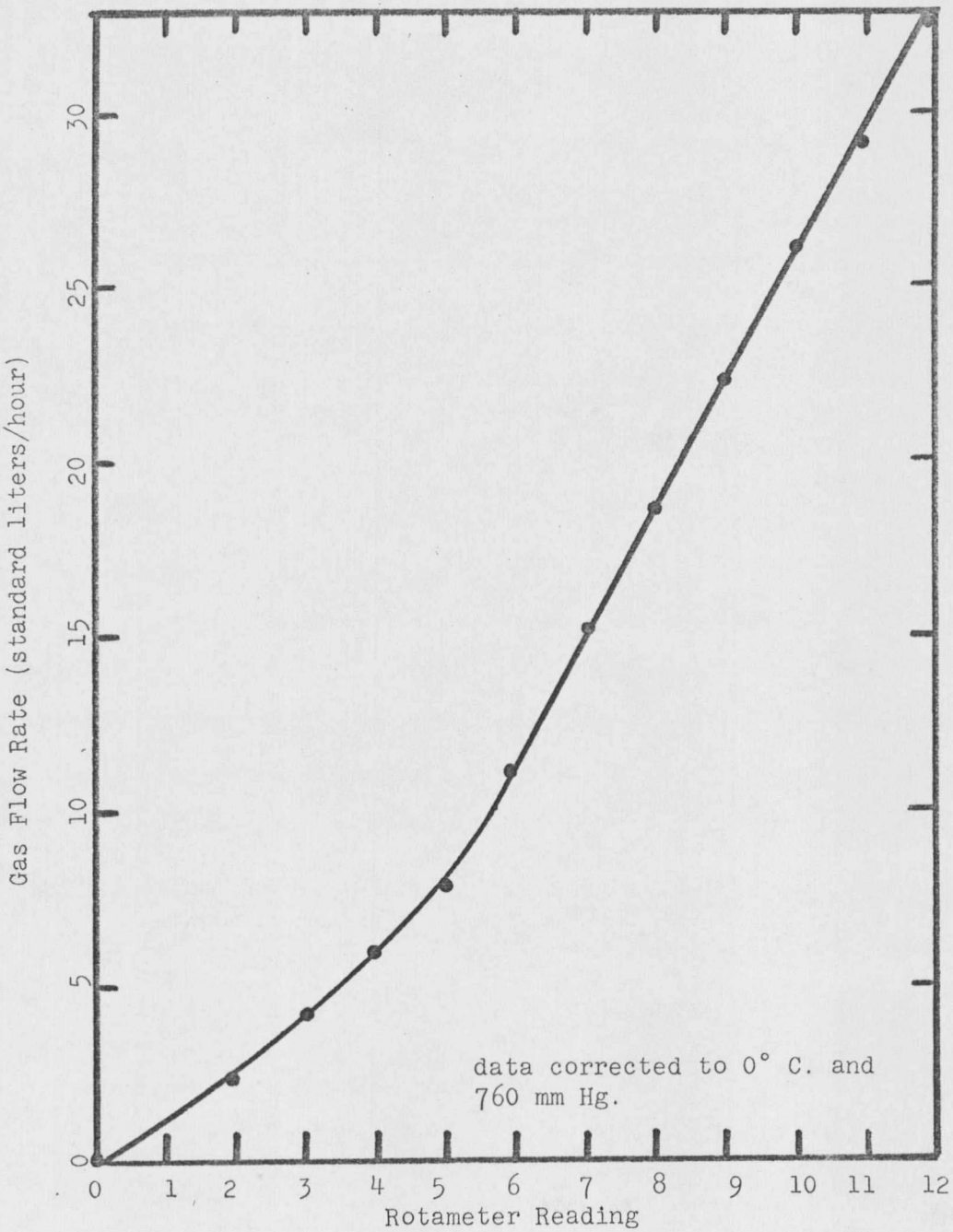

Figure 10: Rotameter Calibration Plot from Wet Test Meter (corrected to standard conditions).

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