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Publication Date
1993-05-01
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*(Ph.D. Thesis)

May 1993
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SYNTHESIS AND DEVELOPMENT OF PROCESSES FOR THE RECOVERY OF SULFUR FROM ACID GASES


Part II: Development of a Zero-Emissions Process for Recovery of Sulfur from Acid Gas Streams

by

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May, 1993

* Ph.D. Dissertation. This work was supported by the Morgantown Energy Technology Center, Assistant Secretary for Fossil Energy, Office of Coal Utilization, Advanced Research and Technology Development, Division of Surface Coal Gasification through the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
Abstract

Synthesis and Development of Processes for the Recovery of Sulfur from Acid Gases

Limestone can be used more effectively as a sorbent for $\text{H}_2\text{S}$ in high-temperature gas-cleaning applications if it is prevented from undergoing calcination. Sorption of $\text{H}_2\text{S}$ by limestone is, however, impeded by sintering of the product CaS layer. Sintering of CaS is catalyzed by $\text{CO}_2$, but is not affected by $\text{N}_2$ or $\text{H}_2$. The kinetics of CaS sintering was determined for the temperature range 750 - 900 °C. A reactor containing a moving-bed of limestone particles would absorb $\text{H}_2\text{S}$ and also be very effective for filtering particulate matter from the coal gas.

When hydrogen sulfide is heated above 600 °C in the presence of carbon dioxide elemental sulfur is formed. The rate-limiting step of elemental sulfur formation is thermal decomposition of $\text{H}_2\text{S}$. Part of the hydrogen thereby produced reacts with $\text{CO}_2$, forming CO via the water-gas-shift reaction. The equilibrium of $\text{H}_2\text{S}$ decomposition is therefore shifted to favor the formation of elemental sulfur. The main byproduct is COS, formed by a reaction between $\text{CO}_2$ and $\text{H}_2\text{S}$ that is analogous to the water-gas-shift reaction. Smaller amounts of $\text{SO}_2$ and $\text{CS}_2$ also form. Molybdenum disulfide is a strong catalyst for $\text{H}_2\text{S}$ decomposition in the presence of $\text{CO}_2$. A process for recovery of sulfur from $\text{H}_2\text{S}$ using this chemistry is as follows: Hydrogen sulfide is heated in a high-temperature reactor in the presence of $\text{CO}_2$ and a suitable catalyst. The primary products of the overall reaction are $\text{S}_2$, CO, $\text{H}_2$ and $\text{H}_2\text{O}$. Rapid quenching of the reaction mixture to roughly 600 °C prevents loss of $\text{S}_2$ during cooling. Carbonyl sulfide is removed from the product gas by hydrolysis back to $\text{CO}_2$ and $\text{H}_2\text{S}$. Unreacted $\text{CO}_2$ and $\text{H}_2\text{S}$ are removed from the product gas and recycled to the reactor, leaving a gas consisting chiefly of $\text{H}_2$ and CO, which recovers the hydrogen value from the $\text{H}_2\text{S}$. This process is economically favorable compared to the existing sulfur-recovery technology and allows emissions of sulfur-containing gases to be controlled to very low levels.
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Acknowledgements

There are many people to whom I am indebted for help that I have received during my time in Berkeley, but none more so than my adviser, Professor Scott Lynn. His patience, his humor, and above all his incredible knowledge of chemistry and all aspects of chemical engineering design were a constant inspiration and set a standard to which I hope to aspire in my own work. No apprentice could wish to study under a greater master.

I am grateful to all my labmates over the years for support, entertainment and for putting up with my sense of humor. In particular, it was a pleasure to work with Laurent Fenouil on the limestone project; I am grateful to him for producing the pictures used in Part I and also for being so understanding when my attention was diverted by teaching and the ZESP project. Dave Koch and Rob Broekhuis gave invaluable help with my computing difficulties and John Markels helped me work harder, drink more, understand America better and get a lot more out of my time here.

To my girlfriend Caroline I owe my health, happiness, sanity and much more besides. Her love and support gave me strength when I needed it most and I will always be indebted to her and her family for the love and kindness they have showed me.

I found all the staff of the Chemical Engineering Department to be friendly and helpful, especially Kay Ekman and Ferne Kasarda in the Graduate Student's Office. Their guidance in manoeuvering through the famed University bureaucracy was much appreciated, as were our many conversations on travel, and all things cultural. I truly believe that the chemical engineers must be the best looked-after graduate students in the University. Special thanks are also owed
to Tom Lawhead and Cathy Sigler of the college glass shop, without whose superb craftsmanship this research would have been impossible. They not only produced complicated glassware to sub-millimeter specifications, but also maintained their composure when I brought it back in pieces and asked how long it would take to fix.

This research was funded by the Morgantown Energy Technology Center, Assistant Secretary for Fossil Energy, Office of Coal Utilization, Advanced Research and Technology Development, Division of Surface Coal Gasification through the U.S. Department of Energy under contract DE-AC03-76SF00098.
Part I

Development of a High-Temperature Process for Removal of H$_2$S from Coal Gas Using Limestone:
Thermodynamic and Kinetic Considerations
1. Introduction

1.1 Background

One of the greatest challenges faced in the energy-conversion field is the problem of how to extract energy from coal while causing a minimum amount of damage to the environment. The major contaminant that must be removed from the coal is sulfur, which in conventional plant is oxidized to sulfur dioxide, SO$_2$, and removed from the combustion flue gases in a flue-gas-desulfurization (FGD) plant. FGD plants are costly, do not recover the sulfur in a usable form, and often generate large amounts of solid waste. An alternative is to gasify the coal. Coal gasification plants do not require FGD units as gasification converts the sulfur to hydrogen sulfide, H$_2$S, which can be easily recovered by classical techniques such as absorption. A further advantage of coal gasification is that the coal gas can be used as a fuel for gas turbines, allowing exploitation of recent advances in combined-cycle power-generating technology. It has been shown by Squires et al. (1971), that removing the sulfur and other contaminants from the coal gas at high temperature and pressure offers numerous advantages over other methods of gas cleaning, most notably higher thermal efficiency and reduced volume (hence cost) of processing vessels.

One possible strategy for high-temperature, high-pressure (HTHP) gas cleaning is to add limestone to the gasification reactor. Moderately successful recovery of H$_2$S is achieved; however, the limestone conversion is low (typically less than 50%) and large amounts of mixed sulfided and sulfated limestone/slag solid waste are produced. The poor conversion is due to the conditions prevalent in the gasifier (for reasons discussed below).
An alternative strategy would be to contact the limestone and coal gas in a separate vessel, whose operating conditions would be optimized for $H_2S$ sorption. This would prevent the limestone from mixing with the slag from the coal and permit regeneration and recycle of the sorbent. A further advantage of contacting the $H_2S$ and limestone in a separate vessel is that if a moving-bed reactor is used then it will also remove aerosol contaminants from the gas by filtration. This dissertation describes an investigation of some of the chemical and physical processes that are important in the design of such a high-temperature gas cleaning device.

1.2 Previous Work

Limestone is an abundant sedimentary rock of varying composition, consisting mainly of $CaCO_3$ with $CaSO_4$ and $MgCO_3$ as the major impurities. Natural limestone has very low porosity, typically less than 8% (Borgwardt and Roache, 1984). Upon heating, limestone dissociates to calcium oxide and $CO_2$, a process known as calcination:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1.1}$$

If the fugacity of $CO_2$ is sufficient to prevent calcination then at high temperatures $CaCO_3$ reacts with $H_2S$ according to:

$$CaCO_3 + H_2S = CaS + H_2O + CO_2 \tag{1.2}$$

referred to as sulfidation of limestone. If the limestone is calcined then the reaction which occurs is sulfidation of calcium oxide:

$$CaO + H_2S = CaS + H_2O \tag{1.3}$$

For both calcination (Reaction 1.1) and sulfidation (Reaction 1.2) of limestone the external dimensions of solid particles are observed to remain constant (Borgwardt et al., 1984),
therefore as the reaction proceeds the porosity of the solid increases. From the densities of these materials it can be calculated that the porosity should increase to roughly 57% of solid volume on calcination and ~28% on sulfidation. Since the pore structure opens up on reaction both reactions might therefore be expected to proceed to 100% conversion of the solid phase. This is not true for the sulfidation of calcium oxide (Reaction 1.3), where the stereochemical effect of substituting S for O leads to the formation of a surface layer of CaS causing the reaction to proceed by a solid state diffusion mechanism (Hartman and Trnka, 1980; Bhatia and Perlmutter, 1981).

The increase in internal surface area due to reaction is partially offset by a decrease due to rearrangement of either the product or unreacted limestone — a process known as sintering. The sintering of CaO formed by calcination is a well known process discussed by numerous authors (good examples being Ruth et al., 1972, and Borgwardt et al., 1984). Sintering of calcium oxide has been cited by Borgwardt and Roache (1984) as a reason for the poor performance of CaO as a sorbent for H₂S. Borgwardt (1989) found that the sintering of CaO was catalyzed by the presence of CO₂ or H₂O in the gas phase. Borgwardt and Roache (1984) also suggested that sintering of CaCO₃ might inhibit the sulfidation of limestone, as discussed in Chapter 5. Fuller and Yoos (1987) suggest that impurities in the rock serve as fluxes which promote sintering; however, they provide no experimental evidence. The sintering properties of CaS have not been reported in the literature.

The calcination of limestone was investigated over a wide range of temperatures and pressures by Baker (1962) who correlated the calcination temperature as a function of the partial pressure of CO₂. The kinetics of calcination have been the subject of much work, largely of very
poor quality. Khraisha and Dugwell (1989) observed that much apparent contradiction in the literature is due to empiricism, lack of rigorousness and failure to differentiate between chemical, heat- and mass-transfer steps before extracting the genuine chemical rate. Sotirchos et al. (1988) and Khraisha and Dugwell (1989) also point out that results obtained from experiments in thermogravimetric analyzers (TGAs) may not be immediately relevant to the performance of industrial calcining systems with very different heat- and mass-transfer characteristics.

The decomposition of limestone occurs via a shrinking-core-model mechanism with a definite boundary between the CaO and unreacted CaCO₃. Most writers agree that the rate-determining step is chemical reaction, as first observed by Satterfield and Feakes (1959) and Ingraham and Marier (1963). Dennis and Hayhurst (1986, 1987) found chemical reaction control for 0.4 to 2.0 mm particles, as did Borgwardt (1985) for small diameter (10 to 90 μm) particles and Baruto and Searcy (1974) for single crystals in vacuo. Hills (1968) found the decomposition of large spheres (10 mm in diameter) was controlled by both heat and mass transfer in the calcined layer. Fuller and Yoos (1987) failed to identify a rate-controlling mechanism. For the purposes of this study the exact mechanism is unimportant and it is sufficient to note that calcination of limestone will occur rapidly at high temperatures if the equilibrium fugacity of CO₂ is low enough.

A close mineral relation of limestone is dolomite, which has approximate chemical composition CaCO₃·MgCO₃. Dolomite calcination was observed by Dennis and Hayhurst (1987), who found the MgCO₃ calcines very rapidly followed by slower calcination of the CaCO₃.

\[
[CaCO₃·MgCO₃] = [CaCO₃·MgO] + CO₂ = [CaO·MgO] + 2CO₂ \tag{1.4}
\]
Dolomite or half calcined dolomite may also be reacted with $\text{H}_2\text{S}$; however, only the calcium fraction undergoes sulfidation from either the carbonate or oxide form.

As noted above, most studies to date have investigated the addition of limestone to the gasification reactor or furnace itself. Under the high temperatures encountered in these vessels calcination occurs much more rapidly than sulfidation and the main sulfur-capturing reaction is therefore:

$$\text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O}$$  \hspace{1cm} (1.3)

This reaction has been very thoroughly investigated since the use of limestone as a sorbent for $\text{H}_2\text{S}$ was first proposed by Squires et al. (1971). The problem with using this reaction for sulfur removal is that the sulfidation of calcium oxide results in a net decrease in porosity, therefore a tight inert layer of CaS is formed over the CaO. Calcium oxide is also known to sinter very rapidly. Complete conversion of the solid phase thus requires diffusion of ions through the product layer (Hartman and Trnka, 1980; Bhatia and Perlmutter, 1981). The diffusivities involved were estimated for six different limestones by Borgwardt et al. (1987).

Intuitively one might expect that the limestone sulfidation reaction would proceed more rapidly than the sulfidation of calcium oxide, due to the increase in porosity described above. Early studies by Ruth et al. (1972) found that half-calcined dolomite had a much greater reactivity than fully calcined at temperatures up to 800 °C (they speculated that the high temperature limit was due to sintering of $\text{CaCO}_3$). Their greatest interest was in CaO, however, so no further investigation was made until Borgwardt and Roache (1984).

Borgwardt and Roache state that Ruth et al. (1972) found that half-calcined dolomite
reacted according to:

\[
\frac{d(CaCO_3)}{dt} = k_2 \cdot (CaCO_3) \cdot C_{H_2S}
\]  

(1.5)

where \((CaCO_3)\) is the fraction of \(CaCO_3\) unreacted, \(C_{H_2S}\) is the gas phase concentration of \(H_2S\) and \(k\) is a rate constant. This expression does not actually appear in Ruth et al. Borgwardt and Roache studied the sulfidation of limestone over the temperature range 570 to 850 °C for particles of size 1.6 to 100 μm. They found the rate of reaction to be inversely proportional to particle size and to be high initially, but to fall off rapidly above ~11% conversion. They speculated that this was due to a loss of the initial porosity of the \(CaCO_3\). Attar et al. (1979) studied the sulfidation of calcite (pure, trigonal crystals of calcium carbonate) and found the rate-limiting step to be chemical reaction on the flat crystal surface until about 80 CaS layers are formed. After this the reaction rate becomes limited by solid-state diffusion through the CaS crust. These results are consistent with Borgwardt and Roache's (1984) observation of a steep decline in the sulfidation rate of μm-sized pellets after 11% conversion: 80 molecular layers corresponds to about 10% of the volume of a 1-μm-diameter \(CaCO_3\) grain. Both Ruth et al. (1972) and Borgwardt and Roache (1984) investigated the effect of other constituents of the coal gas on the limestone/\(H_2S\) reaction. Both found that adding \(CO_2\) and \(H_2O\) promoted the reaction. Ruth et al. found that adding hydrogen had no effect, but Borgwardt and Roache found it to be inhibitive. Unfortunately neither set of workers appeared to be aware of the equilibration of the water gas shift reaction at high temperatures, therefore the gas-phase concentrations reported are highly inaccurate. This casts some doubt on the findings of their work and suggests the need for more thorough research in this area. These and other common faults in the limestone literature are discussed in more detail in Section 2.2.
2. Thermodynamics

2.1 Importance of Gas Composition

Coal gas is a multicomponent gas mixture consisting chiefly of CO, H₂, CO₂, H₂O, CH₄, H₂S and N₂, with small but significant amounts of COS, NH₃ and various volatilized salts in aerosol form. The composition of the gas is set by the equilibrium of a number of reactions; however, at the temperatures at which sorption would be carried out the most important of these is the water-gas shift reaction:

\[ CO + H₂O = CO₂ + H₂ \]  \hspace{1cm} (2.1)

It is well known that at high temperatures this reaction equilibrates rapidly compared to the timescale for other reactions (see any reference on coal gasification, e.g. Denn and Shinnar, 1987). Therefore, since the four species involved are the main constituents of the coal gas, the equilibrium fugacity of each species can be assumed to be set by the water-gas shift equilibrium.

Because of the complex nature of these high-temperature, multicomponent gas mixtures and their interactions with the solid phase, calculation of the thermochemical equilibrium composition is nontrivial. Such calculations were performed using a computer simulation previously developed in this Department (Whitney et al. 1987) named COALNEAT. This program calculates the equilibrium composition, given a feed stream composition, together with a temperature and pressure. The calculation is performed by selecting a set of independent chemical reactions, determining material balances for all elements present and then solving iteratively using a robust, multi-dimensional Newton-Raphson iteration procedure. Use of this simulation allowed investigation of the way the equilibrium composition of the gas phase changes.
with temperature, pressure and feed composition. This was useful in:

i) analyzing previous research efforts,

ii) selecting the best conditions for our own experiments, and

iii) performing process simulation calculations.

In carrying out experiments on the high-temperature sulfidation of limestone, two gas/solid reactions are important, namely calcination and sulfidation itself. If we wish to observe the sulfidation of CaCO₃ (rather than CaO) then we must maintain an equilibrium fugacity of CO₂ high enough to prevent calcination from occurring:

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]  \hspace{1cm} (1.1)

The sulfidation reaction leads to the formation of CO₂ and H₂O:

\[ \text{CaCO}_3 + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O} + \text{CO}_2 \]  \hspace{1cm} (1.2)

If no CO is present then the gas mixture is oxidizing in nature, which can cause problems. Calculations showed that CO₂ is capable of oxidizing CaS to CaSO₄, which would effectively prevent the sulfidation reaction by pore blocking. A sufficient amount of either CO or H₂ must therefore be added to the gas to prevent this from occurring. Calculations show that the ratio of CO to CO₂ needs to be greater than 1:100 to prevent oxidation of calcium sulfide.

It is possible that any of the four main gas-phase species (CO, H₂, H₂O and CO₂) may exert an influence upon the kinetics of the sulfidation reaction, either directly or through their influence on the other species via the water-gas shift reaction. The gas species may also exert an influence on physical processes such as sintering. It is therefore necessary to evaluate the
effect of each constituent while keeping the others as near constant as possible. This is made more difficult by the water-gas shift reaction, which though relatively weakly temperature-dependent over the range of study, is still capable of causing major fugacity changes with temperature, particularly for species present in low concentrations. Considerable care is therefore necessary in selecting the gas composition. There is no evidence of such care being taken in much of the previous work in this field.

2.2 Failures of Previous Work

In the course of examining the literature available on high-temperature gas cleaning it became apparent that most previous studies contained major flaws due to misunderstanding the nature of the systems involved. A few key errors that were common to a number of research efforts are described below.

Many researchers reported results in terms of gas-phase concentrations, in some cases even failing to report the pressure at which experiments were carried out. In gas/solid reactions it is the partial pressure (or, strictly, the fugacity) of any gas-phase species that should be used in modelling reaction kinetics, therefore the effect of pressure must be included. More importantly, where several species are present in the gas phase, the equilibrium fugacity may be strongly dependant upon composition and temperature. At the high temperatures used for experiments on limestone calcination and sulfidation the gases behave ideally except under pressures much higher than normally encountered experimentally. It is, however, possible for the gas composition to alter due to any of several high-temperature gas-phase reactions. For example, if H$_2$ and CO$_2$ are present in the feed, then the gas composition in the reactor will be
set by the water-gas shift equilibration (which will of course change with temperature).

An important result of this high-temperature equilibration is that great care must be taken in the selection of an experimental gas-feed composition. Most researchers appeared unaware of the effect of high-temperature gas-phase reactions on the gas composition. They therefore performed experiments in which the gas composition varied widely with temperature, or in which water-gas shift equilibration had reduced the equilibrium fugacity of $\text{CO}_2$ to the point at which calcination of limestone would have occurred. Another problem already described above is that if the equilibrium fugacity of $\text{CO}_2$ is high enough relative to that of CO then CaS can be oxidized to $\text{CaSO}_4$, which may be responsible for the results observed by Borgwardt and Roache (1984). Data from experiments in which the gas-phase composition was varying with temperature in an undetermined manner are obviously of little utility.

Another fault common to several research efforts was poor apparatus design. Section 4.1.1 discusses the different types of reactors used for studying high-temperature gas / solid reactions. It was found by Gallagher and Johnson (1973) that isothermal reactors (in which the solid is usually held at a single location in the reactor) perform significantly better than dynamic reactors (in which the solid moves through the reactor, experiencing different temperatures at different points in the trajectory) when studying limestone calcination. Despite this many researchers use dynamic reactors, even though the variation in temperature (and hence gas composition) that the particle experiences as it passes through the reactor makes correlation of the results exceedingly complicated (a fact conveniently ignored by assuming gas composition to be temperature-independent).
2.3 Selection of Experimental Atmosphere

In view of the factors discussed above, considerable care was taken in selecting experimental atmospheres for performing experiments to study the sulfidation of limestone. The atmosphere used for kinetic studies must:

i) Contain sufficient CO$_2$ to allow a range of temperature operation close to the process operating temperature (973 °C / 1784 °F) so as to allow extrapolation of data into the range likely to be used by any high-temperature gas cleaning process (but note that the upper temperature is determined by calcination).

ii) have a CO$_2$ partial pressure similar to that used under process conditions, or as close as possible. For a typical coal gas stream the partial pressures of the gas components under process conditions are:

<table>
<thead>
<tr>
<th>H$_2$</th>
<th>CO$_2$</th>
<th>CO</th>
<th>H$_2$O</th>
<th>H$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.4</td>
<td>2.33</td>
<td>18.4</td>
<td>2.42</td>
<td>0.42</td>
</tr>
</tbody>
</table>

iii) contain a sufficiently high partial pressure of CO to prevent oxidation of CaS to CaSO$_4$ as described above. This requires roughly 1 % CO in CO$_2$. This CO concentration can be achieved by adding H$_2$, due to rapid equilibration of the water-gas shift reaction at these temperatures.

iv) maintain constant partial pressure for as many species as possible over an appreciable
temperature range so as to allow decoupling of the effects due to temperature and those due to composition changes. This can be achieved by "flooding" — using such a large fraction of one component that the mass balance restricts the other component concentrations from fluctuating significantly.

v) contain sufficient \( \text{H}_2\text{S} \) to allow a high equilibrium conversion in the limestone sulfidation reaction. Note that this requires more \( \text{H}_2\text{S} \) as the partial pressure of \( \text{CO}_2 \) increases.

Furthermore, we know from Pell *et al* (1971) that the kinetics are first order with respect to the partial pressure of \( \text{H}_2\text{S} \), therefore using more \( \text{H}_2\text{S} \) will shorten reaction times.

Bearing all these considerations in mind it was decided to use a mixture "flooded" with \( \text{CO}_2 \). An \( \text{H}_2\text{S} \) concentration of roughly 1 % at 1 atm pressure is sufficient for experimental purposes. This gives a lower partial pressure of \( \text{H}_2\text{S} \) than normally found in coal gas; however, since we seek to develop a process that reduces the \( \text{H}_2\text{S} \) partial pressure to a low level, a low concentration is appropriate for our study. A small amount of \( \text{H}_2 \) was also added to the mixture, which could form \( \text{CO} \) and \( \text{H}_2\text{O} \) via the water-gas shift reaction at high temperatures. This eliminated the need for using a \( \text{CO} \) supply in early experiments, reduced the safety hazards associated with the experiments and guaranteed a reducing atmosphere with respect to the oxidation of \( \text{CaS} \) to \( \text{CaSO}_4 \).

Test runs were carried out using the COALNEAT program to determine the optimum \( \text{CO}_2 \) partial pressure. It was found that the calcination temperature is not significantly changed by varying the \( \text{CO}_2 \) composition between 90 and 96 % at 1 atm. The composition therefore used
for preliminary experiments was set at an initial feed composition:

\[
\begin{align*}
\text{CO}_2 & \quad \text{H}_2 & \quad \text{H}_2\text{S} \\
0.95 & \quad 0.04 & \quad 0.01
\end{align*}
\]

At 1 atm this gives a calcination temperature of 890 °C, at which temperature the composition in equilibrium over limestone is:

\[
\begin{align*}
\text{CO}_2 & \quad \text{H}_2 & \quad \text{CO} & \quad \text{H}_2\text{O} & \quad \text{H}_2\text{S} \\
0.912 & \quad 0.0016 & \quad 0.038 & \quad 0.048 & \quad 4.8e-5
\end{align*}
\]

For this feed the simulation predicts that only the fraction of H\textsubscript{2} changes by more than 1% over a 100 K range below the calcination temperature. The other criteria described above are all satisfied within the limits imposed by operating at one atmosphere total pressure. Some of the H\textsubscript{2}S present in the feed will be converted to elemental sulfur and COS, as discussed in Part II of this Dissertation. Hydrogen sulfide dissociation was minimized by use of high gas flowrates and the H\textsubscript{2}S partial pressure was always several orders of magnitude greater than the equilibrium value shown above.
3. Theory

As stated in Chapter 1, a limestone-based sulfur-removal process must achieve greater than 50% conversion of the limestone if it is to compete with existing technology. Most previous work on the kinetics of limestone sulfidation dealt with the initial rate of reaction; however, if we seek to react the limestone to completion, we must concern ourselves with processes that influence the rate during the entire course of the reaction.

Previous studies suggest that full conversion of the limestone is very difficult to obtain (Chapter 1) and that this may be due to the sintering of CaCO$_3$ (Borgwardt and Roache, 1984). Sintering is an internal rearrangement of the solid structure that occurs at high temperatures; typically, at temperatures greater than six-tenths of the melting point. The driving force for sintering is usually minimization of the surface energy, and sintering leads to a decrease in the specific surface area. In particular, small pores in the solid can be lost entirely during the sintering process. This loss of porosity can cause the formation of a tight product layer over the solid surface rather than the porous "ash-layer" usually considered in gas-solid reaction theory. In the event of such a layer forming, further reaction requires the diffusion of ions through this product layer. This is a very slow process, hence it is difficult to obtain full conversion.

It will be shown (Chapter 5) that sintering is of great importance in the limestone/H$_2$S/coal gas reaction system. If full conversion of the limestone is to be achieved then we must understand the circumstances under which sintering occurs, in order to anticipate and prevent excessive sintering in our designs. This chapter describes theoretical approaches to sintering and introduces two alternative models that are used in analyzing experimental data on
sintering.

3.1 The German and Munir Model

The most commonly used model for the initial rate of sintering is that of German and Munir (1976). German and Munir showed that in the initial stages of sintering the most important driving force is the chemical potential gradient produced by variations in mean curvature across the surface. They considered several geometries (German and Munir, 1975, a,b,c,d) including neck growth between sintering spheres and wires, from which they developed a generalized kinetic expression (German and Munir, 1976)

$$\left( \frac{\Delta S}{S_o} \right)^\gamma = Kt \quad (3.1)$$

where $\Delta S$ is the surface area reduction, $S_o$ the initial surface area, $K$ is a constant and $t$ is time. The constant $K$ varies with temperature and can be correlated by an Arrhenius expression with activation energy $E_a$ and pre-exponential constant $K_\circ$. They found that for sintering of monosized spheres the exponent $\gamma$ could be related to the particle coordination and the mechanism of mass transport (viscous flow, volume diffusion, surface diffusion, etc.) and normally is in the range 1 to 3.6. For non-ideal cases, or where more than one mass-transfer mechanism is important, it is, however, necessary to treat $\gamma$ as an adjustable parameter. Considerably higher values of $\gamma$ have been reported for cases where the gas phase is able to catalyze sintering (Borgwardt, 1989). Rearranging equation (3.1) gives:

$$\log \left( \frac{\Delta S}{S_o} \right) = \gamma \log Kt \quad (3.2)$$

hence if the German and Munir model is satisfied a graph of $\log (\Delta S/S_o)$ vs. log time yields a
It is important to recognize that German and Munir only intended for their model to be applied to ideal geometries. They note (German and Munir, 1976) that, for aggregations of particles where there are large deviations in shape or size distribution, anomalous effects are produced for which their model does not account.

The model was derived from a consideration of neck growth between particles, therefore it will also break down at the point when neighboring necks begin to intersect one another, which German and Munir found to be roughly $\Delta S/S_0 = 50\%$ for monodisperse spheres. Although the case of sintering within a porous solid is geometrically very different from the aggregation of a collection of particles, small pores in the solid have very high curvature, consequently it is not unreasonable to expect the German and Munir model to be useful in analyzing the initial rate of sintering. At longer times the influence of curvature becomes less significant and we must use the surface energy model discussed below.

3.2 The Surface Energy Model

As stated previously, the main driving force for sintering through much of the sintering process is surface free energy reduction. Schlaffer et al (1957, 1965) proposed the empirical kinetic model:
\[
\frac{dS}{dt} = -k_s S^m
\]  

(3.3)

where \(S\) is the surface area and \(k_s\) and \(m\) are constants. This model was found to give reasonable agreement with the data for the sintering of many catalysts, though it did not perform so well in analyzing the sintering of metals (Rhines et al., 1969).

If we differentiate equation (3.1) we obtain

\[
\frac{dS}{dt} = -\frac{KS_o}{\gamma} \left( \frac{S_o}{S_o - S} \right)^{\gamma-1}
\]  

(3.4)

We therefore see that comparing the two models in the limit \(S \rightarrow S_o\), the rate predicted by equation (3.3) is finite, whereas that predicted by equation (3.4) is infinite. This provides further evidence that the German and Munir model is the more appropriate model for the initial stages of sintering.

A further disadvantage of the surface energy model given above is its differential form. Calculation of sintering rates from experimental data is not easy except when the rate of change in the specific surface area is low (i.e., at longer times). Integration of equation (3.3) yields:

\[
S^{(1-m)} - S_o^{(1-m)} = (m-1) k_s t
\]  

(3.5)

which clearly cannot be arranged to yield a straight line plot without prior knowledge of \(m\).

Because of the factors discussed above, the German and Munir model is recognized as the most suitable model for the initial stages of sintering. Chapter 5 will discuss attempts to use this model in analyzing experimental data from the limestone/H\(_2\)S/coal gas system.
4. Experimental

4.1 Reactor Configuration

4.1.1 Reactor Selection

There are three principal types of reactor used for analysis of gas/solid reactions at high temperatures, namely thermogravimetric analyzers, differential tube reactors and suspension reactors. The effectiveness of each type has been discussed by Sotirchos et al. (1988) whose conclusions are summarized in Table 4.1. An experimental investigation by Gallagher and Johnson (1973) also found the performance of isothermal reactors to be significantly better than that of dynamic reactors in observing the kinetics of limestone calcination.

Because of the variation of gas atmosphere with temperature discussed in Section 2.1, it is of vital importance that the exact conditions at the solid surface be known. In particular, extreme care must be taken to ensure that calcination does not occur. As a result of this it can be seen from Table 4.2.1 that the differential tube reactor is the most suitable for this research, and consequently was selected.

4.1.2 Reactor Design

As noted in Table 4.1 the principal drawback of differential tube reactors is that if the solid phase is being monitored (rather than the gas phase) then their use can be very time consuming, since only one time of exposure can be obtained per experiment before the solid must
be removed for analysis (unlike thermobalances such as T.G.A.s which allow continuous monitoring of weight change). In order to improve the efficiency of the experimental procedure it was therefore necessary to design a reactor that would allow for rapid changeover of solid samples and thermal equilibration.

Table 4.1 Comparison of Gas / Solid Reactor Systems

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Thermogravimetric Analyzer (T.G.A.) | allows several data points per experiment  
can detect conversion of solid instantaneously without needing to quench | reaction conditions in the vicinity of the solid may be poorly known  
stable and noise-free operation requires low flowrates, which give low heat- and mass-transfer coefficients  
low flowrates may not give differential conversion in the gas phase |
| Differential Tube Reactor  | conditions at the solid surface are well known  
external heat- and mass-transfer effects can easily be eliminated  
differential conversion in the gas phase is guaranteed | only one data point can be obtained per experiment  
frequent sample changes make operation repetitious and time consuming |
| Suspension Reactor         | allows several data points per experiment (continuous operation)  
differential conversion can be obtained | difficult to carry out isothermal experiments  
no precise knowledge of gas composition along the particle trajectory  
there can be difficulties with solid sampling |
Other properties required of the reactor were:

i) A flat temperature profile over a sufficient length to give constant temperature at the solid sample.

ii) Accurate measurement of the temperature at the solid.

iii) The ability to heat and quench solid samples rapidly.

iv) High flow in the vicinity of the solid.

v) The ability to sample the gas from the vicinity of the solid if necessary.

With these considerations in mind a design was produced loosely adapted from the reactor used by Borgwardt (Borgwardt et al., 1984) and illustrated in Fig. 4.1. The reactor consists essentially of two quartz tubes having outer diameters 7 mm and 30 mm. Gas mixture enters the outer tube and flows through the countercurrent heat-exchange section before entering the furnace. The gas then flows over the solid sample and exits via the inner tube, where it is cooled by heat exchange with the incoming gas (this arrangement also serves to pre-heat the feed gas and gives a flatter temperature profile). The hot end of the reactor contains a quartz thermowell to allow measurement of temperature at any point along the reactor and also an inlet tube, which allows sampling of gas from the vicinity of the solid sample (and is also used for purging the reactor between runs).

The solid sample is weighed into a quartz boat, which is placed in the opening of the inner tube. The cold-end stopper contains a gas-tight seal, which allows the inner tube to be inserted and withdrawn from the outer tube and thereby allows rapid quenching of the sample. The cold-end stopper can be removed without needing to cool the outer tube, which allows
changeover of samples to take place while the heater is still running and saves a considerable amount of time between experiments (the exact procedure for loading and removing samples is described in Section 4.3). Quartz wool insulation is used wherever this will not interfere with the mechanical operation of the reactor, in order to maintain a flatter temperature profile.

Fig. 4.1 Differential Tube Reactor

4.2 Apparatus

The apparatus used to react samples of limestone with H₂S is shown in Fig. 4.2. Industrial grade (99.9% pure) gases were metered through low-flow control valves and rotameters and mixed into a combined gas stream. This stream could be sent either through the reactor or directly to a gas-scrubber system designed to remove H₂S before sending the gas to vent. The gas entered the outer tube of the reactor described in the previous section, was heated and passed over the solid sample in the inner tube before exiting the reactor and going to the scrubbers. A separate flow-control and metering system allowed the reactor to operate under an atmosphere of CO₂ only. This permitted the reactor to be heated under CO₂ and the sample introduced and
heated in an atmosphere inert to CaCO₃. While the reactor was heating, the reaction-gas mixture was established and sent to the scrubbers. When the reactor reached thermal steady state, the stream of reaction gas was sent to the reactor and the flow of pure CO₂ was stopped. After the desired reaction time the solid was removed from the furnace by withdrawing the inner tube and cooled while still under the reaction-gas mixture. Once the solid had cooled, the reaction gas was switched back to the scrubber and the reactor was purged with CO₂, allowing the sample to be removed and a fresh sample inserted. The reactor was fitted with a water dip-tube relief valve, which indicated the pressure in the system as well as preventing overpressure by allowing gas to vent to the scrubbers. Temperature measurement was carried out using a type K (chromel/alumel) thermocouple inserted in the reactor thermowell. Several sample points were built into the apparatus to allow samples of gas to be withdrawn for GC analysis if necessary.
A piping and instrumentation diagram and detailed instructions on the sequence of valve switching required to operate the apparatus are included in Appendix I.A.

Samples of industrial-quality limestone were provided by the Great Lakes Calcium Corporation (Green Bay, WI). The chemical composition of these samples is shown in Table 4.2. There is some variation to be expected in the composition, since the samples are from natural quarried rock. Purified calcium sulfide powder (100%) was obtained from Fisher Scientific Co. (Fair Lawn, NJ). The sources and purities of the gases used are given in Appendix I.B.

<table>
<thead>
<tr>
<th>Species</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
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</tr>
<tr>
<td>Mg</td>
<td>0.47</td>
</tr>
<tr>
<td>C</td>
<td>11.97</td>
</tr>
<tr>
<td>Fe</td>
<td>0.105</td>
</tr>
<tr>
<td>Al</td>
<td>0.068</td>
</tr>
<tr>
<td>S</td>
<td>0.065</td>
</tr>
<tr>
<td>O</td>
<td>Bal</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>97 - 99</td>
</tr>
<tr>
<td>MgCO₃</td>
<td>0.5 - 2</td>
</tr>
</tbody>
</table>

Table 4.2 Average Composition of Limestone Used

4.3 Analytical Procedures

Several analytical procedures were used to follow the physical and chemical changes occurring in the solid phase. Both quantitative and qualitative methods were used to provide not
only the data necessary for modelling the behavior, but also information to assist in choosing the right models.

4.3.1. Chemical Analysis

Elemental analysis of the unreacted limestone samples was carried out by the Chemistry Department microanalysis labs. Carbon, nitrogen and hydrogen were detected using a Perk and Elmer 240C CH&N combustion analyzer. Metallic elements (chiefly Ca, Mg, Na and Al) were detected using a Perk and Elmer 2380 Atomic Absorption Spectrometer. Phosphorus was detected by a gravimetric wet chemistry procedure. Sulfur and chlorine were detected by subcontractors using X-ray fluorescence and combustion analysis respectively. The chemical composition of unreacted limestone samples is shown in Table 4.2.

The progress of the reaction / sintering was followed gravimetrically by weighing the samples before and after exposure to the hot gas. Although satisfactory for CaCO₃, this method was found to be inadequate for CaS, since the CaS was in powder form and handling errors during loading and unloading usually caused losses of the order of 5%.

Analysis of reacted or sintered samples was made using Electron Dispersive Spectroscopy (EDS). This method allows the determination of the concentration of any atomic species larger than boron in the outer 2.5 μm of the particle and hence is very useful for determining the composition of the solid surface layer. EDS analysis was carried out using an EDAX® system manufactured by North American Philips Corporation (Mahwah, NJ).
4.3.2 Physical Analysis

Physical analysis of the treated samples was made by determining their specific surface areas by Brunauer, Emmett and Teller (BET) analysis. This was carried out using a Quantasorb Surface Area Analyzer (Quantachrome Corp., Greenvale, NY). Details of the calibration and operation of this device are given in Fenouil (1992).

4.3.3 Qualitative Observation

In some cases visual inspection of the samples was sufficient to observe that changes had taken place (e.g. samples of CaS which had sintered formed pellets which could be seen when the sample was tipped out of the sample boat). Magnification up to 400X was achieved using a Nikon EPIPHOTME Optical Microscope (Nikkon Kogaku K.K., Japan). Pictures were also taken at magnifications up to 10,000X using an ISI-DS 130 Dual Stage Scanning Electron Microscope (SEM) made by International Scientific Instruments, Inc. (Santa Clara, CA). Details of the preparation of samples for SEM analysis are described in Fenouil (1992).

4.4 Experimental Strategy

In order to evaluate the suitability of using limestone as a high temperature sorbent for \( \text{H}_2\text{S} \) a sequence of experiments was conducted to investigate the physical and chemical parameters likely to determine the reaction behavior.
4.4.1 Characterization of Apparatus

The first experiments performed were to test the apparatus and determine the correct operating practices for later experiments. Flow and temperature measurement devices were calibrated and reactor thermal profiles evaluated. The thermal profiles for the range of temperatures of interest are shown in Fig. 4.3. It was found that the thermal profile was independent of gas flowrate over the range used experimentally. The maximum in the thermal profile occurred at a distance of 18 cm from the cold end, consequently the sample holder and temperature detector were marked such that they could rapidly be adjusted to position both sample and detector at this point. The length of the sample boats was ca. 15 mm, which was not negligible compared to the length scale over which the temperature was varying. However, by locating the sample at the maximum in the temperature profile the temperature variation within the sample was minimized. The error in the temperature recorded due to location of the sample was found to be ± 0.5 °C.

An investigation of the effect of the procedure described in Section 4.2 on the temperature recorded by the detector determined the time for the system to reach thermal steady state after the insertion of a sample. Fig. 4.4 shows a thermal response curve for the reactor, which takes the form typical of variables under feedback control. The time to reach true steady state was of the order of 20 minutes at all temperatures. However, after 2 minutes the temperature had reached within 2 °C of the steady state value, therefore some short-time experiments were permitted (see Section 5.3). It should be noted though, that the shorter-time experiments have a higher degree of uncertainty in the thermal history.
Fig. 4.3 Variation of Temperature With Distance Along Reactor

experienced by the sample. The effect of time variation was found to decrease if the furnace was run for an extensive period, probably because the thermal capacity of the apparatus acted to damp temperature variations. The error in temperature due to time variation was $< \pm 1.5 ^\circ C$.

The difference between the temperature shown by the detector and the temperature experienced by the sample was investigated by performing the standard procedure with a thermocouple inserted along the sample tube. The result of this test was found to be that the temperature of the detector under-predicts the temperature at the sample by ca. 10 $^\circ C$; however, the two thermometers track each other closely. Both the temperature detector and sample are located in 7-mm diameter quartz tubes at the same radial position inside the outer reactor tube, therefore their heat-transfer properties are identical except for two factors:
Fig. 4.4 Variation of Detector Temperature With Time

i) The hot gas exits through the inner tube at high velocity, giving heat transfer by convection from the hot gas with a large heat-transfer coefficient.

ii) The temperature detector loses some heat by conduction through the thermocouple wires.

This experiment was repeated for each of the temperatures at which sintering or reaction experiments were carried out, thereby determining the appropriate temperature correction to apply to the detector temperature at any temperature and time. The cumulative effect of all errors in temperature detection, once the correction between sample and detector temperature is made, is an error of $\pm 2 ^\circ C$ ($< 0.2 \%$ of the absolute temperature).
4.4.2 Sintering of Limestone

Experiments were carried out to investigate physical changes in the structure of limestone at high temperatures. Borgwardt and Roache (1984) suggested that the low conversion of the solid phase, which they observed in limestone sulfidation experiments, may have been due to sintering of CaCO₃. Borgwardt and Roache (1984) studied limestone sintering using a very fine limestone powder (micrometer size) with a relatively high initial surface area (0.75 to 4.5 m²/g). For such small particles, two neighboring grains could create a zone of very high curvature around their contacting region, causing rapid sintering and agglomeration of the particles. This is confirmed by Borgwardt and Roache's discovery that the average particle size increased from 1.6 μm to 3.5 μm. For larger particles, contact between external surfaces is reduced and there is a lower driving force for sintering. Larger particles are also more suitable for use in coal-gas cleaning, for reasons discussed in Chapter 6. We therefore investigated the sintering behavior of millimeter-sized limestone particles to determine what impact sintering might have on the sulfidation reaction. Samples of limestone were heated under an atmosphere of CO₂, to prevent calcination and to extend the range of temperatures observable. The samples were then analyzed using the procedures described above. Results are discussed in Section 5.2.

4.4.3 Sulfidation of Limestone

These experiments were intended to develop a quantitative analysis of the limestone sulfidation reaction. Limestone samples were heated and then exposed to an atmosphere selected according to the principles described in Section 2.3. This series of experiments was curtailed for two reasons:
i) The sulfidation yield was lower than expected, and the focus of the experiments was shifted to determining what was responsible for this low yield.

ii) An interesting and unexpected side result was observed during the first sulfidation experiment, which led to the work described in Part II of this Dissertation.

4.4.4 Sintering of Calcium Sulfide

The low yield observed in the preliminary sulfidation experiments could be explained in a number of ways. Having already ruled out sintering of CaCO₃ (Section 5.1) the next most obvious effect to investigate was the sintering of the CaS product layer. This had not been investigated previously. Samples of analytical grade CaS powder were weighed and loaded into the apparatus. The correct gas mixture was then established and the sample was given a timed heat exposure before being removed, re-weighed and analyzed using the procedures described above. Strong sintering was observed (Section 5.3), therefore experiments were carried out to determine which gas-phase species influenced the sintering rate and develop a model to describe the sintering behavior. Results are given in Section 5.3.
5. Results

5.1. Reaction of Limestone and Hydrogen Sulfide

Because of doubts over the experimental conditions used in previous studies (see Chapter 2) we performed our own experiments on limestone sulfidation. A gas mixture was selected according to criteria discussed in Section 2.3 and samples of 3/8-inch/6-mesh limestone were exposed to the gas at high temperatures. After 60-minutes exposure at 800 °C the conversion was found gravimetrically to be only 8.2%. Increasing the temperature to just below the calcination temperature gave a conversion of 13% in the same time. These results confirmed the poor conversions observed by Borgwardt and Roache (1984); however, we were able to improve our understanding of limestone sulfidation by examining the internal and external morphology of the reacted solid.

Figure 5.1 (magnification = 4800 X) shows the external surface of a sample of limestone that had been exposed to the gas 1 % H₂S, 4 % H₂, 96 % CO₂ for 60 minutes at 800 °C. Comparison with Figure 5.6 (limestone heated under CO₂) and Fig. 5.8 (sintered CaS) suggests that the smooth features of the reacted limestone surface are more similar to those of sintered CaS. EDS analysis confirmed that CaS is the major species present on the solid surface.

Figure 5.2 (magnification = 800 X) was taken from a sample that had been sectioned using a razor blade. The blade fractured the limestone through the weakest parts of the solid (cracks, etc.), therefore this may be taken as a view of the inside of a pore. Once again we see a smooth surface similar to that of sintered CaS. To confirm that CaS had formed an even layer...
Fig. 5.1 Sulfided Limestone (60 min. at 800 °C, 1 % H$_2$S; mag. 4800 X)

Fig. 5.2 Sectioned Sample of Sulfided Limestone (60 min. at 800 °C, 1 % H$_2$S; mag. 800 X)
over the limestone surface, samples were polished to allow X-ray mapping. CaS is fluorescent under X-rays, which allows clear identification of regions that have undergone sulfidation. Comparison of X-ray and SEM pictures of the same sample showed that lighter gray regions on the SEM pictures correspond to zones rich in CaS, whereas darker grey areas correspond to unreacted limestone. Figure 5.3 shows an SEM picture of a sectioned, polished sample (magnification = 250 X) that had been exposed to 1 % H₂S for 60 minutes at 900 °C. It can be seen that CaS has been formed around the pores throughout the particle, but is not present in the core of any of the CaCO₃ grains. H₂S has not been prevented from reaching the core of the particle; however, CaS has only formed surface layers on the CaCO₃ grains. There is no evidence of cracks forming in the CaS layers, which suggests that a sintering process must be canceling out the volume change associated with the reaction.

Fig. 5.3 Sectioned, Polished Sample of Sulfided Limestone (60 min. at 900 °C, 1 % H₂S; mag. 250 X)
Figure 5.4 Surface Area Distribution of Unreacted Limestone

Average = 0.266
Standard Deviation = 0.047

Fig. 5.5 Untreated Limestone (Mag. 2960 X)
5.2. Sintering of Limestone

5.2.1 Analysis of Untreated Limestone

Experiments were carried out to characterize the limestone prior to reaction or heat treatment. The porosity of the limestone was estimated at 8 to 9% using a Quantachrome Porosimeter. The initial surface area averaged $0.27 \, \text{m}^2/\text{g}$ with a standard deviation of $0.05 \, \text{m}^2/\text{g}$. The distribution of specific surface area measurements for untreated limestone is shown in Fig. 5.4, and is largely attributable to natural variations within the rock. The error in the BET measurements is estimated as $0.05 \, \text{m}^2/\text{g}$ (Fenouil, 1992). Figure 5.5 is an SEM picture (magnification 2960 X) of untreated limestone, from which it can be seen that the limestone has a coarse structure composed of an agglomeration of grains in the micrometer size range.

5.2.2 Surface Area Evolution

Sintering experiments were carried out by heating 3/8-inch/6-mesh limestone particles under carbon dioxide (to prevent calcination). Limestone particles were exposed to temperatures ranging from 800 to 910 °C for various durations. Results are shown in Table 5.1.

The results average $0.28 \, \text{m}^2/\text{g}$ with standard deviation $0.07 \, \text{m}^2/\text{g}$; i.e., there is no significant difference between the treated and the untreated samples. No correlation in surface area evolution can be identified, either with respect to temperature or to exposure time. We therefore conclude that there is negligible sintering for 3/8-inch to 6-mesh limestone under a CO$_2$ atmosphere for times up to two hours (a typical residence time for sorbents in a high-temperature gas cleaning process) as long as the calcination temperature is not exceeded. Scanning electron
microscopy (SEM) pictures support this conclusion: Figure 5.6 (magnification 3100 X) shows the inside of a limestone particle that had been held at 900 °C for 120 minutes (the strongest heat treatment performed). Figures 5.5 and 5.6 have roughly the same magnification and may therefore be compared directly. It can be seen that there is no obvious difference between the two pictures.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>5</th>
<th>20</th>
<th>40</th>
<th>80</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C</td>
<td></td>
<td></td>
<td>0.32</td>
<td></td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.29</td>
</tr>
<tr>
<td>850 °C</td>
<td></td>
<td>0.25</td>
<td>0.30</td>
<td>0.33</td>
<td>0.26</td>
</tr>
<tr>
<td>900 °C</td>
<td>0.23</td>
<td>0.24</td>
<td>0.21</td>
<td>0.23</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td>0.31</td>
<td>0.28</td>
<td>0.33</td>
<td>0.25</td>
</tr>
<tr>
<td>910 °C</td>
<td></td>
<td></td>
<td>0.22</td>
<td></td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 5.1 Surface Area of Limestone After Annealing for Different Temperatures and Times

On one experimental run the temperature measured was 913.5 °C, which is somewhat higher than the expected calcination temperature. Of fourteen stones in the batch, two changed color from gray to white. The other twelve stones were unaltered and their specific surface area remained at 0.24 ± 0.04 m²/g, typical for the limestone studied. The two white stones were found to have calcined and their specific surface area had increased to about 1 m²/g. This large increase in area was not found for any of the other samples, confirming that calcination had not taken place in any of the other experiments.
Fig. 5.6 Limestone Heated for 120 minutes at 900 °C (Mag. 3100 X)

Fig. 5.7 Untreated CaS Powder (Mag. 6000 X)
Our results show that for large limestone particles with low specific area, sintering does not significantly reduce the particle area under the conditions typically found in a coal-gas cleaning system. This does not contradict the findings of Borgwardt and Roache (1984) since they worked with much smaller particles of higher specific surface area where inter-particle interactions (agglomeration) were more important. However, our results rule out CaCO$_3$ sintering as a potential explanation for the poor conversion of the sulfidation reaction observed for large particles (diameter larger than 100 μm). This turned our attention towards the behavior of the CaS product layer.

5.3. Sintering of Calcium Sulfide

Sintering experiments were performed on pure CaS powder (Fischer Scientific Company). The specific surface area of this powder averages 1.32 m$^2$/g with a standard deviation of 0.05 m$^2$/g. The density of calcium sulfide is 2.61 g/cm$^3$, therefore the average equivalent grain diameter is estimated as 1.7 μm. This is supported by scanning electron microscopy measurements. CaS powder was exposed to temperatures ranging from 750 °C to 900 °C, for several durations and gas compositions. Physical changes undergone by the solid were followed by BET surface area measurements, optical- and scanning electron microscopy. Electron dispersive spectroscopy (EDS) analysis was used to determine if chemical reaction was responsible for the observed surface area reduction upon heat treatment.

It was found that the gas composition had a strong effect on the CaS sintering rate. Table 5.2 shows the surface areas of CaS samples that had been held at 850 °C for 40 minutes under different gas atmospheres. It can be seen from Table 5.2 that CaS does not sinter under a N$_2$ or
H₂ atmosphere, whereas significant area loss is found in all cases when CO₂ is present in the gas phase, even at concentrations as low as 5 % in N₂. It is impossible to probe the influence of CO on the sintering rate independently, since in the absence of CO₂ the carbon monoxide will disproportionate into CO₂ and solid carbon with the latter contaminating the CaS samples. This phenomenon was observed to a slight extent in the two experimental runs with CO.

The influence of H₂O on CaS sintering was not investigated; however, comparison of the last three results of Table 5.2 indicates that there is no significant difference in CaS sintering between samples exposed to pure CO₂ and those exposed to CO₂ containing some H₂O (formed by the water-gas-shift reaction). It is not possible to conclude whether H₂O has a catalytic effect on CaS sintering but we expect this effect to be less important than that of CO₂.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated CaS</td>
<td>1.32 ± 0.06</td>
</tr>
<tr>
<td>100 % N₂</td>
<td>1.29 ± 0.17</td>
</tr>
<tr>
<td>90% N₂ / 10% H₂</td>
<td>1.41 ± 0.18</td>
</tr>
<tr>
<td>100% CO₂</td>
<td>0.73 ± 0.09</td>
</tr>
<tr>
<td>95% CO₂ / 5% CO</td>
<td>0.61(1) ± 0.09</td>
</tr>
<tr>
<td>90% CO₂ / 10% CO</td>
<td>0.71(1) ± 0.09</td>
</tr>
<tr>
<td>5% CO₂ / 95% N₂</td>
<td>1.01 ± 0.09</td>
</tr>
<tr>
<td>96% CO₂ / 4% H₂</td>
<td>0.70 ± 0.04</td>
</tr>
<tr>
<td>90% CO₂ / 10% H₂</td>
<td>0.69 ± 0.09</td>
</tr>
</tbody>
</table>

(1): may be underestimated since the sample was contaminated by carbon deposits ("coking").

**Table 5.2 CaS Surface Area Evolution After 40 Minutes at 850 °C Under Different Gas Atmospheres**
5.3.1 Kinetics of Calcium Sulfide Sintering

A 96% CO₂ / 4% H₂ gas mixture was used to conduct a kinetic study of calcium sulfide sintering. This feed composition gives a gas mixture at high temperature containing sufficient CO to prevent oxidation of CaS to CaSO₄. It also maintains a relatively constant composition over the temperature range 750 °C to 900 °C, due to the high fraction of CO₂. Consequently, the temperature and the exposure time were the only parameters that varied significantly in these experiments.

To confirm that CaS had not been oxidized to CaSO₄, CaS samples exposed to 850 °C for 40 minutes under an atmosphere of pure CO₂ were analyzed by EDS. The spectra obtained were identical to those for untreated CaS, confirming that no significant chemical reaction took place during the heat treatment and the surface area loss is purely due to a physical rearrangement. This does not rule out involvement of the gas phase in the sintering mechanism; in fact any sintering mechanism must account for the strong influence of the gas-phase composition already described.

Scanning Electron Microscope pictures also demonstrate that CaS undergoes morphological changes when exposed to atmospheres containing CO₂ above 750 °C. Figure 5.7 (magnification 6000 X) shows CaS powder prior to heat treatment; Figure 5.8 (magnification 6000 X) shows the same powder after 20 minutes at 850 °C. The powder grains in Figure 5.8 have a "smooth" surface, typically encountered in sintered solids. The grain boundaries are clearly identifiable and it can be seen that originally disjoint grains are now merging. Figure 5.9 (magnification 6000 X) shows a CaS sample heated under N₂ and it can be seen that there is no
Fig. 5.8 Sintered CaS (20 minutes at 850 °C under CO₂; mag. 6000 X)

Fig. 5.9 CaS Heated Under Nitrogen (40 minutes at 850 °C under N₂; mag. 6000 X)
noticeable structural difference between this and the untreated sample shown in Figure 5.7. This is consistent with the absence of a reduction in specific surface area for CaS powder heated under 100% nitrogen.

5.3.2 Kinetic Model

If the German and Munir kinetic expression were satisfied, then a plot of \( \ln(1-S/S_0) \), where \( S_0 \) is the initial surface area, versus \( \ln(t) \) should give straight lines with identical slopes, \( 1/\gamma \), for the four different temperatures. Figure 5.10 shows that this is satisfied within the bounds of experimental error for the two lower temperatures (750 °C and 800 °C) with \( \gamma \) equal to 4.4 and 4.8 respectively. At higher temperatures the \( \gamma \) values do not agree as well; moreover, they are much higher than the values usually encountered when applying the German and Munir model. The German-Munir theory is therefore not applicable to our high-temperature data. This result was expected since the surface area data for 850 °C and 900 °C are 40% below the initial surface area, and consequently outside of the normal range of applicability of the German and Munir model. Data taken at shorter sintering times may allow extension of the model to higher temperatures, but this would require exposure times shorter than five minutes, which would introduce a high error due to thermal equilibration time if the current apparatus were used.

The German-Munir expression was fitted to the 750 - 800 °C experimental data, with the value of \( \gamma \) fixed at 4.6 (the average of the values 4.4 and 4.8 obtained from the ln-ln plot). An iterative, non-linear fit was performed on Sigma-plot™ software (Jandel Scientific, Corte Madera, CA) using the German and Munir model with two free parameters (\( K_s \) and \( E_s \) as defined in Chapter 3).
The results were found to obey the expression:

$$\left( \frac{\Delta S}{S_\gamma} \right)^{4.6} = 2 \times 10^6 \left\{ \exp \left( \frac{-48,000}{RT} \right) \right\} \cdot t \tag{5.1}$$

where $t$ is in minutes

$R$ is in cal/mole K

Results from the model, together with experimental data, are shown in Figure 5.11. The fit is relatively good for all the data above 0.70 m$^2$/g.

At the highest temperatures (850 and 900 °C) the rate of surface area decrease is slow
after the initial rapid loss. In their study of calcium hydroxide sintering Irabien et al. (1990) correlated the surface area by a linear expression in this region. This approach is purely empirical, but other, more physical, models give no better correlation using more adjustable parameters (and often yield unrealistic values for their physical parameters, especially activation energy). Our results ($t > 5\ min$) may be correlated by:

\[
S = 0.813 - 0.00224 \ t \quad \text{at } T = 1128 \ K
\]

\[
S = 0.713 - 0.00193 \ t \quad \text{at } T = 1181 \ K
\]

where $S$ is the surface area in $\text{m}^2/\text{g}$ and $t$ is the time in minutes.
5.4 Future Work

It has been shown that uncalcined limestone is not suitable for use as a sorbent for H$_2$S at high temperatures and low pressures, due to sintering of the product CaS layer. It is, however, possible that this sintering may be avoided under certain circumstances. The experiments hitherto carried out used hydrogen sulfide partial pressures of the order of 500 Pa (because of the apparatus construction and the need for a high partial pressure of CO$_2$). In coal gasification plants the H$_2$S partial pressure would be roughly 42 kPa; i.e., two orders of magnitude greater. It is therefore possible that under processing conditions the kinetics of sulfidation may be more rapid than those of sintering. This is particularly likely at lower temperatures (700 - 750 °C) where the sintering rate is found to be slow. This cannot be investigated properly without using a high-pressure reactor; however, some experiments were run with higher concentrations of H$_2$S (92 % CO$_2$, 6 % H$_2$, 2 % H$_2$S) and limestone conversions of roughly 50% were found. This was not investigated further at the time, since attention was transferred to the project described in Part II of this dissertation; however, it is to be the subject of future research by Laurent Fenouil.

Another possibility is that the presence of magnesium salts in the limestone may reduce the effect of sintering. Ruth et al. (1972) found that half-calcined dolomite performed better than limestone as a sorbent for H$_2$S above the calcination temperature. This was probably due to MgO preventing the CaO from sintering fully. A similar effect may be found for the calcium sulfide product layer below the calcination temperature, therefore the effect of Mg content on the rates of limestone sintering and sulfidation will also be found.
6. Removal of Particulate Matter

Among the contaminants that must be removed from coal-gas before it is suitable for use as a fuel in gas turbines are particles known as gasifier fines. The coal-gas exiting the gasifier contains an aerosol mixture consisting of small lumps of ash, char and tar, together with droplets formed by the vaporisation and subsequent re-condensation of alkali salts from the coal. The detrimental effects of particulate matter on gas turbines are reviewed by McCarron and Grey (1980) and by Menguturk and Sverdup (1979).

It has been shown (Clift, 1983; Roberts et al., 1981) that during steady operation two or three stages of cyclone suffice to remove particulates to a level acceptable to a gas turbine, however, because of excursions in cyclone operation it appears necessary to provide tertiary cleaning (Ghadiri et al., 1986). A good review of the technology available for HTHP tertiary gas cleaning is given by Saxena et al. (1982). A number of devices have been investigated (Zaharchuk and Rubow, 1986; Bedick and Dellefield, 1986). In particular, it has been found (Zaharchuk and Rubow, 1986) that one of the most promising designs is the moving granular bed filter (GBF) developed by the Combustion Power Co. (CPC) and described in numerous reports (Wilson, 1986; Haas et al., 1988).

The initial objective of this dissertation was to design a moving bed reactor for absorption of H_2S from the coal-gas using limestone. Such a reactor would have the added advantage of effecting part (or all) of the tertiary cleanup duty. If a suitable solid sorbent for H_2S can be found then the moving bed reactor will continue to provide a useful way of removing both gaseous and aerosol contaminants from the gas simultaneously. This chapter therefore proposes
a model for the filtration behavior of such a reactor system and uses the model to predict the expected collection efficiency as a function of particle diameter. The sensitivity of collection efficiency to important process parameters is investigated and areas requiring further investigation are outlined. Due to major differences in flow configuration it is not yet possible to compare the model with experimental data for industrial GBF systems.

6.1 Previous Work

Information on particle capture in packed beds is usually expressed in terms of a dimensionless quantity called the single grain capture efficiency, denoted \( \eta \). This is the ratio of the actual deposition onto the \( i \)th grain, to the idealized rate \( nU/A_i \) calculated assuming that particles move in straight lines with constant superficial velocity \( U \). The local concentration of aerosol particles is \( n \) and \( A_i \) is the projected area of the grain. To avoid confusion the aerosol material filtered by the bed is hereafter referred to as particles, whereas the material of which the bed is composed is referred to as grains. For a uniform bed, depth \( L \), packed to solids fraction \( \alpha_o \) with grains distributed in area \( A_i \) and volume \( V_i \) the penetration \( P = n_{\text{out}}/n_{\text{in}} \) of particles through the bed is given by:

\[
- \ln P = \alpha_o L \left( \sum \eta_i A_i \right) / \Sigma V_i
\]  

(6.1)

If the bed is packed with identical spherical grains of diameter \( D_o \), Eq. 6.1 reduces to:

\[
- \ln P = 3 \alpha_o L \eta / 2 D_o
\]  

(6.2)
The total bed collection efficiency is simply $\eta_{\text{TOT}} = (1-P)$

The single grain capture efficiency depends on particle size, shape, density and electric charge, similar grain properties, bed voidage, particle loading in the bed, gas velocity, gas physical properties and externally imposed force fields. Capture may be by several mechanisms, including Brownian diffusion, sedimentation, interception, inertial impaction, electrostatic drift and thermophoresis (D'Ottavio and Goren, 1983). Different mechanisms will be important for different particle sizes and gas velocities; furthermore, the analysis is complicated by the fact that not all the particles striking a collector will adhere to it, the sticking probability also being dependant on many variables. For a moving bed reactor there is no accumulation of particles in the bed at steady state, however the concentration of absorbed particles will be greatest at the base of the bed and there may thus be a spatial variation in the physical properties of the bed surface.

Because of this complexity most theoretical work has been limited to determining suitable dimensionless parameters for use in correlating experimental data. For gas turbine applications we are chiefly concerned with removing larger particles (particularly those with diameter $> 5 \mu m$), since these particles make up most of the particulate mass, are least likely to be removed by burning in the combustor and have the most detrimental effects on turbine machinery (Goren and Kalinowski, 1984). The most important mechanism for removing particles in this size range is inertial impaction, as discussed by D'Ottavio and Goren (1983). From a consideration of the flow over a single particle, they concluded that the single grain capture efficiency $\eta$ could be expressed as a function of the three dimensionless groups $\alpha_0$, $Re = \rho D_0 U / \mu$, and $St = \rho_p D_p^2 C_p U / 18 \mu D_0$ -- where $\rho$ and $\mu$ are the density and viscosity of the gas, $\rho_p$ and $D_p$ the density
and diameter of the particles and $C_p$ is the Cunningham slip correction factor for the particle.

Goren (1978) showed that to determine $\eta$ at small Stokes numbers it is sufficient to know the gas flow field only in the region close to the collecting surface. From the gas continuity equation and no-slip boundary condition it can be shown that close to the forward stagnation point the velocity of the gas must be of the form:

$$u_y = 3A(\alpha_0, Re) \frac{U y \sin \theta}{D_g}$$

$$u_r = -6A(\alpha_0, Re) \frac{U y^2 \cos \theta}{D_g^2}.$$  \hspace{1cm} (6.3)\]

(Spielman, 1977; Goren, 1978) where $u_r$ and $u_y$ are the radial and tangential gas velocities, $\theta$ is the angle measured from the forward stagnation point and $y$ is the distance measured into the gas from the surface of the sphere. The factor $A$ depends on bed hydrodynamics and is equal to 1 for an isolated sphere at low $Re$. For very small Reynolds number flow in packed beds, the dependence of $A$ on $\alpha_0$ can be predicted using cell models. D’Ottavio and Goren (1983) recommend Happel’s model (Happel, 1958), which results in:

$$A_H(\alpha_0) = \frac{(6 - 6 \alpha_0^{5/3})(6 - 9 \alpha_0^{1/3} + 9 \alpha_0^{5/2} - 6 \alpha_0^2)}{6 - 9 \alpha_0^{1/3} + 9 \alpha_0^{5/2} - 6 \alpha_0^2}.$$ \hspace{1cm} (6.4)

where $A_H$ is the value of $A$ predicted by the Happel model for low $Re$. For high Reynolds number flows, boundary layer flow past an isolated sphere with the modification that free stream velocity match the interstitial velocity yields $A = 1.14 Re^{1/2} (1-\alpha_0)^{3/2}$ (D’Ottavio and Goren, 1983). Since there is no intermediate range theory D’Ottavio and Goren approximated $A(\alpha_0, Re)$
over the entire range of Re as the sum of its two asymptotic values, i.e.:

\[
A(\alpha_0, \text{Re}) = A_\text{H}(\alpha_0) + 1.14\text{Re}^{1/2}(1-\alpha_0)^{-3/2}
\] (6.5)

D’Ottavio and Goren (1983) showed that near the surface of a grain in a packed bed the gas velocity field \( \tilde{u} \) is given by:

\[
\tilde{u} = A \ U \ \tilde{u}(r^*)
\] (6.6)

where \( \tilde{u}^* \) is dimensionless and depends only on the dimensionless position \( r^* = r/D_0 \). By substituting this into the equations of motion of a particle and making those equations dimensionless, they were able to show that the dimensionless particle trajectory depended only on \( \text{AST} \) and the starting streamline. Consequently the single grain capture efficiency depends only on the group \( \text{AST} \), which they called the effective Stokes number, \( \text{St}_{\text{eff}} \). Their data for liquid aerosols were successfully correlated by this approach over the experimental range \( (0.1 < \text{St}_{\text{eff}} < 2.0) \), and they were able to fit the data using the empirical formula:

\[
\eta = \text{St}_{\text{eff}}^{3.55}/(1.67 + \text{St}_{\text{eff}}^{3.55})
\] (6.7)

For smaller particles it is necessary to consider sedimentation and diffusion as collection mechanisms. The theory for these regimes is more complex and is discussed in detail by Mann and Goren (1984). Once again, a satisfactory correlation for the single particle capture efficiency can be derived after using theoretical arguments to determine dimensionless groups upon which it might depend.
Defining a group

\[ \beta = 2^{1/3} A^{1/3} \text{Pe}^{2/3} \text{Grv}^{1} \]  \hspace{1cm} (6.8) 

where: \( \text{Pe} = 3 \pi \mu D_{p} D_{o} U / k T_{p} \) (k is Boltzmann’s constant, T is temperature), \[ \text{Grv} = \rho_{p} D_{p}^{2} C_{p} g / 18 \mu U \] and A is defined by Eq. 6.5, they showed that for Grv \(<< 1\), Pe \(>1\) and interception number \( R = D_{p} / D_{o} \) \(<< 1\) the experimental results were correlated by:

\[ \eta / \text{Grv} = 1 + 1.9 \beta - (1.9 \beta / (1 + 1.9 \beta)) \] \hspace{1cm} (6.9) 

For the intermediate region between these regimes it is proposed to follow the standard practice in aerosol science of summing the contributions due to each separate mechanism.

Other correlations have been produced more recently, e.g. that of Yoshida and Tien (1985) which was based on data from nine sources, but failed to take account of the hydrodynamic factor A, and that of Jung et al. (1989) based on their own data and those of D’Ottavio and Goren (1983). Jung et al. used three different particle counters to gather data and (possibly as a result of this) their data exhibit a very wide scatter, therefore the present study makes use of the earlier and simpler correlation.

A number of pilot scale trials of granular bed filters have been made, most notably by Kawasaki Heavy Industries Ltd. (Hozumi et al., 1986) and by Combustion Power Co. as part of the DOE high-temperature gas-cleaning program (Wilson, 1986; Haas et al., 1988). The fluid mechanical arrangement of these pilot filters is substantially different from that of the vessel
under consideration. In the case of CPC the filter involves zones of cross-flow and co-current flow in addition to countercurrent flow (see Fig. 6.1), therefore their results are not suitable for direct comparison with predictions from the model.

![Diagram of HTHP Gas Cleaning Devices](image)

**Fig. 6.1 Flow Patterns in HTHP Gas Cleaning Devices**

6.2 Data Sources and Procedure

Coal-gas is taken to have the composition given in Table 6.1. The density of the gas was taken as the ideal gas density (since we are concerned only with high temperatures), while the gas viscosity was found following the procedure recommended by Perry and Green (1985). This involved using the correlation of Dean and Stiel (1965) taking critical data from Prausnitz et al. (1986) and viscosities of pure gases from Beerman (1982). The density of gasifier fines was taken as 1.2 g cm\(^{-3}\) (a "reasonable" value since gasifier fines consist of char with a varying
ash and tar content and specific gravity from 1.0 to 1.4). The bed was approximated as consisting of randomly packed non-uniform spheres, for which the porosity varies between 0.38 and 0.39 (Mann and Goren, 1984). A value of 0.385 was therefore used for the void fraction ($\alpha_0 = 0.615$). The specific gravity of limestone was taken as 1.5 (Perry and Green, 1985). All other input data were treated as process design variables and were varied over a likely range as part of the sensitivity analysis. In performing the sensitivity analysis, one parameter would be varied while every other parameter was assigned its base value. The base values and ranges investigated for each design parameter are shown in Table 6.2. The ranges correspond to the values likely to be encountered in a HTHP gas cleaning process. In each study the collection efficiency was evaluated for a range of particle sizes from 0.1 to 100 µm.

Table 6.1 Typical Composition of Coal Gas

<table>
<thead>
<tr>
<th>Species</th>
<th>CO</th>
<th>H$_2$</th>
<th>CO$_2$</th>
<th>H$_2$O</th>
<th>CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>50</td>
<td>30</td>
<td>5</td>
<td>10</td>
<td>.5</td>
</tr>
</tbody>
</table>

Table 6.2 Design Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base Case</th>
<th>&quot;Worst&quot; Case</th>
<th>Range of Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>750</td>
<td>750</td>
<td>700 - 800</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>18</td>
<td>18</td>
<td>18 - 18</td>
</tr>
<tr>
<td>Bed Depth (m)</td>
<td>5</td>
<td>5</td>
<td>1 - 10</td>
</tr>
<tr>
<td>Average Grain diameter (mm)</td>
<td>2</td>
<td>3.5</td>
<td>1 - 3.5</td>
</tr>
<tr>
<td>Gas superficial velocity/ fluidizing velocity, $x$</td>
<td>0.3</td>
<td>0.5</td>
<td>0.2 - 0.5</td>
</tr>
</tbody>
</table>
The superficial gas velocity at minimum fluidization, $U_{mf}$, was found using the correlation of Wen and Yu (1966), based on the smallest size grains in the system ($D_o = 1$ mm). The actual superficial gas velocity was then set to a fraction $x$ of $U_{mf}$, where $x$ was considered a design variable. Haas et al. (1988) observed that for large values of $x$ ($x < 1$) plugging due to absorbed particles could lead to fluidization of the bed, with potentially disastrous consequences for the $\text{H}_2\text{S}$ removing reactions. They recommended a value of $x = 0.25$ to avoid fluidization, but since this study bases $U_{mf}$ on the smallest grains rather than on average grain diameter the base case was taken as $x = 0.3$.

Once the velocity had been found the dimensionless groups $\text{Re}$, $\text{Grv}$, $\text{St}_{cr}$ and $\text{Pe}$ were evaluated and substituted into the correlations of D'Ottavio and Goren (1983) and Mann and Goren (1984) to give single particle collection efficiencies in each regime. These were then added (and truncated at 1 if necessary) to give a total single particle collection efficiency, as described above. The total bed collection efficiency was estimated by making the assumption that the grains were identical spheres of diameter $D_o$, yielding:

$$\ln(1-\eta_{\text{TOT}}) = -3 \alpha_o \eta \frac{L}{2 D_o}$$

where $\eta_{\text{TOT}}$ is the overall bed collection efficiency.

6.3 Results

The particle collection efficiency predicted for the base case is shown in Fig. 6.2, which is of the characteristic form for all particle removal devices, evincing a minimum in collection
efficiency at \( D_p \sim 1 \, \mu m \), \textit{i.e.} in the accumulation mode. Fig. 6.2 also shows a "worst case" curve, calculated for a bed depth of 5 m using the most inefficient value of every other design parameter. Note that in both cases the collection efficiency is greater than 99.9\% for particles in the critical size range \((D_p > 5 \, \mu m)\), although the worst case design gives considerably poorer results for smaller diameters.

\[ \text{Fig. 6.2 Particle Collection Efficiency for Base Case and Worst Case} \]

The effect of bed depth on collection efficiency is shown in Fig. 6.3. The collection efficiency is a sensitive function of bed depth, as might be expected from Eq. 6.2. Collection efficiency was found to be insensitive to temperature, as can be seen from Fig. 6.4. Changes in temperature affect the gas viscosity (hence \( U_{mf}, \text{Re}, \text{Pe}, \text{Gr}_v \text{ and } \text{St} \)), density (hence \( \text{Re} \text{ and } U_{mf} \)), and diffusivity (hence \( \text{Pe} \)). The range of temperature investigated was 1023 K \pm 4.9\%; this 4.9\% change in temperature gives an average 4.1\% change in viscosity (increases with increasing temperature) and 1.3\% change in superficial velocity (decreases with increasing temperature). Diffusivity is directly proportional to temperature and density is inversely proportional. We can
Fig. 6.3 Effect of Bed Height on Particle Collection Efficiency

note, however, that the only part of the collection curve where the efficiency is not unity (i.e. where we would be able to detect any effect of temperature variation) is in the diffusion-dominated regime. The important dimensionless number in this regime is $Pe$, which is proportional to the group $\mu U/T$ (the temperature dependence comes from the diffusivity), hence the changes in viscosity and temperature effectively cancel out over a small temperature range giving the observed insensitivity.

The effect of superficial gas velocity on particle-collection efficiency is shown in Fig. 6.5. Perhaps unexpectedly, we see that an increase in velocity reduces the fraction of particles collected. This is because in the inertial-deposition-dominated regime ($D_p > 5 \mu m$) collection is $\approx 100\%$ efficient at all velocities considered but for smaller particles ($D_p < 5 \mu m$) the dominant deposition mechanisms (diffusion and sedimentation) are more efficient if the particulates have a greater residence time in the bed. Increasing the superficial velocity therefore has the effect of sweeping the particles through the bed before they have time to deposit and consequently reduces collection efficiency.
Fig. 6.4 Effect of Temperature on Particle Collection Efficiency

![Graph showing the effect of temperature on particle collection efficiency.]

Fig. 6.5 Effect of Superficial Gas Velocity on Particle Collection Efficiency

![Graph showing the effect of superficial gas velocity on particle collection efficiency.]

Fig. 6.6 shows the effect of grain diameter on collection efficiency. The volume of solid material per unit volume of bed is simply given by the solids fraction $\alpha_G$. The number of grains per unit volume is therefore $N_G = 6\alpha_G/\pi D_G^2$, hence the exposed surface area per unit volume of
The surface area for collection per unit bed volume is thus inversely proportional to \( D_0 \) and we therefore expect collection efficiency to decrease with increasing grain diameter, as is indeed observed. In practice this part of the analysis is necessarily approximate since there will be an (as yet undetermined) distribution of grain sizes and the total collection efficiency will be found using Eq. 6.1 rather than the idealized Eq. 6.2; however, this shows that on average smaller grains make more efficient collectors. A lower limit is placed on the grain size by hydrodynamic factors such as pressure drop and fluidization.

6.4 The Effect of Retention

The results presented merely show the efficiency of the bed at collecting particles. To predict the removal of particles from the gas, it is necessary to know something about how well the grains are able to retain particulate material after the initial collision. A number of processes play a role in determining the retention, chiefly whether particles adhere to the grain or "bounce"
on initial impaction, whether abrasion between grains causes re-entrainment of adsorbed particles and whether particles can agglomerate on the surface of the grains forming larger particles that are more likely to be removed by abrasion (as postulated by D'Ottavio and Goren, 1983). Each of these will depend on the properties of the particulate material; therefore, it is necessary to base our analysis on data appertaining to gasifier fines, the only detailed study of which is that of Ghadiri et al. (1986).

Ghadiri (1980) found that for solid aerosols collected on clean surfaces, retention efficiency is generally low because high relative velocity between the aerosol and the collector, whilst favoring collection by inertial impaction, also favors rebound (Coury, 1983; Clift, 1984). For any given system, the particle bounce is related to the kinetic energy of the particles (Dahneke, 1971; Loeffler, 1974). There is, however, no reliable way of estimating impact velocities in packed beds. D'Ottavio and Goren (1983) were able to evaluate sticking probabilities for solid potassium biphthalate (KHP) particles by comparing measured capture efficiencies with results calculated using a correlation developed for liquid aerosols. They plotted their results against an effective kinetic energy based on a velocity AU (as defined above) and found that, below an effective kinetic energy of $10^4$ ergs, the sticking probability was unity. It is likely that a similar threshold will exist for gasifier fines, although the work of Ghadiri et al. (1986) does not allow this to be determined. The effect of bounce can be reduced if the particle deforms plastically on impact (Boehme et al., 1964; Dahneke, 1971). This can be achieved by operating at higher temperatures where the solids are more likely to undergo sintering, but since this would conflict with the reactor operating requirements such a strategy must be ruled out for the design under consideration, as must other retention improvement techniques such as adding a liquid retention aid as suggested by Ghadiri et al. (1985).
At high particle loadings the issue of retention is further complicated by re-entrainment of particulates due to abrasion between the grains. Increased loading increases the efficiency of packed beds (Walata et al., 1986; Michaels and Goren, 1987) due to decreased porosity, but should not affect the porosity of a moving bed, since the grains are free to rearrange themselves. The effect of re-entrainment of particles has been mentioned by a number of investigators, notably D'Ottavio and Goren (1983), but no quantitative analyses are reported in the literature. In any case the effect of high particulate loading will probably only be felt in a very small part of the moving bed reactor near the solid discharge, and so may be of small significance compared with the problem of bounce.

Because of the difficulties outlined above and lack of quantitative information on retention, no attempt has been made to include retention in the model and the data have been reported as collection efficiencies. The collection efficiency may be viewed as a theoretical maximum particulate removal efficiency which in practice will be reduced due to the effects described above. How severely the actual removal efficiency will be reduced depends on the physical properties of gasifier fines under operating conditions and cannot as yet be determined. The single particle removal efficiency will generally be given by:

\[ \eta = \eta_c \eta_R \]  

(6.10)

where \( \eta_c \) is the collection efficiency as determined previously and \( \eta_R \) is the retention efficiency.
6.5 The Effect of Loading

Another factor important in the design of a moving-bed filter is bed loading, i.e., the amount of particulate material removed per bed grain. At high loadings the bed capture efficiency is reduced (Michaels and Goren, 1987); for a moving bed filter this is usually a cause for concern for particle loadings greater than 3 weight %. A detailed analysis of the effect of loading is given by Michaels and Goren (1987).

If a moving-bed reactor containing limestone were used as a gas-filtration device several factors would be important in determining how its performance would be affected by loading. Firstly, the reactor would normally be considered as a tertiary cleanup system for the particulates, i.e., there would be several cyclone stages between the gasifier and the absorber. Typical gasifier outlet particulate concentrations range from 1000 to 10,000 ppmw, depending on the type of gasification reactor. These concentrations would be considerably reduced by the time the gas entered the absorber, depending on the number of cyclone stages used. Secondly, the effect of particulate loading is likely to be most severe in the region where the gas enters the bed; however, this is also the region where the solid absorbent leaves the bed, therefore higher loadings may be achieved than in a fixed bed, depending on the solids flow rate. A further complication is that the nature of the particulate material may also be important -- material that is easily re-entrained will tolerate lower loadings than material that is harder to re-entrain.

A full analysis of bed performance with respect to loading should therefore be based on experiments under conditions that closely resemble process operating conditions. We can note, however, that if a coal gas containing 1 wt % H₂S and 1000 ppmw particulates is desulfurized
by a moving bed containing a stoichiometric amount of limestone, the bed loading is roughly 0.034 g particulates/g limestone.
7. Conclusions

Limestone has been much studied as a sorbent for hydrogen sulfide in coal gasification processes. If the limestone is added directly to the gasification reactor then the conversion of limestone to sulfur-containing compounds (chiefly sulfate and sulfide) is usually less than fifty percent. This is because limestone undergoes calcination under the conditions prevalent in the gasifier and the calcium oxide thus formed is a poor sorbent for $\text{H}_2\text{S}$ for stereochemical reasons.

An alternative strategy is to contact the coal gas with limestone under conditions where calcination does not occur. From stereochemical considerations $\text{CaCO}_3$ might be expected to be a better sorbent than $\text{CaO}$. The molar density of $\text{CaS}$ is greater than that of limestone and the external dimensions of the solid remain constant on reaction, therefore the internal porosity of the solid should increase upon reaction, guaranteeing full conversion. Experiments showed that this is not the case, and that a layer of calcium sulfide forms over the surface of the calcium carbonate grains, with no evidence of cracks or pores in this layer. The absence of cracks or pores causes the reaction to proceed by a solid-state diffusion mechanism and conversion of the limestone in processing timescales is therefore very low.

The formation of a tight product layer over the $\text{CaCO}_3$ grains can be explained by sintering of either the limestone or the product $\text{CaS}$. Sintering of limestone was found to be unimportant for large diameter particles, although for fine powders it may be significant due to agglomeration and loss of external area rather than internal porosity. Calcium sulfide does not sinter when heated under $\text{N}_2$ or $\text{H}_2$, but shows a marked decrease in specific surface area if heated in the presence of $\text{CO}_2$. Similar gas-phase catalysis of sintering has been observed for calcium
hydroxide (Borgwardt, 1989). Electron Dispersive Spectroscopy analysis showed that the CaS had not undergone reaction and thus confirmed that the loss in surface area resulted from a purely physical process.

At moderately high temperatures (700 °C - 800 °C) the sintering of CaS can be described by the German-Munir sintering model, with exponent 4.6 and an activation energy of 46 kcal/mole. These values are typical of those found in gas-catalyzed sintering processes. At higher temperatures (850 °C - 900 °C) the initial rate of sintering was too rapid for the German-Munir model to be accurately fitted to data gathered using the available apparatus; the results were therefore correlated using an empirical expression. Measurements of surface area reduction were supported by scanning electron microscopy pictures that showed the evolution of the limestone and calcium sulfide during reaction and sintering.

The effectiveness of a moving-bed reactor at removing aerosol contaminants from the coal gas was also studied. Our calculations suggest that under high-temperature, high-pressure conditions such a reactor will achieve satisfactory tertiary particle clean-up and the system is very robust to changes in process conditions such as temperature, sorbent particle size and gas superficial velocity. The retention of gasifier fines is not yet understood; however, retention is expected to be high at high temperatures.

It may be possible to develop a high-temperature, high-pressure gas-cleaning process using such a moving-bed reactor, but containing a better sorbent for H₂S than limestone. A suitable candidate might be half-calcined dolomite, CaCO₃·MgO, for which the presence of MgO may help retard the sintering of product CaS. This will be the subject of future investigation.
NOMENCLATURE

Nomenclature Used in Chapters 1 - 5

BET Brunauer, Emmett and Teller
EDS Electron Dispersive Spectroscopy
FGD flue-gas desulfurization
HTHP high-temperature, high-pressure
SEM Scanning Electron Microscope
TGA thermogravimetric analyzer

Ea German-Munir model activation energy
k₂ second order rate constant
kₙ surface energy model kinetic constant
K German-Munir model constant
K₀ German-Munir model pre-exponential constant
m surface energy model exponent
S surface area
S₀ initial surface area
ΔS change in surface area
t time

γ German-Munir model exponent
Nomenclature Used in Chapter 6

A  flow hydrodynamic factor
A_H low Re asymptote of A
A_i projected area of i_th grain
C_p Cunningham slip correction
D_o diameter of grain
D_p diameter of particle
g gravitational "constant"
k Boltzmann's constant
L bed depth
n local concentration of aerosol
N_o number of grains per unit volume of bed
P penetration of particles through bed
r* dimensionless radius
T temperature
U gas superficial velocity
U_{mf} gas superficial velocity at fluidization
u_r radial velocity
u_s tangential velocity
u* dimensionless velocity
V_i volume of i_th grain
x = U/U_{mf} gas velocity as fraction of velocity required to cause fluidization
\(\alpha_0\)  solids volume fraction in bed

\(\eta\)  single grain capture efficiency

\(\eta_c\)  single grain collection efficiency

\(\eta_R\)  single grain retention efficiency

\(\eta_{TOT}\)  total bed capture efficiency

\(\mu\)  gas viscosity

\(\rho\)  gas density

\(\rho_p\)  particle density

\[ Grv = \rho_p D_p^2 \rho_g / 18 \mu U \]  - gravity number

\[ Pe = 3 \pi \mu D_p D_0 U / k T C_p \]  - Peclet number

\[ R = D_p / D_0 \]  - interception number

\[ Re = \rho D_0 U / \mu \]  - Reynolds number

\[ St = \rho_p D_p^2 C_p U / 18 \mu D_0 \]  - Stokes number

\[ St_{eff} = A St \]  - effective Stokes number for impaction regime
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Part II

Development of a Zero-Emissions Process
For Recovery of Sulfur from Acid Gas Streams
1. Introduction

Part I of this dissertation describes an investigation into the high-temperature reaction between limestone and hydrogen sulfide. In the course of this investigation it was noticed that when hydrogen sulfide and carbon dioxide were heated together at temperatures above 800 °C and cooled rapidly, a substantial fraction of the $\text{H}_2\text{S}$ was converted to elemental sulfur. This was found to be due to shifting of the equilibrium of the $\text{H}_2\text{S}$ thermal decomposition reaction:

$$\text{H}_2\text{S} \rightleftharpoons \text{H}_2 + \frac{1}{2} \text{S}_2$$

by the equilibrium of the water-gas-shift reaction:

$$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$$

Carbon dioxide and $\text{H}_2\text{S}$ are acid gases that occur commonly in fossil fuel gases (e.g., refinery gases, coal gas, some natural gases, etc.) and must be removed from these gases to prevent damage to catalysts and, in the case of $\text{H}_2\text{S}$, to comply with environmental legislation. It therefore seemed very attractive to develop a process based on the chemistry described above, whereby $\text{H}_2\text{S}$ and $\text{CO}_2$ would be converted to elemental sulfur and a mixture of CO and H$_2$ known as synthesis gas.

The following chapters describe the synthesis and development of such a process, which we named the U.C. Berkeley Zero-Emissions Sulfur Process. Chapter 2 describes current practices in sulfur-recovery technology and gives more details on the experimental discovery that led to the process. Chapter 3 discusses previous work relevant to this field and Chapter 4 contains a thermodynamic study of the equilibrium behavior of mixtures of $\text{CO}_2$ and $\text{H}_2\text{S}$ at high temperatures. The kinetics of the $\text{CO}_2/\text{H}_2\text{S}$ system were investigated experimentally in order to
develop models that could be used for process reactor design: this is described in Chapter 5. Chapter 6 contains a description of the synthesis and development of the process and Chapter 7 discusses some areas of particular engineering interest.
2. Background and Discovery

2.1 Sulfur Recovery Technology

The recovery of sulfur from fossil fuels is of major importance in the chemical and energy industries. Sulfur must be removed from fuels in order to comply with legislation designed to prevent environmental damage due to acid precipitation. Sulfur must also be removed from petrochemical feedstocks to prevent degradation of catalysts used in downstream processing. If this sulfur can be recovered in a usable form then its sale will partially offset the cost of its removal from the fossil fuel. Therefore, as environmental regulations have become more stringent, there has been an increase in the amount of sulfur recovered from fossil fuels, to the point where in 1991 roughly 62% of all sulfur consumed in the United States was produced by this method. (Chemical and Engineering News, June 29, 1992).

The first stage in all commercial sulfur recovery processes consists of converting the sulfur into hydrogen sulfide gas. In some cases this is unnecessary; for instance, in many "sour" natural gases the sulfur naturally occurs as H₂S. In most cases though, the organically bound sulfur must be removed by a hydrogenation process. For oil this can be accomplished as a part of hydroprocessing, a standard refinery technique that also improves the quality of the oil for other refinery uses. An important feature of hydrotreatment processes is that they require more hydrogen than is produced by the reforming processes in refineries. The excess hydrogen required must therefore be produced from hydrocarbon feedstocks at the expense of refinery products. In the case of coal, both gasification and liquefaction processes convert most of the organic and inorganic sulfur to H₂S. Coal gasification and liquefaction are not yet economically
attractive in the United States; however, they offer considerable advantages for sulfur recovery over direct-burning processes, which may be an important factor in their eventual implementation. The vapor pressure of \( H_2S \) at 25 °C is roughly 20 atmospheres, thus hydrogen sulfide is present as a gas under all conditions found in fuel treating plants. The hydrogen sulfide must therefore be removed from the hydrocarbon gas (e.g. refinery gases, coal gas, etc.) - - a process known as gas sweetening. In some cases natural gas or refinery gas may also contain carbon dioxide, and since this is also an acid gas, it too can be removed by sweetening processes if so desired.

![Diagram of Absorber Stripper Loop for Sour Gas Sweetening](image)

**Fig. 2.1 Absorber Stripper Loop for Sour Gas Sweetening**

Typical sweetening processes involve contacting the hydrogen sulfide with a suitable sorbent, usually in aqueous solution, in an absorption column, as shown in Fig. 2.1. The sorbent absorbs the acid gases (\( H_2S \), and \( CO_2 \) if required) leaving a "sweet" gas whose sulfur content
meets the legislative or process requirements. The "rich" solution, containing the absorbed acid gases, is then sent to a stripper column, where heat is used to drive off the acid gases and regenerate a "lean" solution of sorbent. If CO₂ and H₂S are to be removed from the gas then two stages of absorption and stripping, using different sorbents or operating conditions, may be necessary.

The most commonly used sorbents are the alkanolamines, usually monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA). There are, however, a number of other sorbent-based processes, including some which lead to direct sulfur recovery. A good review of these is given in Kirk and Othmer's Encyclopedía (West, 1984). The direct recovery processes are usually complex and involve the accumulation of unwanted, sulfur-containing by-product species, which must be purged to prevent build-up. They are therefore not widely used industrially. Instead, most industrial sulfur recovery is carried out using the Claus Process, a schematic for which is shown in Fig. 2.2.

The Claus process was invented in 1883, but not widely deployed until the 1950's (West, 1984). The principle reaction upon which it is based is:

\[ 2H₂S + SO₂ = 3S + 2H₂O \] (2.1)

In order to provide the SO₂ for this reaction, a part of the H₂S is burned in air, which leads to several problems described below. The gas mixture then passes through several stages of catalytic conversion, with condensation and removal of product sulfur between stages.

Because of the introduction of air to the process there is a considerable amount of nitrogen flowing through the Claus plant (> 60 % of any gas stream downstream of the
Fig. 2.2 Simplified Schematic of the Claus Process With Three Catalytic Stages
This inert material must be removed as tail gas; however, after three or four conversion stages the tail gas still contains some sulfur-containing species. The tail gas must therefore be sent to a treatment plant to remove these contaminants to an acceptable level. A number of tail-gas processes are reviewed by West (1984). Of these, the process most widely used industrially is the SCOT process; however, a SCOT unit may cost as much as the Claus plant itself (West, 1984).

If a sulfur-removal process is run in conjunction with a Claus plant and tail-gas cleanup process then overall recovery of sulfur may be as high as 99.8% (West, 1984). This technology allows economic recovery of sulfur, however it is very costly because of the large number of processing steps needed to prevent sulfur emissions, and it does not recover the chemical or fuel value of the hydrogen from the \( \text{H}_2\text{S} \). Any process which reduced both capital cost and sulfur emissions, and recovered the hydrogen in a usable form, would be a substantial improvement over the existing technology.

### 2.2 Initial Observation

The process described in this dissertation was conceived after an unexpected chemical reaction was observed experimentally. Experiments were being made to investigate the suitability of limestone for use as a high-temperature sorbent for \( \text{H}_2\text{S} \) (for more details see Part I of this dissertation). These experiments involved heating limestone in an atmosphere containing \( \text{H}_2\text{S} \) in the apparatus shown in Fig. 2.3. In order to prevent calcination of the limestone, the bulk of the gas (96 mole%) was carbon dioxide, with 4 mole \% hydrogen (for reasons discussed below) and 1 \% \( \text{H}_2\text{S} \). It can be seen from Fig. 2.3 that the reaction-gas mixture entered the outer tube of
the reactor, passed into the furnace, and was withdrawn through the inner tube. The difference in diameters between these tubes was such that the residence time in the inner tube was one-thirtieth the residence time in the outer tube. The gases exiting the reactor were consequently quenched very rapidly from high to low temperature, by counter-current heat-exchange with the cooler incoming gases.

Fig. 2.3 Apparatus Used for Limestone Experiments

When these experiments were carried out at a temperature of 800 °C it was observed that a yellow deposit formed inside the inner tube in the region where the tubes exited the furnace, Fig. 2.4. After the experiment had been run for four hours a substantial amount of this yellow material had accumulated inside the inner tube. Upon dismantling the apparatus the deposits were found to be soluble in carbon disulfide, and, given the feed composition, must therefore have been elemental sulfur. The formation of elemental sulfur under these conditions had not been
expected, in fact later calculations showed that several aspects of the experimental design were of great importance in allowing the observation to be made. The flow pattern in the reactor was perhaps the most important factor. The exit of the hot reaction-gas through the inner tube caused it to cool rapidly, thereby preventing the gas-phase species from attaining equilibrium at a lower temperature. The thermodynamics of sulfur formation are described in detail in Chapter 4; however, higher temperatures favor elemental sulfur over H₂S, therefore rapid quenching preserved a higher proportion of the sulfur than would have been seen had the gas cooled more slowly. The concentration of elemental sulfur in the gas at the lower temperatures was therefore sufficient to cause condensation and permit the sulfur to be observed.

![Fig. 2.4 Location of Sulfur Deposits](image)

The composition of the feed gas also played an important role. Had the feed concentration of H₂S been lower there may not have been enough sulfur in the product gas to cause condensation. A small amount of hydrogen was also present in the feed-gas to prevent CO₂ from oxidizing the calcium sulfide produced in the sulfdiation of limestone. At high temperatures the H₂ reacts with CO₂ via the water-gas shift reaction:

\[ CO + H₂O = CO₂ + H₂ \]  \hspace{1cm} (2.2)

The CO thus formed reduces the oxidizing power of the CO₂. For 1 mole% H₂S in 96 % CO₂
it was necessary to have CO present, otherwise significant amounts of SO₂ would have formed, and again elemental sulfur deposition might not have been seen. Finally, the experimental temperature was in exactly the right range for sulfur formation. Increasing the temperature favors both partial oxidation of H₂S to sulfur and complete oxidation to SO₂. Sulfur dioxide is more strongly favored, however, and had the temperature been a few hundred degrees hotter then sulfur formation might not have been observed.

A computer program for calculating the chemical equilibrium composition of a gas mixture (see Chapter 4) was used to analyze the experimental findings. It was calculated that at high temperature we should indeed expect to see a significant fraction of the sulfur present in the form of S₂. The apparent reaction by which sulfur formation occurs is:

\[
CO_2 + H_2S \rightarrow CO + H_2O + \frac{1}{2} S_2
\]  

which will be shown to be the sum of the hydrogen sulfide decomposition reaction:

\[
H_2S \rightarrow H_2 + \frac{1}{2} S_2
\]  

and the water-gas shift reaction. Other calculations were performed to investigate the thermochemical behavior of the system and the results are discussed in Chapter 4.

It was immediately realized that Reaction (2.3) is similar to the Claus reaction (2.1) and therefore could be used as the basis for a sulfur-recovery process. Furthermore, the by-product of Reaction (2.3) is carbon monoxide, which can be reacted with steam to generate hydrogen, thereby effectively recovering the H₂ from the H₂S. The development of a process based on this chemistry is described in Chapter 6.
3. Previous Work

A great deal has been written on the oxidation of H$_2$S by SO$_2$ as required in the Claus process. There has also been much research into the thermal decomposition of H$_2$S as a source of hydrogen, including some efforts that tried to react the H$_2$S with CO to form COS and H$_2$. Very little research has been reported addressing the partial oxidation of H$_2$S with CO$_2$.

The most important early paper on the oxidation of hydrogen sulfide was that of Garnson and Elkins (1953). Their very thorough article not only covered the thermodynamics and kinetics of the reactions pertinent to the Claus process, but also included process considerations and evaluated the effectiveness of several modifications of the basic Claus process. A good review of more recent developments in Claus process technology is given by Goar (1986). Garnson and Elkins (1953) were also the first to realize that the Claus process leads to the formation of a mixture of sulfur-containing compounds, including S$_2$, S$_4$ and S$_8$, for which they allowed in their calculations. Later experiments using more sophisticated apparatus (Rau et al, 1973) showed that significant amounts of S$_3$, S$_4$ and S$_7$ can also be present in sulfur vapor in the range 900 - 1200 K. Rau et al (1973) used density measurements to determine the equilibrium constants for the formation of each allotrope from S$_2$, then fitted thermodynamic properties from these data. They report sufficient data to permit calculation of the equilibrium composition of the gas phase, allowing for all sulfur species in the range S$_1$ - S$_8$. Kaloidas and Papayannakos (1987) performed equilibrium calculations for the decomposition of H$_2$S to form hydrogen and elemental sulfur (S$_2$, ..., S$_8$) and compared their results with experimental data. They found that for sulfur vapor 91% of the S was present as S$_2$ for temperatures above 1000 K at 1 atm. In H$_2$S/H$_2$/S$_i$ mixtures (2 < i < 8) they found that for temperatures above 1000 K and pressures from 1 to 4 atm 99.8 %
of the elemental sulfur was present as $S_2$.

North American interest in the thermal decomposition of $H_2S$ began with a paper by Raymont (1975), although it had received some attention in Japan prior to that date (Kotera, 1976). The main focus of Raymont's work (and much of that which followed) was on $H_2S$ decomposition as a source of hydrogen, rather than as a means of $S$ recovery. Raymont found the decomposition of $H_2S$:

$$H_2S = H_2 + \frac{1}{2} S_2 \quad (2.4)$$

to be thermodynamically unfavorable at temperatures below 1800 K. His kinetic studies showed that the reaction proceeds rapidly to equilibrium without requiring catalyst at temperatures above 1250 K, though he did not state the residence time of the reactor in which these experiments were carried out. Below this temperature catalysis is required to achieve a rapid rate; however, Raymont did not identify a particular catalyst. Raymont also correctly observed that the equilibrium conversion of $H_2S$ could be enhanced by combining the decomposition reaction with a more favorable reaction. Because of his emphasis on $H_2$ recovery, he chose the reaction:

$$2CO + S_2 = 2COS \quad (3.1)$$
giving the overall reaction:

$$H_2S + CO = H_2 + COS \quad (3.2)$$

The COS could then be converted to $S_2$ via:

$$2COS + SO_2 = 2CO_2 + 3/2 S_2 \quad (3.3)$$

the $SO_2$ being produced in a manner similar to the Claus process. He suggested that Reaction (3.2) be carried out under conditions that allowed continuous separation of $H_2$ from COS, i.e.,
in a reactor with metal-alloy-membrane walls. Since this technology was (and is) not available, attention shifted to continuous removal of sulfur instead.

Fukuda et al (1978) were able to obtain 95% conversion of H₂S to hydrogen and sulfur by continuous removal of sulfur and intermittent separation of hydrogen, using molybdenum disulfide as catalyst at 800 °C. The catalytic properties of molybdenum disulfide for H₂S decomposition were described by Katsumoto et al (1973) and Kotera (1976). Kotera (1976) had also investigated the decomposition route via reaction (3.1), but found this pathway to be complicated by the reaction:

\[ 2\text{COS} \rightarrow \text{CO}_2 + \text{CS}_2 \]  (3.4)

He therefore switched his attention to the thermal decomposition route.

Fukuda et al (1978) described the kinetics of H₂S decomposition over molybdenum disulfide. They were, however, unable to develop a commercially-attractive process due to the high energy costs associated with separating H₂ from H₂S. Fukuda et al (1978) also determined that tungsten disulfide is a slightly less effective catalyst than molybdenum disulfide, whereas NiS is much less effective, due to the formation of NiS₂. Chivers et al (1980) performed similar tests and found that Cr₂S₃ gave similar performance to WS₂, while FeS, CoS and a range of copper sulfides (Cu₂S, Cu₆S₅ and CuS) were not effective as catalysts. Chivers et al also found that MoS₂ was the most effective catalyst above 600 °C, but WS₂ and Cr₂S₃ were more effective below 600 °C. Possible mechanisms for H₂S decomposition over MoS₂ are described by Sugioka and Aomura (1984) and Katsumoto et al (1973). Roth et al (1982) investigated the mechanism of thermal decomposition of H₂S at low concentrations (<200 ppm) and high temperatures (>1965
K) as part of an investigation of sulfur conversion in flames. They found the primary mechanism to be second order:

\[ H_2S + M = HS + H + M \]  \hspace{1cm} (3.5)

with a rate constant:

\[ k = 7.7 \times 10^{10} \exp (-41,500/T) \]  \hspace{1cm} (cm^3/mol.s)

It should be noted, however, that their experimental temperatures were significantly higher than those of interest to this study. Kaloidas and Papayannakos (1989) investigated the non-catalytic thermal decomposition of \( H_2S \) in the temperature range 600-860 °C and pressure range 1.3-3.0 atm. They developed a kinetic model based upon a free-radical mechanism with the splitting of \( H_2S \) into free-radical intermediates as the rate-limiting step. The model gave good agreement with their experimental results and they found the rate of decomposition to be given by:

\[ r = k_1 P_{H_2S} \]

where:

\[ k_1 = 784.1 \exp (-23,600/T) \]  \hspace{1cm} (mol/cm^3.s.atm)

and \( P_{H_2S} \) is the partial pressure of \( H_2S \) in atm.

They demonstrated clearly that the rate of thermal decomposition was first-order in \( P_{H_2S} \), therefore their results are to be preferred to those of Roth et al (1982). Kaloidas and Papayannakos (1989) also cite numerous references confirming the presence of \( H^* \), \( HS^* \) and \( S^* \) radicals in gaseous systems containing \( H_2S \) at high temperatures (Bradley and Dobson, 1967a,b; Levy and Merryman, 1965; Merryman and Levy, 1967, 1972 and Norrish and Zeelenberg, 1957). They also determined that alumina (\( Al_2O_3 \)) does not catalyze the decomposition reaction.
Banderman and Harder (1982) developed the first realistic process flow diagram for H$_2$S decomposition. Their process used continuous separation of sulfur by condensation and semicontinuous separation of H$_2$ and H$_2$S by pressure-swing adsorption, allowing recycle of unreacted H$_2$S. They were skeptical about the ability of this process to compete with the Claus process economically, largely as a result of its very large energy requirements. The use of pressure-swing adsorption would also impose scale-up limitations on the process. They were, however, able to demonstrate the feasibility of the process on a bench-scale. A process via the COS route was patented by the Standard Oil Co. of Ohio (Herrington and Kuch, 1984), however this process did not appear to account for the formation of side products as mentioned above, and was not deployed industrially.

Chivers and co-workers at the University of Calgary continued to investigate catalysts for H$_2$S decomposition. Chivers and Lau (1985) reported catalytic activity for Li$_2$S. They also found that sodium and potassium sulfides (Na$_2$S, K$_2$S) and polysulfides (Na$_2$S$_2$, K$_2$S$_2$, Na$_2$S$_3$, K$_2$S$_3$, Na$_2$S$_4$, and K$_2$S$_4$) were not catalytically active, though they were able to react with the gas forming amorphous mixed polysulfide products. Chivers and Lau (1987) investigated vanadium sulfide, V$_2$S$_3$, and mixed sulfide systems (V$_2$S$_3$/FeS, V$_2$S$_3$/Cu$_x$S$_y$ and V$_2$S$_3$/ZnS) in both flow and thermal-diffusion-column reactors at temperatures between 400 and 800 °C. They found that V$_2$S$_3$ performed better than MoS$_2$ in flow reactors and identified the catalysis mechanism as being via thermal decomposition of V$_2$S$_3$:

\[
V_2S_3 = 2VS + 1/2S_2 \quad (3.6)
\]

\[
2VS + H_2S = V_2S_3 + H_2 \quad (3.7)
\]
The mixed sulfide systems performed no better than MoS₂ at temperatures above 600 °C, with the exception of the mixture V₂S₃/Cu₅S₅ which gave significantly better performance. Chivers and Lau used X-Ray Diffraction to identify the solid-phase species formed from the sulfide mixture at high temperatures as being Cu₃VS₄, and thus postulated that the thio-anion V₅S₄⁻ is a better catalyst for H₂S decomposition at high temperatures than MoS₂. It should, however, be noted that Chivers and Lau used a recirculating reactor system rather than a once-through system, therefore it is possible that their results may have been distorted due to liberation of sulfur from the solid phase. Without information on the solid and gas inventories in their apparatus it is impossible to quantify this error; however, they report the times for the reactor to reach steady-state. For MoS₂ the time required is ca. 20 minutes, whilst the mixed sulfide system required 70 minutes. This seems to be convincing evidence of the superior catalytic properties of MoS₂.

Al-Shamma and Naman (1989) also investigated V₂S₃ as well as V₂S₃/V₂O₅ mixtures (Al-Shamma and Naman, 1990). They report kinetic data and mechanisms, however their data suggest that the processes they were observing were reactive rather than catalytic. Although they used a once-through flow apparatus, the concentration of hydrogen produced never reached a steady-state level. Instead it increased slowly to a maximum after ca. 200 minutes, before falling off more rapidly. This would be consistent with sulfidation of the V₂O₅ followed by catalysis by VS as described above.

Recently interest in the COS route (exploiting reaction 3.2 or otherwise) has revived. Gangwal et al (1991) proposed using coal gas to reduce SO₂ to elemental sulfur via:
\[ 2CO + SO_2 = 2CO_2 + \frac{1}{n} S_n \] (3.8)

and suggested that coal gas would also react with COS and H₂S to form elemental sulfur. The maximum temperature they investigated was 650 °C and they suggested a process pressure of 20 atm. Their experiments showed that a high conversion of H₂S to elemental sulfur could be obtained in a system containing coal gas and SO₂, however they did not appear to realize that the H₂S must be undergoing oxidation by CO₂ as well as SO₂ in this system.

Fellmuth et al. (1987) examined the reaction of H₂S and CO₂. They were, however, chiefly interested in zeolite deactivation and did not extend their studies above 300 °C. The main reaction they observed was therefore:

\[ H_2S + CO_2 = COS + H_2O \] (3.9)

which they found to be catalyzed by basic zeolites. This reaction will be seen to be the main route for COS formation in our system (Chapter 5). Bowman (1991) observed the same experimental effect that was described in Chapter 2 while researching thermochemical cycles for hydrogen manufacture, and used this to design and patent a process. (We were unaware of this process until a late stage in the design of the Zero-Emissions Sulfur Process owing to the delay between granting of the patent and its appearance in Chemical Abstracts). The process described by Bowman (1991) was based on a somewhat incomplete set of equilibrium calculations and took no account of kinetic considerations. It therefore contains serious economic and operability flaws and should not threaten the patentability of the Zero-Emissions Sulfur Process, though it may cause licensing difficulties owing to the similar chemistry used. The only other paper found in the literature addressing the reaction between H₂S and CO₂ is that of Rice et al. (1988). This was a theoretical treatise on the nature of HOCCO complexes formed under very low pressures and is
not strictly relevant to the sulfur recovery field.
4. Thermochemical Analysis

4.1 Introduction and Method

We have two aims in analyzing the thermochemical behavior of the H$_2$S/CO$_2$ system at high temperatures. Firstly, calculation of the thermodynamic equilibrium composition can determine the fraction of elemental sulfur formed at equilibrium, and can also be used to examine how this equilibrium is affected by process variables such as temperature, pressure, feed composition, etc. This provides useful information for establishing process operating conditions. Secondly, we can recognize that all reactions do not occur at the same rate, therefore some reactions will reach equilibrium more rapidly than others. This is of particular importance when cooling the gas mixture from a high temperature. A key part of this research involves exploiting high-temperature equilibria that favor sulfur formation, then cooling rapidly to lower temperatures at which the reaction kinetics are too slow for a less favorable equilibrium composition to be formed within the processing timescale. The rate of cooling necessary is determined by kinetic considerations (see Chapter 5); however, if the cooling is not fast enough some of the more rapid reactions will re-equilibrate as the gas is cooled. The effect of this re-equilibration can be investigated by performing calculations on a smaller sub-set comprising only the more rapid reactions. This is described in Section 4.5.

The calculations were carried out using a modified version of a computer simulation previously developed in this Department (Whitney et al 1987) named COALNEAT. This program calculates the equilibrium composition, given a feed stream composition, together with a temperature and pressure. The calculation is performed by selecting a set of independent
chemical reactions, determining material balances for all elements present and then solving iteratively using a robust, multi-dimensional Newton-Raphson iteration procedure. For the high temperatures (> 600 °C) and low pressures (< 10 bar) of interest to this study it was reasonable to assume that all gas-phase species behave ideally, therefore fugacity corrections were not made. Thermochemical data were taken from the JANAF Thermochemical Tables (Chase et al. 1985).

Following the findings of Kaloidas and Papayannakos (1987), S\(_2\) was considered to be the only elemental sulfur species present. In practice, small amounts of other sulfur allotropes will also exist, therefore the calculations may slightly underpredict the fraction of elemental sulfur in the gas at equilibrium. This is a safe-side approximation that considerably shortens calculation time and obviates the selection of a thermodynamic database for the other elemental sulfur species. The sensitivity of the results to this assumption is discussed in Section 4.3.5.

4.2 Verification of Experimental Observation

The first calculations determined what equilibrium conversion of \(\text{H}_2\text{S}\) to elemental sulfur would be obtained under the conditions used in the original limestone experiments. The feed was 95 mole% \(\text{CO}_2\), 4% \(\text{H}_2\) and 1% \(\text{H}_2\text{S}\); the temperature was 789 °C, and the pressure was 1 atm. Species considered to be present in the gas phase were \(\text{CO}_2\), CO, \(\text{H}_2\), \(\text{H}_2\text{O}\), \(\text{H}_2\text{S}\), \(\text{S}_2\), \(\text{COS}\), \(\text{CS}_2\), and \(\text{SO}_2\). The equilibrium composition was calculated for the gas phase only, i.e., neglecting the presence of the limestone, and is shown in Table 4.1. This confirmed that we should indeed expect to see a substantial amount of elemental sulfur formed if the gas had reached high-temperature equilibrium.
### Table 4.1 Equilibrium Composition for Limestone Experiment Conditions

(789 °C, 1 atm, 95 mole \% CO₂, 4 \% H₂, 1 \% H₂S)

<table>
<thead>
<tr>
<th>Species:</th>
<th>CO₂</th>
<th>CO</th>
<th>H₂</th>
<th>H₂O</th>
<th>H₂S</th>
<th>S₂</th>
<th>COS</th>
<th>CS₂</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium composition (mol%):</td>
<td>90.6</td>
<td>4.1</td>
<td>0.2</td>
<td>4.3</td>
<td>0.46</td>
<td>0.10</td>
<td>0.29</td>
<td>2 ppm</td>
<td>360 ppm</td>
</tr>
<tr>
<td>Fraction of sulfur-containing species:</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.467</td>
<td>0.207</td>
<td>0.289</td>
<td>2x10⁻⁴</td>
<td>0.036</td>
</tr>
</tbody>
</table>

#### 4.3 Thermodynamic Survey

Calculations were performed to investigate the effect of important variables on the equilibrium composition of the gas phase for CO₂ and H₂S mixtures. The results are discussed below.

The sulfur-containing species included in the calculations were H₂S, S₂, SO₂, CS₂, COS and SO₃. Results for CS₂ and SO₃ are not reported, however, as neither ever accounted for more than two-thousandths of the total sulfur present. The results are presented in the form of graphs showing the fractional distribution of sulfur, i.e., the molar fraction of the total sulfur present as each species.

In discussing the results of the survey it is useful to note that since we consider eight chemical compounds (CO₂, CO, H₂, H₂O, H₂S, S₂, SO₂ and COS) containing four elements (C,
H, O and S), we require four reaction equations to specify the equilibrium composition of the gas phase. For the purposes of this discussion these will be taken as being the water-gas-shift reaction:

\[ CO + H_2O = CO_2 + H_2 \]  \hspace{1cm} (2.2)

the \( H_2S \) decomposition reaction:

\[ H_2S = H_2 + \frac{1}{2} S_2 \]  \hspace{1cm} (2.4)

the Claus reaction:

\[ 2 \ H_2S + SO_2 = \frac{3}{2} S_2 + 2 \ H_2O \]  \hspace{1cm} (2.1)

and the formation of COS from CO and \( S_2 \):

\[ 2 \ CO + S_2 = 2 \ COS \]  \hspace{1cm} (3.1)

It will be seen that of these reactions, the water-gas-shift reaction plays the greatest role in determining the equilibrium composition by shifting the equilibria of the other reactions.

4.3.1 The Effect of Temperature

Figure 4.1 shows the equilibrium sulfur distribution given by the decomposition of \( H_2S \) as a function of temperature at 1 atm in the absence of CO\(_2\). Fig. 4.2 shows the distribution for an initial feed of 50 \% \( H_2S \), 50 \% CO\(_2\). Comparing the figures it can be seen that the fraction of \( S \) present as elemental sulfur at equilibrium has been enhanced by a factor of roughly two at all temperatures, demonstrating the effectiveness of the water-gas-shift reaction for shifting the equilibrium of \( H_2S \) decomposition.
The equilibrium yield of $S_2$ increases with increasing temperature, due to the endothermic
nature of $\text{H}_2\text{S}$ decomposition (Reaction 2.4). Increasing $\text{H}_2\text{S}$ decomposition causes an increase in the amount of $\text{H}_2\text{O}$ present in the gas, which helps drive the reverse of the Claus reaction (2.1), therefore the equilibrium fraction of $\text{SO}_2$ also increases with temperature. This will be found to impose an important limit on the operating conditions for the sulfur-recovery process (see Sections 6.2, 7.1.2). The formation of $\text{COS}$ is favored by low temperatures, since Reaction 3.1 is exothermic as written.

4.3.2 The Effect of Pressure

![Fig. 4.3 The Effect of Pressure on the Equilibrium Distribution of Sulfur-Containing Species at 900 °C for a 50 % $\text{H}_2\text{S}$, 50 % $\text{CO}_2$ Feed](image)

The water-gas-shift reaction (Reaction 2.3) is equimolar and therefore its equilibrium composition is independent of pressure. All of the elemental-sulfur-forming reactions lead to a net increase in the number of moles, consequently the amount of $\text{S}$ present as elemental sulfur decreases with increasing pressure as can be seen in Fig. 4.3. An interesting, and perhaps
unexpected, result is that the equilibrium fraction of \( \text{SO}_2 \) also decreases. If we consider the ratio (number of moles of products)/(number of moles of reagents) for the \( S_2 \)-forming reactions, we find that for reactions (2.4) and (3.1) the ratio is 1.5, whereas for the Claus reaction it is only 1.17. COS formation and \( \text{H}_2\text{S} \) decomposition are therefore much more sensitive to pressure than the Claus reaction, and consequently when the pressure is increased \( S_2 \) is more likely to be converted to \( \text{H}_2\text{S} \) or COS via these routes than to \( \text{SO}_2 \) via the Claus reaction. Obviously this is somewhat dependent on the initial composition of the gas (particularly the amount of \( \text{H}_2\text{O} \) present) since the water-gas-shift equilibrium is pressure-independent.

4.3.3 The Effect of the \( \text{CO}_2/\text{H}_2\text{S} \) Ratio

Figure 4.4 shows the effect of increasing the initial mole fraction of \( \text{H}_2\text{S} \) in \( \text{CO}_2 \) on the equilibrium distribution of sulfur compounds. At very low \( \text{H}_2\text{S}/\text{CO}_2 \) ratios, \( \text{SO}_2 \) is the most
favored product; however, the fraction of the S present as SO₂ falls rapidly as the initial H₂S concentration is increased and the mixture becomes more reducing in nature.

The fraction of sulfur present as S₂ passes through a maximum at around 6 % H₂S in CO₂, since increasing the amount of H₂S present not only makes the mixture less oxidizing in nature, but also lowers the S₂ fraction by dilution with H₂S. A similar effect is observed for COS. It should be noted that the results for COS are plotted on an expanded scale (4x magnification) and that the COS fraction is therefore much less sensitive to the feed composition than the S₂ fraction.

4.3.4 The Effect of H₂O

For processing reasons, it is likely that any gas stream containing H₂S and CO₂ would also contain a small amount of water vapor. (This arises from the use of absorber/stripper loops for acid-gas cleaning — the acid gas stream usually leaves the stripper saturated with water at cooling-water temperature). It is therefore important to understand the effect of the initial H₂O concentration on the equilibrium distribution of sulfur-containing species.

Fig. 4.5 shows this variation at 900 °C and 1 atm, for a feed containing 1:1 CO₂ and H₂S, as the water fraction is increased from 0 to 10 %. At 1 atm pressure, 10 % initial water concentration corresponds to the feed gas being saturated with water at 46 °C.

Perhaps the most salient feature of Fig. 4.5 is that none of the species is strongly affected by increasing the H₂O fraction over this range. In particular, the equilibrium fraction of S₂
Fig. 4.5 The Effect of Initial Water Concentration on the Equilibrium Distribution of Sulfur Containing Species for a 1:1 H$_2$S:CO$_2$ feed at 1 atm, 900 °C

decreases only from 0.32 to 0.29, a change of under 10 %.

Increasing the water content helps drive the reverse Claus reaction, thus the SO$_2$ fraction increases, though not strongly. The effect of increasing the feed H$_2$O content on the water-gas-shift reaction is to drive the reaction over towards CO$_2$ and H$_2$, thereby tending to reduce H$_2$S decomposition. This also reduces the CO concentration and hence favors the reverse of Reaction (3.1), leading to COS decomposition and causing the COS fraction to decrease as the H$_2$O fraction increases. The increased COS decomposition to some extent counteracts the reduced H$_2$S decomposition, giving rise to the observed weak dependence of S$_2$ fraction on H$_2$O content.
4.3.5 The Effect of Sulfur Allotropes

In the introduction it was mentioned that elemental sulfur can exist as a number of allotropes \( S_2, \ldots, S_8 \) under the conditions of this study. In order to confirm the results of Kaloidas and Papayannakos (1987) cited above, the base calculation (1 atm, 900 °C, 50:50 \( H_2S:CO_2 \)) was repeated with the sulfur species \( S_3, \ldots, S_8 \) included in addition to the species included in the calculations described above. The results are shown in Table 4.2. The fraction of \( S \) present as elemental sulfur was 32.40 % in the case where only \( S_2 \) was considered and 32.56 % in the case where all \( S \) allotropes were allowed. This confirms that the effect of including the compounds \( S_3, \ldots, S_8 \) is negligible.

Table 4.2 The Effect of Including Sulfur Allotropes

<table>
<thead>
<tr>
<th>Species</th>
<th>Fraction of Sulfur-Containing Species Considering ( S_2 ) only</th>
<th>Considering ( S_2, \ldots, S_8 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_2 )</td>
<td>0.324</td>
<td>0.318</td>
</tr>
<tr>
<td>( S_3 )</td>
<td>0</td>
<td>0.00649</td>
</tr>
<tr>
<td>( S_4 )</td>
<td>0</td>
<td>0.000303</td>
</tr>
<tr>
<td>( S_5 )</td>
<td>0</td>
<td>0.00005</td>
</tr>
<tr>
<td>( S_6 )</td>
<td>0</td>
<td>0.000123</td>
</tr>
<tr>
<td>( S_7 )</td>
<td>0</td>
<td>0.000107</td>
</tr>
<tr>
<td>( S_8 )</td>
<td>0</td>
<td>0.000024</td>
</tr>
<tr>
<td>( H_2S )</td>
<td>0.614</td>
<td>0.613</td>
</tr>
<tr>
<td>( SO_2 )</td>
<td>0.000811</td>
<td>0.000798</td>
</tr>
<tr>
<td>( COS )</td>
<td>0.0607</td>
<td>0.0604</td>
</tr>
<tr>
<td>( CS_2 )</td>
<td>0.0000087</td>
<td>0.0000087</td>
</tr>
</tbody>
</table>

4.4 Reactor Yield

The calculations presented above showed the fraction of sulfur present as each species at equilibrium. If we multiply the fraction present as elemental sulfur by the feed \( H_2S \) fraction,
we obtain the yield of elemental sulfur, i.e., the number of moles of elemental sulfur (S) formed per mole fed to the reactor. The reactor yield is an important process design parameter that determines the size of the recycle, and hence the size of the furnace and second absorption sections of the Zero-Emissions Sulfur Process (see Chapter 6).

Figure 4.6 shows the reactor yield at 900 °C, 1 bar, as a function of the concentration of H₂S in the feed (dry basis). The solid lines in Fig. 4.6 are for a dry feed, in which the maximum yield is 16.7% at an initial concentration of 67% H₂S in CO₂. This represents an improvement of 36% over the yield in the absence of CO₂. This could raise the question whether the presence of CO₂ is necessary to the process; however, it must be remembered that the water-gas-shift reaction significantly lowers the hydrogen concentration, thereby preventing back-reaction during the quench. It is therefore much easier to maintain a high yield in the presence of CO₂ than in its absence.

As noted in Section 4.3.4, the feed will normally contain some H₂O, therefore calculations were repeated for a feed saturated with water at 40 °C, 1 atm. The results are shown as the dashed lines in Fig. 4.6. In this case the maximum yield of elemental sulfur per mole feed gas is 14.52% at a feed fraction 71% H₂S in CO₂. This is somewhat lower than the previous case, mainly due to dilution: if we correct the results to a dry basis the yield is 15.7%, i.e., an improvement of 27.7% over the yield in the absence of CO₂.

This suggests that to optimize reactor performance for the Zero-Emissions Sulfur Process, the reactor feed should be roughly 70% H₂S in CO₂. Reactor yield is also improved by reducing
the feed H₂O fraction. This can be achieved by operating the strippers and water condensers under slightly higher pressure than the furnace section. For example, if the stripper is run at 2 bar instead of 1 bar, the feed H₂O fraction is reduced from 7.4 % to 3.7 %; however, increasing the pressure in the stripper impairs its performance somewhat. The trade-off between reactor yield and stripper performance ultimately depends on process economics and is something that must be addressed at the detailed design stage. In determining the optimum reactor feed for the process we must consider other factors as well as reactor yield. This is discussed in Section 6.2.

4.5 The Effect of Cooling

If the reactor gas is cooled slowly enough then some of the reactions will be fast enough to re-equilibrate, while other, less rapid, reactions will not, and hence will be quenched. In
particular, we expect the $\text{H}_2\text{S}$ decomposition reaction (reaction 2.4) to be the slowest to reach equilibrium during cooling. Not only is this reaction known to be relatively slow (Chapters 3 and 5), but also, on cooling, the equilibrium favors $\text{H}_2\text{S}$ formation by recombination of sulfur and hydrogen. In our system the hydrogen concentration is considerably lowered by the water-gas-shift reaction, which further reduces the rate of back-reaction.

If the cooling rate is too rapid for re-equilibration of reaction 2.4, but too slow to quench the other reactions, then the net effect is that the other species re-equilibrate as if $\text{H}_2\text{S}$ were not present. (We had eight compounds, four mass balances and four reaction equations - removing one reaction equation means we must consider one less compound at equilibrium). In this case the distribution of sulfur-containing species is different from the case where $\text{H}_2\text{S}$ is in equilibrium with the other species during cooling. It is important to examine this case to determine what would occur if the quench were not rapid enough.

Figure 4.7 shows the distribution of sulfur-containing species as a function of temperature for the cooling conditions described above. Slow cooling strongly favors formation of COS at the expense of elemental sulfur. Since COS is hydrolyzed to $\text{CO}_2$ and $\text{H}_2\text{S}$ and recycled to the reactor (see Section 7.1.1), the effect of high COS formation is to lower reactor yield and increase the size of the recycle. This is not desirable; therefore the quench rate must be high enough to prevent re-equilibration of the COS-forming reactions. The same can also be said for $\text{CS}_2$.

For sulfur dioxide the fraction present decreases if the cooling rate is slow enough for re-equilibration. By 600 °C the $\text{SO}_2$ concentration in the gas is roughly 4 ppm under the
conditions calculated. Low SO$_2$ concentrations are very beneficial to process operation (see Section 7.1.2), therefore this is to be desired. In practice the Claus reaction is quite rapid at temperatures above 400 °C, so although we might not achieve complete re-equilibration during quenching, we expect to find significantly lower fractions of SO$_2$ in the cooled gas than were present at the highest temperatures. This was confirmed experimentally (see Chapter 5).
5. Kinetic Analysis

5.1 Experimental Strategy

A series of experiments was conducted to investigate the kinetic behavior of \( \text{H}_2\text{S}/\text{CO}_2 \) mixtures at high temperatures. We are primarily interested in the interplay between the water-gas-shift reaction:

\[
\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2
\]  

and the thermal decomposition of \( \text{H}_2\text{S} \):

\[
\text{H}_2\text{S} = \text{H}_2 + \frac{1}{2} \text{S}_2
\]

The kinetics of reaction 2.4 was investigated by Kaloidas and Papayannakos (1989); a description of their results is given in Chapter 3. For a complete understanding of the system, however, we must also consider the reactions that form \( \text{COS} \) and \( \text{SO}_2 \):

\[
2\ \text{H}_2\text{S} + \text{SO}_2 = 3/2 \text{S}_2 + 2\ \text{H}_2\text{O}
\]  

\[
2\ \text{CO} + \text{S}_2 = 2\ \text{COS}
\]

For the purposes of equilibrium calculations reaction (3.1) is sufficient to describe the presence of \( \text{COS} \); however, it is not necessarily the rate-limiting reaction of \( \text{COS} \) formation. This is discussed in more detail below.

Carbonyl sulfide may be removed from the reactor product gases by hydrolysis (see Section 7.1.1), and therefore may be considered as a reaction byproduct that merely lowers the product yield-per-reactor-pass and hence increases process recycle rate. Sulfur dioxide is a less
desirable product, for reasons discussed in Section 7.1.2; however, the kinetics of reaction (2.1) is known to be rapid at the temperatures of interest, and it was shown in Chapter 4 that we do not expect to find significant SO\textsubscript{2} formation.

If the gas mixture is given a sufficiently long time at high temperature then the equilibrium of these four reactions will determine the distribution of sulfur-containing species, as described in Chapter 4. It was also shown in Section 4.3.1 that the formation of elemental sulfur is strongly favored by high temperatures. It is therefore desirable for process reasons (see Sections 6.2, 7.3) that the gas be allowed to approach equilibrium at high temperature, then be quenched rapidly to a temperature at which the kinetics of the important reactions are very slow, so that the reactions are unable to re-equilibrate at the lower temperature.

For process design purposes we wish to predict the size of reactor required to achieve a given H\textsubscript{2}S conversion for a given flow of feed gas, and also the rate at which the products must be cooled if excessive COS formation and back-reaction are to be prevented (Section 4.5). Experiments therefore concentrated on determining which of the reactions given above was the rate-limiting step, and on developing a kinetic model that could predict the conversion of H\textsubscript{2}S. The effect of varying quench rate on the level of COS formation was also investigated experimentally.

Once the rate-limiting step had been determined it became possible to improve the process design by applying a catalyst to this step. A thorough investigation of the effect of catalysis, and the effect of the reaction mixture on the catalyst, would be beyond the scope of this work; however, a few preliminary experiments were carried out to demonstrate feasibility. Results of
these experiments are described in Section 5.5.

5.2 Apparatus

5.2.1 Description

Experiments were carried out in the continuous-flow apparatus shown in Fig. 5.1. The CO₂ and H₂S (industrial grade, supplied by Mattheson Gas Products, Newark, CA) were mixed at the desired flowrates using high-precision, low-flowrate rotameters (Omega Engineering Inc., Stamford, CT), before being sent to the reactor. The reactor consists of two concentric quartz tubes mounted in a high-temperature furnace. The gas enters the outer tube of the reactor, where it is pre-heated by contact with the exiting gas and by heating tape around the outside of the reactor. The gas is then further heated in the furnace section of the reactor before exiting through the inner tube. The difference in the tube diameters causes the residence time in the inner tube to be roughly 4% of that in the outer tube, which, together with the temperature profile obtained in the reactor and judicious selection of flowrates, ensures that the gas spends long enough at high temperature to guarantee significant conversion of H₂S, before being cooled rapidly as it exits the furnace.

The gas leaving the reactor passes through a condenser that collects elemental sulfur formed during the reaction. The condenser is designed to recover more than 99% of the sulfur formed on reaction. The piping between the reactor and condenser is heat-traced to prevent blockages due to sulfur deposition. After leaving the condenser the gas passes through a U-tube cold trap and filter (which remove remaining traces of sulfur from the gas) and a sample point,
Fig 5.1 Experimental Apparatus
before being fed to caustic scrubbers that absorb any remaining acid gases. The sample point allows samples of gas to be sent to an SRI 8610 Gas Chromatograph (SRI Instruments, Torrance CA), which is used to detect for CO$_2$, CO, COS, H$_2$S and SO$_2$. This, together with knowledge of the feed rates, allows us to calculate the composition of the gas leaving the reactor.

At the end of each experiment the sulfur formed was collected from the condenser (for experiments with high conversions some sulfur was also precipitated in the reactor inner tube). Some of the sulfur could be run out of the condenser via the tap at the bottom; the remainder was removed by washing with carbon disulfide. The sulfur collected was weighed and used to calculate the conversion. Although not as accurate as the G.C. results (due to losses during the experiment, rinsing etc.), this provided a second measure of conversion independent of the first.

5.2.2 Characterization of Apparatus

![Fig. 5.2 Reactor Dimensions](image)

The physical dimensions of the reactor are given in Fig. 5.2. These dimensions are of
great importance in the modelling of the reactor; each dimension is the average of several measurements (taken at different points of the reactor where possible).

![Diagram of Reactor Temperature Profile](image)

**Fig. 5.3 Reactor Temperature Profile**  
\(T_{\text{set}} = 800 \, ^\circ\text{C}, F = 2F\)

The temperature profile of the reactor was measured for different heater set-points and gas flowrates (using CO₂ instead of reactor feed gas). The profile was found to vary slightly with flowrate, therefore three standard flowrates (denoted \(F_S\), \(0.5F_S\), and \(2F_S\)) were selected and the temperature profile was measured for each. A typical temperature profile for the reactor is shown in Fig. 5.3.

The temperature profile in the inner tube was found by removing the condenser and inserting a thermocouple into the tube. Since heat losses by conduction through the thermocouple wires are negligible, this gives a reasonably accurate measure of the temperature in the inner tube. The temperature in the outer tube was measured by a thermocouple in the reactor.
thermowell. This measurement was less accurate, since the detector was not in direct contact with the gas and the temperature of the thermowell was necessarily higher than that of the gas flowing over it. (The thermowell gains heat by radiation from the furnace, reactor walls, etc. and can only lose heat by conduction along the wires or by convection to the incoming gas, therefore its temperature must be greater than that of the gas). The temperature measured in the thermowell did indeed show this behavior, starting out roughly 30 - 50 °C cooler than the temperature measured in the inner tube, it increased as we approached the center of the furnace until it was of the order of 20 °C hotter than the temperature in the inner tube by the time the maximum in the temperature profile was reached (Fig. 5.4).

We know, however, that the bulk temperature of the gas when it reaches the entrance to the inner tube is the same as the temperature measured at the opening of the inner tube, therefore the difference between the two temperatures must go to zero at the entry to the inner tube. Furthermore the reactor was designed (using experience form Part I) so that the inner tube opening would be at the flattest part of the temperature profile (the maximum temperature). Since the temperature of the gas in the outer tube was obviously not greater than the temperature of the gas in the inner tube the following procedure was used to correct the temperature profile measured in the thermowell. The difference between the thermowell and inner tube temperatures (ΔT) was calculated:

\[ ΔT = T_{\text{inner}} - T_{\text{thermowell}} \]

the data for ΔT > 10 °C were then fitted to the expression
\[ \Delta T = a \left( 1 - \exp(b \cdot x) \right) \]

where \( x \) is the distance from the entry to the inner tube

\( a \) and \( b \) are constants

It can be seen that this expression has the correct form, i.e., \( \Delta T \) tends to zero as \( x \) tends to zero.

Least-squares numerical best-fit was performed using "Sigma-Plot" software (\textregistered Jandel Scientific Corp.). The temperature of the gas in the outer tube was then taken as:

\[
\begin{align*}
T_{\text{gas, outer}} &= T_{\text{thermowell}} & (\Delta T > 10 \, ^\circ C) \\
T_{\text{gas, outer}} &= T_{\text{inner}} - \Delta T & (\Delta T < 10 \, ^\circ C)
\end{align*}
\]

where \( \Delta T \) is calculated using the correlation developed above. A typical set of measured and corrected profiles are shown in Fig 5.4. The dashed line through the squares is the corrected profile for the gas in the outer tube and the solid line through the circles represents the temperatures measured in the inner tube.

Since the profiles measured by either thermocouple are relatively flat in the region near the inner tube entry the error introduced by this approximation is small (\( \pm 3 \, ^\circ C, \text{i.e.,} < 0.3 \% \)). The effect of this error on the model prediction of conversion is discussed in Section 5.4.5.

The effect of radial variations in temperature was investigated by rotating the reactor and repeating the measurements. It was found that the bottom of the furnace is slightly hotter than the top and that the temperature measured in the inner tube could be decreased by roughly 3 \( ^\circ C \) if the inner tube was screened from the bottom of the furnace by the thermowell. In all
experiments the inner tube and thermowell were kept in the same relative positions to minimize the impact of such effects.

Fig. 5.4 Measured and Corrected Temperature Profiles 
\( T_{set} = 850 \, ^\circ C, \, F = F_2 \)

Knowledge of the temperature-distance profile and the gas flowrate allows calculation of the reactor temperature-time profile, \( i.e. \), the temperature history experienced by the gas as it passes through the reactor. We can also calculate the quench rate from the highest temperature attained to any lower temperature. Such calculations were incorporated into the kinetic models described in the next section. A typical temperature-time profile is shown in Fig. 5.5.

5.3 Kinetic Modelling

This section discusses the approach taken towards modelling the experimental apparatus.
Some relatively simple models that were initially used are described in Section 5.3.1. The more complex models that were ultimately found to give the best prediction of the experimental data are described in Section 5.3.2. A short sensitivity analysis of the model behavior under various limiting conditions is also described.

In all of these models the reactor is assumed to be in plug flow. This assumption is discussed in Section 5.4.5.2. The reactor is divided into sections corresponding to the intervals at which the temperature was measured. For each interval the average temperature can be found, and hence, knowing the feed flowrate and pressure, the time the gas spends in the interval may be calculated. In the more advanced models the flowrate is also corrected to allow for the increase in molar flowrate that occurs on reaction. Given the residence time and temperature for each interval we can use a suitable algorithm to find the concentration of each species at the end of the interval. The algorithms used are described below. By treating the intervals as a set of
plug-flow reactors in series we eventually obtain a prediction of the final outlet concentration.

For the simpler models these calculations can be performed using spreadsheet software such as "Quattro" (Borland International, Scotts Valley, CA). For the more complex models it was necessary to use iterative solution methods; a series of FORTRAN programs were therefore written.

5.3.1 Simple Models

The simplest model that can be constructed for $H_2S$ decomposition is one in which the decomposition reaction is assumed to be irreversible and is considered to be the only reaction present:

$$H_2S \rightarrow H_2 + S_2$$

(5.1)

The kinetics of this reaction was discussed by Kaloidas and Papayannakos (1989) and since the reaction is first order we can update the $H_2S$ concentration from one interval to the next using the equation:

$$p_{H_2S,n} = p_{H_2S,n-1} \exp (-k_{1,n} \Delta t_n)$$

(5.2)

where:

- $p_{H_2S,n}$ is the $H_2S$ partial pressure at the end of the $n^{th}$ interval
- $k_{1,n}$ is the first order rate constant for $H_2S$ decomposition, evaluated at the temperature of the $n^{th}$ interval
- $\Delta t_n$ is the residence time in the $n^{th}$ interval
This can be seen to be the equation for a first-order irreversible reaction in a plug-flow reactor with no change in the number of moles (as noted above we can allow for the change in molar flowrate by correcting the interval time). This model is obviously grossly oversimplified, and the first correction we can make is to allow for the reverse of the H₂S decomposition reaction:

\[
H_2 + \frac{1}{2} S_2 \rightarrow H_2S
\]  

(5.3)

In this case the algorithm for updating the H₂S partial pressure is not so simple. The rate of change of the H₂S partial pressure is given by:

\[
\frac{d (p_{H_2S})}{dt} = -k_1 p_{H_2S} + k_2 p_{H_2} \frac{P_{S_2}^{0.5}}{p_{S_2}}
\]  

(5.4)

if the residence time in the interval is short enough, we can use the approximate linear algorithm:

\[
p_{H_2S, n} = p_{H_2S, n-1} + (-k_{1,n} p_{H_2S,n-1} + k_{2,n} p_{H_2,n-1} p_{S_2,n-1}^{0.5}) \Delta t_n
\]  

(5.5)

This is, however, somewhat inaccurate, and is prone to computational difficulties due to overstepping. A better algorithm can be developed if we use suitable average values for the quantities in the second term on the right hand side of equation (5.4) and integrate. This gives the "partially integrated" algorithm:

\[
p_{H_2S, n} = p_{H_2S, n-1} \exp(-k_{1,n} \Delta t_n) + \frac{k_{2,n} p_{H_2,n-1} p_{S_2,n-1}^{0.5}}{k_{1,n}} (1-\exp(-k_{1,n} \Delta t_n))
\]  

(5.6)

The first term in this equation allows for decomposition with no reverse reaction and the second term is a correction to allow for the reverse reaction. It can be seen that in the limit as \(n\) and \(\Delta t_n\) tend to infinity at a constant temperature, the first term goes to zero while the second term approaches the equilibrium concentration.
The concentrations of H$_2$ and S$_2$ for each interval are easily found from S and H mass balances once the concentration of H$_2$S is determined, and may then be used for the calculation of the next interval. The assumption that average values may be used for the parameters in the second term in equation (5.4) is good, as the concentrations of H$_2$ and S$_2$ and the temperature do not vary much from stage to stage over the stages where most of the reaction occurs.

It is possible to develop a fully integrated algorithm for this model, using a modified Euler or Runge-Kutta scheme to solve equation (5.4). This considerably increases the calculational complexity (especially for the more complex models where the concentrations of S$_2$ and H$_2$ depend on the equilibria of a number of reactions) with little benefit in terms of increased accuracy. This was carried out as part of the error analysis and is discussed in Section 5.4.5.3.

This simple model gave good performance in predicting the conversion of an experiment made with H$_2$S in nitrogen, and was also successfully adapted to simulate the experiments of Kaloidas and Papayannakos. In our system, however, the equilibrium of H$_2$S decomposition is significantly shifted by the water-gas-shift reaction. If thermal decomposition of H$_2$S is the rate-limiting reaction (a reasonable assumption, since the water-gas-shift reaction is known to be very fast at these temperatures) then the model developed above is easily extended:

i) $p_{H_2S}$ for each stage is found using the algorithm of equation (5.6).

ii) Having found the number of moles of H$_2$ formed from the H$_2$S decomposition and knowing the number of moles of CO$_2$ fed, the concentrations of CO$_2$, CO, H$_2$ and H$_2$O are found by solving the water-gas-shift reaction equilibrium equation and three mass balances (C, H and O).
iii) The concentration of elemental sulfur is found from a sulfur mass balance.

Since the water-gas-shift reaction equilibrium equation is linear, these equations may be solved analytically. This gives the basic model for our system, which, though simple, is quite good at predicting the $\text{H}_2\text{S}$ conversion. We are, however, unable to account for the presence of COS and $\text{SO}_2$ using this model.

5.3.2 Advanced Models

If we assume that the reactions that form COS and $\text{SO}_2$:

$$\text{CO} + \frac{1}{2} \text{S}_2 = \text{COS}$$

$$2 \text{H}_2\text{O} + \frac{3}{2} \text{S}_2 = 2 \text{H}_2\text{S} + \text{SO}_2$$

are at equilibrium, then we can include them in the same manner as the water-gas-shift reaction. The calculational work is made a little more complex owing to the non-linearity of the equilibrium equations for these reactions; however, the solution converges rapidly if a suitable iterative method is used. FORTRAN programs were written to perform these calculations and to calculate the quench rate from the temperature profile data.

In practice it was found that COS was not formed at equilibrium concentrations, and it was necessary to include information on the kinetics of COS formation. Reaction (3.1) is sufficient to account for COS formation if the COS is present at equilibrium levels, but is not necessarily the main reaction mechanism for COS formation. The equations that were used to model non-equilibrium formation of COS are discussed (in the light of experimental results) in

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Section 5.4.3. The final version of the model therefore assumed H$_2$S decomposition to be the rate-limiting step, assumed the water-gas-shift reaction and Claus reaction to be at equilibrium, and allowed for non-equilibrium formation of COS. The computer code for this model is given in Appendix II.A, together with a sample printout of the results. The success of this model in predicting the experimental results is discussed in Section 5.4.

5.3.3 Test of Model Limits

Before discussing the experimental results it is worth briefly examining the behavior of the model under certain limiting conditions. As noted above, the advanced models are all based on the assumptions that H$_2$S decomposition is the rate-limiting step and that the water-gas-shift reaction is always at equilibrium. Because COS and SO$_2$ are formed at very low concentrations, the simple model that allows for the water-gas-shift reaction incorporates the key features of the advanced models and gives reasonably good prediction of H$_2$S conversion. This model was therefore used, together with the two simpler models, to examine the model behavior in certain important limits.

The first limit is the trivial case where the initial concentration of CO$_2$ is zero. In this case the advanced models should predict the same conversion as the model that considers only the forward and reverse reactions of H$_2$S thermal decomposition. This is indeed what is found.

A more interesting limit is when the feed H$_2$S concentration approaches zero. In this case, for low to moderate conversions the model predicts the same results as are obtained if we allow for only irreversible H$_2$S decomposition. This is because the concentration of hydrogen
is lowered by the water-gas-shift reaction to such an extent that back-reaction is negligible. The overall reaction thus behaves approximately as a first-order irreversible reaction. This approximation in fact holds over quite a wide range: for feed concentrations less than 25 % H$_2$S and to conversions approaching 60 % of equilibrium. Obviously as the conversion approaches its equilibrium value this approximation can no longer hold true; however, most of the experiments were conducted under conditions where the approximation is a good one. For a first-order irreversible reaction in a plug-flow reactor the conversion is independent of the feed concentration, which provides a useful confirmatory test of the validity of the model for describing the experimental data.

5.4 Results

5.4.1 Experimental Results

The most important goal of the kinetic analysis is to develop a model that predicts the kinetic behavior of the H$_2$S/CO$_2$ system at high temperature. The results from a series of experiments, run under different conditions of temperature, flowrate and feed concentration, are shown in Table 5.1. The error in these results is discussed in Section 5.4.5; however most of the points were repeated and some indication of the error can be seen by comparison of repeat points. Experiments labelled with a "Q" correspond to high quench-rate experiments. These experiments are discussed in Section 5.4.2.
### Table 5.1 Experimental Conditions and Results

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>Flowrate (F/F_0)</th>
<th>Feed Concentration (% H₂S in CO₂)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE12</td>
<td>950</td>
<td>1</td>
<td>5</td>
<td>34.4</td>
</tr>
<tr>
<td>SE16</td>
<td>950</td>
<td>1</td>
<td>5</td>
<td>35.2</td>
</tr>
<tr>
<td>SE5</td>
<td>950</td>
<td>1</td>
<td>10</td>
<td>34.0</td>
</tr>
<tr>
<td>SE13</td>
<td>950</td>
<td>1</td>
<td>10</td>
<td>34.4</td>
</tr>
<tr>
<td>SE9</td>
<td>950</td>
<td>0.5</td>
<td>5</td>
<td>54.3</td>
</tr>
<tr>
<td>SE15 (Q)</td>
<td>950</td>
<td>0.5</td>
<td>5</td>
<td>53.1</td>
</tr>
<tr>
<td>SE10</td>
<td>950</td>
<td>0.5</td>
<td>10</td>
<td>43.8</td>
</tr>
<tr>
<td>SE11 (Q)</td>
<td>950</td>
<td>0.5</td>
<td>10</td>
<td>44.3</td>
</tr>
<tr>
<td>SE7</td>
<td>900</td>
<td>1</td>
<td>5</td>
<td>21.5</td>
</tr>
<tr>
<td>SE6</td>
<td>900</td>
<td>1</td>
<td>10</td>
<td>20.0</td>
</tr>
<tr>
<td>SE19</td>
<td>900</td>
<td>1</td>
<td>10</td>
<td>22.2</td>
</tr>
<tr>
<td>SE17</td>
<td>900</td>
<td>0.5</td>
<td>5</td>
<td>36.1</td>
</tr>
</tbody>
</table>

Comparing the experiments at high flowrate (where we are furthest from equilibrium conversion), we can see that the conversion obtained with a feed of 10% H₂S in CO₂ is roughly the same as that obtained with 5% H₂S in CO₂. This shows that we are obtaining the low-H₂S concentration limit first-order-reaction behavior described in the previous section and satisfies the
first criterion for applicability of the model. The experiments run at high temperature and lower flowrates do not satisfy this condition as equilibrium effects are more important for these runs. The conversions calculated from the sulfur collected in the condenser were always slightly less than those found from the gas chromatograph measurements -- this is to be expected as some of the H₂S was converted to COS and some of the sulfur was also lost in the filter, washing and weighing, etc. Experimental errors are discussed in Section 5.4.5.1.

In comparing the results with the model predictions we have a number of options:

i) We could treat the model as being fixed (i.e., containing no adjustable parameters) and examine the results predicted by the model using only the values of the rate constants given in the literature.

ii) We could relax the above condition and allow experimentally-determined parameters from the literature to vary within fixed limits (e.g., ±5%) -- this allows for experimental error in the reported values and in our own experiments.

iii) We could allow the important variables of the model (the activation energy and pre-exponential constant of the H₂S-decomposition rate constant) to vary fully and adjust these parameters to obtain a best fit of the model to the data.

Method (i) is somewhat inflexible and also rather unrealistic, since it assigns absolute values to parameters that necessarily contain an experimental error. Method (iii) is also unsatisfactory, as it involves the complete rejection of the previous work. We therefore seek to establish how well the model can predict the data given a slight variation in the reported kinetic parameters.
To assess how well the model predictions fit the data we use a ratio measurement of the error between the two. If $X_e$ is the conversion found experimentally, $X_m$ is that predicted by the model, and we have $N$ data points, then:

i) defining $r = X_m/X_e$:

$$e_r = \sqrt{\frac{\sum (r-1)^2}{N}}$$

gives a measure of the root-mean-square ratio error between the model and the data.

We can note that $e_r$ tends to magnify errors at low conversions; however these should be the most accurate experiments since the $H_2S$ concentration is highest. From the repeat points and experimental measurement of error (see Section 5.4.5), $e_r$ should be less than 11 %.

It was found experimentally that carbonyl sulfide was formed at rather low concentrations (always < 0.52 mole %). The mechanism of COS formation therefore had only slight impact on the $H_2S$ conversion predicted by the model. It was, however, important that the model be capable of predicting the COS behavior if the process quench conditions were to be adequately described. Before discussing the model predictions of $H_2S$ conversion we therefore digress slightly to examine the formation of COS.
5.4.2 The Effect of Quenching

From the analysis of Section 4.5, it was expected that the reactor quench rate (i.e., the rate at which the gas is cooled) would strongly affect the level of COS formation. To investigate this effect two experiments were run with a glass rod inserted inside the reactor inner tube. This decreased the flow area of the inner tube and hence increased the gas velocity by a factor of roughly 2.6. It was not possible to measure the exact temperature profile in the inner tube under these conditions; however, it is reasonable to assume, for modelling purposes, that the temperature profile is unaltered, since the temperature profile was found to be mainly a function of distance along the reactor rather than flowrate. Experiments performed with a higher quench rate are labelled with a "Q" in Table 5.1.

The outlet compositions found for the high-quench experiments and experiments run under the same conditions with lower quench rates are shown in Table 5.2. The table shows that the outlet compositions for the high-quench experiments are practically identical to those for the corresponding low-quench experiments, i.e., the increase in quench rate gives no added conversion. (The apparent slight increase in COS formation for both quenched experiments is negligible compared with the error in the COS measurements, but see Section 5.4.3). This confirms that the quench rates used in the bulk of the experiments (\( > 1000 \text{ °C/s} \)) were high enough to quench completely both the \( \text{H}_2\text{S} \) decomposition back-reaction and the COS-forming reactions. These results are also useful in analyzing the formation of COS, as described in the next section.
Table 5.2 Outlet Compositions Measured for Quenched and Non-Quenched Experiments

<table>
<thead>
<tr>
<th>Expmt</th>
<th>Quench Rate (K/s)</th>
<th>CO₂</th>
<th>H₂S</th>
<th>CO</th>
<th>H₂ and H₂O</th>
<th>COS</th>
<th>S₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE9</td>
<td>990</td>
<td>0.928</td>
<td>0.0218</td>
<td>0.00973</td>
<td>0.0260</td>
<td>0.00357</td>
<td>0.0112</td>
</tr>
<tr>
<td>SE15 (Q)</td>
<td>2560</td>
<td>0.930</td>
<td>0.0218</td>
<td>0.00884</td>
<td>0.0248</td>
<td>0.00415</td>
<td>0.0103</td>
</tr>
<tr>
<td>SE10</td>
<td>1040</td>
<td>0.873</td>
<td>0.0524</td>
<td>0.0108</td>
<td>0.0408</td>
<td>0.00479</td>
<td>0.0180</td>
</tr>
<tr>
<td>SE11 (Q)</td>
<td>2700</td>
<td>0.872</td>
<td>0.0519</td>
<td>0.0113</td>
<td>0.0412</td>
<td>0.00516</td>
<td>0.0180</td>
</tr>
</tbody>
</table>

5.4.3 Carbonyl Sulfide Formation

A secondary objective of the kinetic analysis is to develop an understanding of the formation of COS in the reactor. In particular, we wish to know what quench rates must be used if excessive COS formation is to be prevented when the gas is cooled.

Table 5.3 shows the outlet COS concentrations measured for each experiment. The random error in the data is quite high, mainly due to the insensitivity of the gas chromatograph thermal-conductivity detector to COS at low concentrations. The apparent equilibrium temperature is the temperature at which the concentration of COS in equilibrium with the reaction-gas mixture would be the same as the outlet COS concentration. The quench rate was taken as the time taken to cool from the highest temperature experienced by the gas to 600 °C.
Table 5.3 Concentrations of COS Formed and Apparent Equilibrium Temperatures

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Outlet COS mole fraction x 10^3</th>
<th>Experimental Error (%)</th>
<th>Apparent Equil. Temperature (°C)</th>
<th>Quench Rate (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE12</td>
<td>4.05</td>
<td>36</td>
<td>725</td>
<td>1843</td>
</tr>
<tr>
<td>SE16</td>
<td>4.43</td>
<td>36</td>
<td>715</td>
<td>1822</td>
</tr>
<tr>
<td>SE5</td>
<td>2.82</td>
<td>13</td>
<td>892</td>
<td>1837</td>
</tr>
<tr>
<td>SE13</td>
<td>3.99</td>
<td>10</td>
<td>840</td>
<td>1837</td>
</tr>
<tr>
<td>SE9</td>
<td>3.57</td>
<td>14</td>
<td>840</td>
<td>988</td>
</tr>
<tr>
<td>SE15</td>
<td>4.15</td>
<td>18</td>
<td>820</td>
<td>2560</td>
</tr>
<tr>
<td>SE10</td>
<td>4.79</td>
<td>7.9</td>
<td>910</td>
<td>1040</td>
</tr>
<tr>
<td>SE11</td>
<td>5.16</td>
<td>10</td>
<td>905</td>
<td>2700</td>
</tr>
<tr>
<td>SE7</td>
<td>3.86</td>
<td>37</td>
<td>897</td>
<td>1701</td>
</tr>
<tr>
<td>SE6</td>
<td>3.36</td>
<td>31</td>
<td>765</td>
<td>1707</td>
</tr>
<tr>
<td>SE19</td>
<td>2.99</td>
<td>37</td>
<td>780</td>
<td>1704</td>
</tr>
<tr>
<td>SE17</td>
<td>3.32</td>
<td>27</td>
<td>750</td>
<td>816</td>
</tr>
</tbody>
</table>

The first thing that is apparent is that the level of COS formation is not as high as would be found if COS were in equilibrium with the gas at the outlet temperature, therefore the COS-
forming reactions are clearly not permanently at equilibrium. The COS concentration is, however, somewhat greater then would be expected if CO and S₂ were in equilibrium with COS at the highest temperature of each experiment.

Secondly, we can see that COS formation is not much affected by quench rate. In particular, the "high-quench" experiments SE11 and SE15 show only small differences from the low-quench analogues SE10 and SE9. This suggests that the COS-forming reactions are not occurring in the exit tube. In fact, SE11 and SE15 have higher COS concentrations (admittedly the difference is small compared to experimental error, but the trend is nonetheless there), which tends to confirm this thesis. It appears, therefore, that COS may actually be back-reacting in the exit tube. Carbonyl sulfide formation must therefore be occurring in the lower-temperature regions of the entry tube.

There are two probable major routes for COS formation. Thermal association-dissociation:

\[ CO + \frac{1}{2} S_2 = COS \quad (3.1) \]

and the reaction:

\[ H_2S + CO_2 = COS + H_2O \quad (3.9) \]

This reaction is clearly a close relative of the water-gas-shift reaction, and for convenience we shall take the liberty of naming it the "sulfur-gas-shift reaction". Since at low temperatures in the entry tube the thermal decomposition of H₂S has not taken place to any great extent, reaction (3.9) must clearly account for the bulk of the COS formation. Reaction (3.1) may be important as a COS dissociation mechanism, but is unlikely to contribute much to COS formation until we
reach higher temperatures and elemental sulfur concentrations, in which region the COS is in any case present at greater-than-equilibrium levels with respect to CO and \( S_2 \), and therefore undergoing net dissociation. We can thus neglect the reaction between elemental sulfur and carbon monoxide entirely, though we must still consider the thermal decomposition of COS.

The kinetics of reaction (3.1) were studied by Schecker and Wagner (1969) in the temperature range 1500 K to 3100 K. They found the rate to be second order and given by:

\[
\frac{d C_{\text{cos}}}{dt} = -10^{14.2} \exp\left(\frac{-61000}{RT}\right) C_{\text{total}} C_{\text{cos}}
\]  

(5.7)

where:  
\( C_{\text{cos}} \) is the concentration of COS (moles/cm\(^3\))  
\( C_{\text{total}} \) is the total concentration (i.e., COS + inerts) (moles/cm\(^3\))

and  \( R \) is the ideal gas constant (cal/mole K)

If the total concentration does not change significantly across the interval of interest, we can approximate this as a first-order reaction with rate constant:

\[
k_{SW} = 10^{14.2} C_{\text{total}} \exp\left(\frac{-61000}{RT}\right)
\]  

(5.8)

The results of Schecker and Wagner (1969) were subsequently confirmed by Chenery et al. (1983). Dokiya et al. (1978) looked at the formation of COS from CO and elemental sulfur. They did not report a kinetic expression; however, their data showed the conversion attained to be strongly influenced by flowrate, indicating that this reaction can be quenched. The kinetic expression given above was incorporated into the model to allow for COS thermal decomposition.

For the sulfur-gas shift reaction (3.9) less information is available. The equilibrium constant, \( K_{sw} \), for this reaction is fitted over the temperature range 450 °C to 1100 °C by the
expression:

\[ K_{eq} = 0.4347 \exp \left( \frac{-2917}{T} \right) \]

The endothermic nature of the reaction and weak temperature-dependance of the equilibrium constant give further evidence to support the comparison with the water-gas-shift reaction. We might also expect this reaction to have equally rapid kinetics. Unfortunately most of the research on this reaction has been related to the development of catalytic processes for COS hydrolysis prior to gas scrubbing (see Section 7.1) and was therefore carried out at low temperatures, typically below 300 °C. Although there is much discussion of the competitive absorption of different species and the nature of the catalytic sites, only one paper was found to give an activation energy for the reaction. George (1974a) found the activation energy to be 12 kcal/mole for COS hydrolysis on cobalt molybdite at 230 °C. The Arrhenius plot he presented showed, however, that this energy was based on a line drawn through only four data points. The line fitted the three points at lower temperatures reasonably well, but substantially underpredicted the point at the highest temperature. There is therefore good reason to believe that George may have overestimated the activation energy, especially when we consider that we are operating several hundred degrees above the temperatures used in his study. In any case, the value 12 kcal/mole is low for an activation energy, confirming the similarity between this and the water-gas-shift reaction and giving us further reason to believe this to be the COS-forming step.

The reaction model was adapted to include the sulfur-gas-shift reaction and COS thermal decomposition. Both the forward and the reverse reactions of the sulfur-gas-shift reaction were accounted for:
\[
\frac{d C_{\text{COS}}}{dt} = -k_{\text{SW}} C_{\text{COS}} - k_{\text{sgs.r}} C_{\text{H}_2\text{O}} C_{\text{COS}} + k_{\text{sgs.f}} C_{\text{H}_2\text{S}} C_{\text{CO}_2} \tag{5.9}
\]

where:
- \( k_{\text{sgs.r}} \) and \( k_{\text{sgs.f}} \) are the forward and reverse rate constants for the sulfur-gas-shift reaction.
- \( C_i \) is the concentration of species \( i \).
- \( k_{\text{SW}} \) is the Schecker and Wagner rate constant for COS thermal decomposition, given above.

We can assume for simplicity that the concentrations do not change much from one interval to the next (this assumption is discussed in Section 5.4.5.3) in which case we can rearrange to give a pseudo-first-order equation with a constant rate of back-reaction:

\[
\frac{d p_{\text{COS}}}{dt} = -(k_{\text{SW}} + k_{\text{sgs.r}} p_{\text{H}_2\text{O}} \frac{C_{\text{total}}}{P}) p_{\text{COS}} + k_{\text{sgs.f}} \frac{C_{\text{total}}}{P} p_{\text{H}_2\text{S}} p_{\text{CO}_2} \tag{5.10}
\]

where:
- \( p_i \) is the partial pressure of species \( i \).
- \( P \) is the total pressure.

This equation is of the same mathematical form as that used to develop the algorithm for \( \text{H}_2\text{S} \) decomposition (equation 5.4), and may be treated in the same way. Clearly \( p_{\text{H}_2\text{S}} \) and \( p_{\text{H}_2\text{O}} \) are subject to much greater variation across each interval than \( p_{\text{COS}} \); however, assuming them to be constant considerably reduces the mathematical complexity of the model and improves its robustness. The sensitivity of the model predictions to this assumption is discussed in Section 5.4.5.3. The algorithm for updating the \( \text{H}_2\text{S} \) composition must also be altered slightly to account for the sulfur-gas shift reaction. The reaction constant \( k_{\text{sgs.r}} \) can be calculated from the equilibrium constant of the sulfur-gas-shift reaction if \( k_{\text{sgs.r}} \) is known (from George, 1974a, or otherwise).

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The final version of the model therefore considers the kinetics of \( \text{H}_2\text{S} \) and \( \text{COS} \) thermal decomposition and the sulfur-gas-shift reaction and assumes the water-gas-shift reaction and Claus reaction to be at equilibrium at all temperatures. The rate constants for \( \text{H}_2\text{S} \) decomposition and the sulfur-gas-shift reaction can both be extrapolated from values outside the temperature range of interest that are reported in the literature. We can also allow constrained variation of these parameters.

5.4.4 Reaction Model Predictions

Table 5.4 shows the experimental results and model predictions obtained using the published values of the activation energies (Kaloidas and Papayannakos, 1989, for \( \text{H}_2\text{S} \) decomposition, and George, 1974, for sulfur-gas-shift). The pre-exponential constants used were \( 6.0 \times 10^6 \text{ s}^{-1} \) for \( \text{H}_2\text{S} \) decomposition and \( 2.4 \times 10^6 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \) for sulfur-gas-shift. The rms ratio error in the conversion is found to be 12.2 %, and the error between the predicted and observed \( \text{COS} \) concentrations is roughly the same as the error in the \( \text{COS} \) measurements.

The error between the model and the data can thus be seen to be almost the same as the experimental error; however, we can also observe that most of the error is due to the two experiments labelled SE10 and SE11 (both of which were run at 950 \( ^\circ \text{C} \), 10 % \( \text{H}_2\text{S} \) in \( \text{CO}_2 \), 0.5 \( \text{F}_2 \)). If we calculate the error in the absence of these points we obtain an rms error \( e_r^* = 7.0 \% \), which is well within experimental error.

It is hard to justify dropping or repeating these two points, since they are repeats of the same experiment. The experiments were run consecutively, however, and therefore it is possible
Table 5.4 Comparison of Experiments and Model Predictions

Using Published Activation Energies

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Conversion (%)</th>
<th>COS outlet mole fraction (x 10^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>Model</td>
</tr>
<tr>
<td>SE12</td>
<td>34.4</td>
<td>35.1</td>
</tr>
<tr>
<td>SE16</td>
<td>35.2</td>
<td>35.4</td>
</tr>
<tr>
<td>SE5</td>
<td>34.0</td>
<td>34.3</td>
</tr>
<tr>
<td>SE13</td>
<td>34.4</td>
<td>34.3</td>
</tr>
<tr>
<td>SE9</td>
<td>54.3</td>
<td>58.6</td>
</tr>
<tr>
<td>SE15</td>
<td>53.1</td>
<td>58.8</td>
</tr>
<tr>
<td>SE10</td>
<td>43.8</td>
<td>55.2</td>
</tr>
<tr>
<td>SE11</td>
<td>44.3</td>
<td>55.2</td>
</tr>
<tr>
<td>SE7</td>
<td>21.5</td>
<td>19.6</td>
</tr>
<tr>
<td>SE6</td>
<td>20.0</td>
<td>19.0</td>
</tr>
<tr>
<td>SE19</td>
<td>22.2</td>
<td>19.0</td>
</tr>
<tr>
<td>SE17</td>
<td>36.1</td>
<td>36.9</td>
</tr>
<tr>
<td>rms ratio error, $e_r$</td>
<td>0.122</td>
<td>0.345</td>
</tr>
<tr>
<td>$e_r^*$</td>
<td>0.070</td>
<td>0.230</td>
</tr>
</tbody>
</table>
that both might contain the same systematic error. Repeating the experiment further might remove this problem and give experimental data that agree better with the model; however, this would be choosing the data that best fit the model and is therefore rejected as bad experimental practice.

We can improve the model predictions somewhat if we allow constrained variation of the activation energy of H\textsubscript{2}S decomposition. This is not unreasonable, since the experiments of Kaloidas and Papayannakos (1989) were performed outside our temperature range and must necessarily contain some experimental error; furthermore, Fukuda et al. (1978) found an activation energy of 42 kcal/mole, which is somewhat lower than the 43.7 kcal/mole found by Kaloidas and Papayannakos. If we use an activation energy 5% lower than that of Kaloidas and Papayannakos (41.5 kcal/mole) we obtain the data given in Table 5.5. The pre-exponential constant in this case is $2.4 \times 10^6$ s\textsuperscript{-1}. The rms ratio error is reduced to 11.3% (6.3% if SE10 and SE11 are excluded), which is of the order of experimental error (see Section 5.4.5). The COS concentration predictions are not affected by this change, as COS formation occurs in the low temperature region of the entry tube, i.e., before the H\textsubscript{2}S conversion is significant.

The difference between the predicted COS concentrations and those observed experimentally is high; however it must be remembered that the experimental error was also high, for reasons discussed above. If we plot the predicted COS concentration versus temperature (Figure 5.6) we can see that the model is also giving the right qualitative behavior. Figure 5.6 also shows the concentration of COS that would be found if COS and S\textsubscript{2} were in equilibrium and the concentration that would be present if COS were only formed from CO and S\textsubscript{2} as predicted by the kinetics of Schecker and Wagner (1969). Clearly neither of these gives an adequate
Table 5.5 Comparison of Experiments and Model Predictions Allowing Constrained Variation of the H₂S Decomposition Activation Energy

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Conversion (%)</th>
<th>COS outlet mole fraction (x 10²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>Model</td>
</tr>
<tr>
<td>SE12</td>
<td>34.4</td>
<td>34.6</td>
</tr>
<tr>
<td>SE16</td>
<td>35.2</td>
<td>34.8</td>
</tr>
<tr>
<td>SE5</td>
<td>34.0</td>
<td>33.8</td>
</tr>
<tr>
<td>SE13</td>
<td>34.4</td>
<td>33.8</td>
</tr>
<tr>
<td>SE9</td>
<td>54.3</td>
<td>57.9</td>
</tr>
<tr>
<td>SE15</td>
<td>53.1</td>
<td>58.1</td>
</tr>
<tr>
<td>SE10</td>
<td>43.8</td>
<td>54.6</td>
</tr>
<tr>
<td>SE11</td>
<td>44.3</td>
<td>54.6</td>
</tr>
<tr>
<td>SE7</td>
<td>21.5</td>
<td>19.8</td>
</tr>
<tr>
<td>SE6</td>
<td>20.0</td>
<td>19.2</td>
</tr>
<tr>
<td>SE19</td>
<td>22.2</td>
<td>19.3</td>
</tr>
<tr>
<td>SE17</td>
<td>.36.1</td>
<td>.37.3</td>
</tr>
<tr>
<td></td>
<td>rms ratio error e_r</td>
<td></td>
</tr>
<tr>
<td></td>
<td>e_r*</td>
<td></td>
</tr>
</tbody>
</table>
description of the results.

We can further improve the prediction of COS concentration by allowing variation of the activation energy of the sulfur-gas-shift reaction. Again this is not unreasonable, due to the somewhat dubious nature of the graph presented by George (1974a). We should also note that although George was studying the reaction in the presence of catalyst, his experiments were carried out 600 °C below ours, so extrapolation may not be justified. If the activation energy for COS hydrolysis is taken as 8 kcal/mole we obtain the results of Table 5.6, which predict both conversion and COS formation to within experimental error. Obviously the model predictions could be further improved by including more reactions in the model, however this merely increases the number of adjustable parameters available and is therefore rejected. Before drawing any conclusions from this analysis it is necessary to discuss the errors involved.

Fig. 5.6 Variation of COS Concentration with Reactor Temperature (Conditions of SE9)
Table 5.6 Comparison of Experiments and Model Predictions
Allowing Variation of Both Activation Energies

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Conversion (%)</th>
<th>COS outlet mole fraction (x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment</td>
<td>Model</td>
</tr>
<tr>
<td>SE12</td>
<td>34.4</td>
<td>34.2</td>
</tr>
<tr>
<td>SE16</td>
<td>35.2</td>
<td>34.5</td>
</tr>
<tr>
<td>SE5</td>
<td>34.0</td>
<td>33.5</td>
</tr>
<tr>
<td>SE13</td>
<td>34.4</td>
<td>33.5</td>
</tr>
<tr>
<td>SE9</td>
<td>54.3</td>
<td>57.5</td>
</tr>
<tr>
<td>SE15</td>
<td>53.1</td>
<td>57.7</td>
</tr>
<tr>
<td>SE10</td>
<td>43.8</td>
<td>54.3</td>
</tr>
<tr>
<td>SE11</td>
<td>44.3</td>
<td>54.3</td>
</tr>
<tr>
<td>SE7</td>
<td>21.5</td>
<td>20</td>
</tr>
<tr>
<td>SE6</td>
<td>20.0</td>
<td>19.2</td>
</tr>
<tr>
<td>SE19</td>
<td>22.2</td>
<td>19.3</td>
</tr>
<tr>
<td>SE17</td>
<td>36.1</td>
<td>37.4</td>
</tr>
</tbody>
</table>

rms ratio error $e_r$ | 0.110 | 0.309

$e_{r,*}$ | 0.0611
5.4.5 Sources of Error

The discussion that follows describes the sources and relative importance of errors in the preceding analysis. There are three main types of error:

i) experimental errors -- arising from measurement accuracy or fluctuation of experimental variables

ii) interpretational errors -- arising from assumptions used in constructing the model

iii) mathematical errors -- due to the mathematical formulation of the model

Mathematical details of the error estimations are given in Appendix II.B. In all cases the error is assessed by examining the experiment whose results are likely to be most sensitive to the error in question. Although this approach involves using different experiments in each case, it enables us to assess the greatest value of the error.

5.4.5.1 Experimental Error

Total Error

The total error is an assessment of the cumulative effect of all other experimental errors, and can be inferred simply by comparing the results of repeated experiments run under the same conditions. The majority of the experiments were repeated, so we can find both average and worst-case total errors in the H₂S conversion. The average error is the error between each of the pair of points and the average of the pair. Over all pairs this gives a combined average of 1.8 %. The worst-case total error is the difference between two points divided by the lower of the
two points. The greatest value of this error is 11 % (SE6 and SE19).

Flowmeter Error

The measurement error from the flowmeters affects the total flowrate, the feed concentration and the experimental conversion calculated from the G.C. results. We can investigate the flowrate and concentration errors using the model and see how the model predictions are affected. The error in total flowrate is < 1.2 %, which gives a 1.1 % maximum change in predicted conversion. The error in concentration is 1.8 %, which gives a negligible error in predicted conversion (< 0.3 %), but an error of 1.7 % in the predicted COS concentration. This is because COS formation occurs at lower temperatures and is therefore more susceptible to small variations in feed concentration than is the overall conversion.

Gas Chromatograph Error

The error in the experimental conversions calculated from the G.C. results is less than 1.9 %. Most of this error is due to the error in the flowmeter measurements, as the G.C. data analysis methods were chosen so as to minimize error (see Appendix II.B). The conversions were calculated from the average of ten G.C. readings taken over two hours once a steady state had been reached in the reactor.

Temperature Error

The error in the temperatures measured was ± 3 °C. The impact of this error can be
tested using the model, by creating temperature profiles in which every temperature is increased or decreased by 3°C. In the worst case this gives an error in model conversion of 3.6 %, though the COS concentration is almost unaffected (error less than 0.29 %).

There is also a small error in the model arising from the measurements of the reactor dimensions. This is estimated to be less than 0.9 %.

5.4.5.2 Interpretational Error

Temperature Profile Calculation

The temperature of the gas in the outer tube could not be measured directly and therefore was approximated using the procedure described in Section 5.2.2. This creates an additional error in the outer tube temperature; however, the temperature at the entry of the inner tube is unaffected by this error and since the gas temperatures in the inner and outer tubes must be equal at this point the outer tube temperature is also unaffected. The exact form of the correlation used therefore makes little difference to the conversion predicted, and the error from this assumption is small compared to the error arising from the temperature measurements.

Reactor Flow

The undoubted greatest source of error in the model is also, unfortunately, the hardest to quantify. The model assumes the reactor to consist of two plug-flow reactors in series, each with a different residence time, corresponding to the inner and outer flow volumes. In practice
the Reynolds numbers used experimentally were 2 or 4 for the outer tube and 48 or 96 for the inner tube, so the flow was laminar in all cases. For a first-order isothermal reaction the conversion in a laminar-flow tubular reactor is somewhat less than that in a plug-flow reactor, mainly due to bypassing by material that flows through the reactor at velocities faster than the average velocity (for laminar flow in a tube, the center-line velocity is twice the average velocity). If the velocity profile is known (e.g., for a simple tube) the conversion can be found mathematically (this involves use of the exponential integral function for a first-order isothermal reaction). In our case, however, the outer tube contains two non-concentric, non-parallel smaller tubes (the inner tube and thermowell) and has a marked longitudinal (and possibly also a slight radial) temperature gradient, all of which make evaluation of the velocity profile a complex computational fluid dynamics problem. There is also a possibility that some mixing may occur in the end space between the inner tube entry and the quartz wool packing (Figure 5.2). This space is small, and the streamline flow should reduce mixing, but the possibility cannot be ruled out. Exact characterization of the laminar-flow reactor is therefore difficult and the plug-flow assumption was thus justified, but this undoubtedly imposes a large error on the model predictions. Experiments that were run with the outer tube entirely packed with quartz wool (as preparation for the catalysis experiments described in Section 5.5) gave somewhat higher conversions than experiments performed in the absence of this packing. It was not clear, however, as to whether the quartz wool was promoting radial mixing and thus bringing the reactor closer to plug flow or whether channeling effects (the quartz wool could not be distributed evenly) were causing changes in the temperature profile experienced by the gas.

To guarantee that the reactor is in plug flow it is necessary to either use a much larger reactor and flowrate, or else to make use of a packing that is well characterized so that the
temperature and flow profiles can be found reliably. This should be borne in mind when designing a reactor for evaluating the processing capabilities of a supported catalyst, as discussed in Section 5.5.3.

5.4.5.3 Mathematical Error

Interval Length

The interval lengths used for the calculations were based on the intervals at which the temperature profile had been measured. If we develop a suitable interpolation formula through these points we can investigate the effect of interval length by doubling the number of intervals. This gives a worst-case error of 1.5 % in the COS concentration and 0.7 % in the conversion. Although not negligible, these errors are small compared with other errors described above, and using the longer intervals permits exclusive use of measured temperature data, i.e., obviates interpolation for the temperature profiles.

Effect of Algorithm Integration Procedure

The "partially integrated" algorithms used to update the H₂S and COS concentrations from one interval to the next assumed average values of all the other species equal to their values at the start of the interval. (The temperature was assumed to be the average temperature for the interval, based on the measured temperature profiles). A more lengthy, but more accurate, procedure is to use a numerical integration method (e.g. Modified Euler, Runge-Kutta, etc.) to calculate the concentration changes. This was tested by adapting the model to use a Modified
Euler procedure. For the most sensitive experiment the error in the H\textsubscript{2}S conversion predicted was 0.17 \%, which is insignificant compared to the errors discussed above.

5.4.6 Discussion

The goal of this study was to develop an understanding of the kinetics that could be used to design a reactor for the Zero-Emissions Sulfur Process. For this purpose the model developed above is adequate, since it describes both H\textsubscript{2}S conversion and the formation of the main reaction byproduct, COS. On a fundamental level, however, the model is somewhat less satisfactory.

At the high temperatures in question it is not reasonable to suppose that the net rate of reaction is affected only by the collisions of molecular species. In practice there are likely to be many short-lived free radical species present at low concentrations (for example, H\textsuperscript{*}, HS\textsuperscript{*}, S\textsuperscript{*}, OH\textsuperscript{*}, SO\textsuperscript{*}, etc.) which probably play an integral part in the reaction mechanism(s) via a series of initiation, chain propagation and termination reactions, much the same as is found in the analysis of combustion systems. The presence of these species was referred to by Kaloidas and Papayannakos (1989) and earlier workers, as noted in Chapter 3. A full analysis of the kinetics would take account of these effects, and also of other minor reactions and byproducts. This is a major piece of work in its own right, and would require rather more accurate data than are presented here, in particular, the flow pattern in the reactor would have to be more accurately described. Such an analysis must therefore be the subject of future work, and a suitable concluding note is that the engineering model developed above will be useful not only in process design, but also in designing an apparatus for more detailed kinetic studies.
5.5 The Effect of Catalysis

Having identified the rate-limiting reaction for the $\text{H}_2\text{S}/\text{CO}_2$ system it is possible to improve the overall reactor performance by applying a catalyst for this reaction. This is of great importance in the development of a process based on this chemistry, as use of catalysis considerably reduces the reactor volume required. It will be seen (Section 7.4) that even with catalysis the reactor is the most expensive capital item in the process designed. Catalysts for the thermal decomposition of $\text{H}_2\text{S}$ were discussed in Chapter 3, and it has been found that of many compounds examined, molybdenum disulfide ($\text{MoS}_2$) is the most effective catalyst for $\text{H}_2\text{S}$ decomposition at high temperatures. A short series of experiments was therefore performed to demonstrate that $\text{MoS}_2$ would act as a catalyst for the $\text{H}_2\text{S}/\text{CO}_2$ system. It should be stressed that this was only a preliminary investigation to demonstrate feasibility for patent purposes. A full analysis of the catalysis of this system would be a major piece of work in its own right and is beyond the scope of this study.

5.5.1 Apparatus

The apparatus described in Section 5.2 was modified by packing the reactor with $\text{MoS}_2$ catalyst supported on quartz wool. Initially, experiments were performed with the reactor packed with quartz wool in the absence of catalyst, so that the effect of the quartz wool could be determined. (Conversions were found to be a little higher than in experiments run under the same conditions without quartz wool. It is not clear whether this was due to improved mixing making the reactor more like a plug-flow reactor, distortion of the temperature profile, or a surface effect). The experiments were then repeated with the same mass of quartz wool onto
which MoS₂ powder had been loaded. The loading was approximately 2.91 g/g, and the total mass of MoS₂ in the reactor was 4.853 g.

Quartz wool was selected as catalyst support as it allowed a quick and flexible modification of the existing apparatus. It also enabled us to increase the catalyst loading if necessary by simply dusting more catalyst onto the quartz wool, although this turned out not to be required. Disadvantages of this method were that it was difficult to guarantee an even distribution of catalyst over the support and impossible to obtain an even distribution of the support within the reactor. This could not be avoided with the reactor used, as it was found that elemental sulfur formed at such high concentrations during the experiments that it condensed in the reactor exit tube at temperatures above 200 °C. It was therefore necessary to remove and clean the inner tube between experiments, which ruled out use of a hard support and probably caused some rearrangement of the quartz wool during the first few experiments, leading to the creation of gaps in the packing that would allow gas bypass. This uneven distribution also made determination of the temperature profile impossible (in fact, different portions of the gas may have experienced quite different temperature profiles). Detailed modelling of the results is therefore impossible at this stage, due to the rather high uncertainties in the experimental conditions. A future study would avoid these problems by using an apparatus specifically designed to be packed with catalyst. Other factors important for the design of future experiments are discussed below.

5.5.2 Results

The experimental conditions and conversions obtained are shown in Table 5.7. In all
cases the feed composition was 5% H$_2$S in CO$_2$. Clearly catalysis gives a significant improvement in conversion at all temperatures studied. The equilibrium conversion at each temperature is also shown.

Table 5.7 Experimental Conditions and Conversions for Catalyst Experiments

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>800</th>
<th>850</th>
<th>850</th>
<th>900</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flowrate</td>
<td>0.5 F$_s$</td>
<td>0.5 F$_s$</td>
<td>F$_s$</td>
<td>F$_s$</td>
</tr>
<tr>
<td>Experiments with quartz wool packing, but no catalyst</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>(SE23) 28.1</td>
<td>(SE25) 32.5</td>
<td>(SE21) 28.9</td>
<td>(SE20) 34.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(SE24) 36.3</td>
</tr>
<tr>
<td>Experiments with quartz wool loaded with MoS$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>(SE31) 76.8</td>
<td>(SE30) 83.4</td>
<td>(SE33) 72.8</td>
<td>(SE32) 82.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(SE34) 83.8</td>
<td></td>
</tr>
<tr>
<td>Results of thermochemical equilibrium calculations</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>77.1</td>
<td>82.7</td>
<td>82.7</td>
<td>87.2</td>
</tr>
</tbody>
</table>

The first few experiments with catalyst gave higher-than-equilibrium conversions; however, this was to be expected as the initial experiments without catalyst or packing also overpredicted the conversion and the apparatus required three or four runs to settle down before giving reproducible results. To eliminate this effect the same sequence of experiments was
repeated until a reproducible result was obtained. It was not worth repeating all of the converged results, however, since quantitative modelling of the experiments could not be attempted for the reasons described above. Only the converged results are shown in Table 5.7.

It can be seen from Table 5.7 that the low-flowrate, high-temperature experiments (SE30 and SE34) have reached equilibrium conversions (within experimental error). It is therefore worthwhile to compare the observed outlet gas composition with the composition calculated for thermochemical equilibrium at (approximately) the same temperature. This is done in Table 5.8.

Table 5.8 Comparison of Experimental Outlet Compositions with High-Temperature Equilibrium Compositions for Experiments with Near-Equilibrium Conversion

<table>
<thead>
<tr>
<th>Composition (mole %)</th>
<th>Experiment</th>
<th>SE30</th>
<th>SE34</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td></td>
<td>89.6</td>
<td>89.3</td>
<td>88.6</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>3.16</td>
<td>3.40</td>
<td>4.00</td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
<td>0.79</td>
<td>0.77</td>
<td>0.86</td>
</tr>
<tr>
<td>H₂ + H₂O</td>
<td></td>
<td>3.96</td>
<td>3.98</td>
<td>4.04</td>
</tr>
<tr>
<td>COS</td>
<td></td>
<td>0.93</td>
<td>0.95</td>
<td>0.65</td>
</tr>
<tr>
<td>S₂</td>
<td></td>
<td>1.47</td>
<td>1.47</td>
<td>1.50</td>
</tr>
<tr>
<td>SO₂</td>
<td></td>
<td>0.086</td>
<td>0.087</td>
<td>0.385</td>
</tr>
</tbody>
</table>
(The H₂ and H₂O compositions could not be determined separately as H₂ was formed at concentrations such that the G.C. could not distinguish between H₂ and the He carrier gas).

It can be seen that the experimental results agree reasonably well with the equilibrium predictions with the following exceptions:

i) The CO₂ fraction is somewhat higher than the equilibrium concentration and CO is somewhat lower, due to re-equilibration of the water-gas-shift reaction on cooling (and possibly also other effects described below).

ii) The COS fraction is somewhat higher than the equilibrium fraction, suggesting that COS formation occurs by the same mechanism as found previously, possibly catalyzed by the formation of HS free radicals in the presence of the catalyst. The higher-than equilibrium COS fraction suggests that for these temperature profiles the gas spent insufficient time at the highest temperatures for the COS concentration to fall to its equilibrium level. This would not be a problem for a process reactor, where the proportion of the residence time spent at the highest temperatures would be much greater.

iii) The SO₂ fraction is lower than the equilibrium fraction by a factor of roughly five. It was expected from thermochemical calculations that the SO₂ fraction would fall during cooling (Section 4.5); however, the mechanism for this back-reaction is not certain. Sulfur dioxide could be reduced by either H₂S (via the Claus reaction) or CO. In both cases, however, the reducing agent is present at low concentrations and the product formed on oxidation by SO₂ (H₂O or CO₂, respectively) is present at much higher concentrations. On cooling, the Claus reaction should
actually favor SO$_2$ formation down to roughly 450 °C, although this equilibrium might be shifted by the water-gas-shift reaction, which favors consumption of water vapor to produce hydrogen under these conditions.

A further possibility is that SO$_2$ loss may have occurred by reaction with H$_2$S in the water that condensed in the U-tube cold-trap. If H$_2$S and SO$_2$ are bubbled through water a yellow, cloudy mixture known as Wackenroder's liquid is formed. This mixture contains colloidal sulfur, thiosulfuric, sulfurous and polythionionic acids (Yost and Russell, 1946). The liquid removed from the U-tube after each experiment met this description, but it is not known whether the volume of liquid present and contact-time with the gas were sufficient to significantly alter the concentration of SO$_2$ in the gas.

For process design purposes the mechanism of SO$_2$ loss is unimportant at this stage. For process reactor feeds the H$_2$S fraction is much greater than 5%; the gas mixture is therefore much more reducing in nature than in these experiments. If gas-phase reduction is involved it will thus be more rapid regardless of whether CO or H$_2$S is the reducing species. If liquid-phase reduction is the mechanism this can be incorporated into the process quite easily, as described in Section 7.1.2.

It can also be seen from Tables 5.7 and 5.8 that the conversion in SE34 is almost identical to that in SE30, despite some 24 hours of running time under 5 % H$_2$S in CO$_2$ and 28 hours of heating/cooling under CO$_2$ between the two experiments. This does not eliminate the possibility that catalyst deactivation is occurring; however, it suggests that if it does occur then it is a rather slow process.
5.5.3 Discussion

As noted above, the experimental conditions are too uncertain to allow detailed modelling of the experiments. It would be possible to extend the model described in Section 5.4 by using the kinetic expression developed for H$_2$S thermal decomposition over MoS$_2$ by Fukuda et al. (1978), but this would not account for the effect of catalysis on the sulfur-gas-shift reaction and hence COS formation. Since the catalytic mechanism is known to involve formation of H, HS and S free-radicals (Katsumoto et al., 1973), it is unreasonable to expect catalysis only to affect the H$_2$S-decomposition reaction. We may however, use the kinetics of Fukuda et al. (1978) as a first-order approximation for process design if we assume the gas reaches the equilibrium concentration (a reasonable assumption in the light of the results above) and the catalyst loading is the same as that used experimentally by Fukuda et al. For a fundamental understanding of the catalytic behavior a more complete analysis is necessary. In carrying out such an analysis the following factors should be borne in mind.

Firstly, the apparatus should be designed for use with catalyst rather than for rapid quenching. A quench rate greater than 1000 °C/s is now known to be adequate to prevent back-reaction in the absence of catalyst. The catalyst support should be chosen so that a uniform distribution of catalyst in the reactor can be obtained, and the reactor and flowrate should be selected so as to give plug flow, to guarantee good radial mixing and a constant radial temperature. This may mean using a significantly larger scale of ancillary equipment to allow higher flows, or else a much smaller reactor. Care must be taken to ensure that any part of the reactor where sulfur condensation may occur can be removed for cleaning without disruption of the catalyst bed. The catalyst-packed section of the reactor should be located in such a way that
the gas leaves the bed in the high-temperature region of the reactor (preferably at a high flowrate) rather than cooling in the presence of catalyst. All of these conditions would be satisfied by performing the reaction in a simple cylindrical tube with a short packed section located at the flattest region of the furnace temperature profile.

Secondly, a great deal more attention should be paid to the method of supporting the catalyst. Fukuda et al. (1978) prepared supported catalyst by soaking γ-alumina in an aqueous alkaline solution of ammonium thiomolybdate and then reducing under hydrogen at 370 °C and calcining at higher temperatures under N₂. Different surface areas and distributions of catalyst over the surface were obtained depending on the calcination temperature. A full analysis would consider such factors and would also attempt to develop higher catalyst loadings than that found by Fukuda et al., since this significantly affects the process capital cost because of its important role in determining the size of the process reactor.

Finally, a full analysis must consider other reactions as well as H₂S decomposition. At the very least, the effect of catalysis of the sulfur-gas-shift reaction must be included, but a better approach would be to identify a free-radical mechanism that could account for all of the reactions and species present in the system.

Although this analysis was somewhat "quick and dirty", the beneficial effect of catalysis has been clearly demonstrated up to high temperatures. Our understanding of the behavior of SO₂ in the H₂S/CO₂ system was also somewhat improved. The success of these experiments justifies the funding of other investigations that would address the preparation of better catalysts and the development of a more fundamental understanding of the reaction chemistry.

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6. Process Synthesis

This chapter discusses the synthesis of the Berkeley Zero-Emissions Sulfur Process (ZESP). The initial development of the process is discussed in Section 6.1, and Section 6.2 gives a description of the base-case process configuration. A flowsheet for the process is presented in Section 6.3.

6.1 Initial Process Synthesis

This section describes the initial steps that were taken in the design of the Berkeley Zero-Emissions Sulfur Process. It is not primarily intended to be a history of the development of the process, but rather to explain how the basic flowsheet arrived at its current form. A detailed description of the process is given in Section 6.2.

The potential for using the interaction between CO$_2$ and H$_2$S for sulfur recovery was realized as soon as the experimental observation that elemental sulfur was formed when the two were heated was confirmed by thermodynamic calculations. The similarity of the apparent reaction:

$$CO_2 + H_2S = CO + H_2O + \frac{1}{2} S_2$$

to the Claus reaction suggested that a similar process could be used. The first flowsheet sketched therefore bore a great resemblance to the Claus Process, employing two high-temperature reactor stages with sulfur condensation and re-heat between them (Fig. 6.1). It differed from the Claus Process in that the reactor feed stream from the absorber/stripper unit contained CO$_2$ and H$_2$S and required no air stream as oxidant. The gas exiting the second sulfur condenser therefore
Fig. 6.1 Initial Sketch of a Sulfur-Recovery Process Using the Reaction Between $\text{H}_2\text{S}$ and $\text{CO}_2$
contained CO₂, H₂S, COS, CO, H₂ and H₂O and was sent to a second absorption stage to recover CO₂, H₂S and COS (which hydrolyses to CO₂ and H₂S during absorption) for recycle.

Initial calculations showed that roughly two-thirds of the sulfur was recovered in the first reactor pass, while cooling and re-heating the gas imposed a considerable burden on the net process energy requirement. The second reactor stage was therefore abandoned. Consideration of the reactor feed composition showed that although the most favorable equilibrium is found with roughly 7% H₂S in CO₂ (Section 4.3.3) the optimum feed contains a much higher H₂S fraction, typically 60 mole % H₂S (see below). In the event that the first absorption and stripping stage cannot be designed to produce such a feed (e.g., if the hydrocarbon gas that is being desulfurized contains no CO₂) it may be necessary to introduce a make-up stream of CO₂.

From the thermodynamic calculations presented in Section 4.3.1 it can be seen that increasing the furnace temperature increases the recovery of elemental sulfur. Calculations showed that operating the furnace at higher temperatures also improves the calorific value of the synthesis gas (CO and H₂) mixture that leaves the second absorber. There are, however, two major drawbacks to increasing furnace temperature. Firstly the range of materials suitable for construction of the furnace tubes becomes very restricted (see Section 7.2) and the cost of the furnace is greatly increased. Secondly SO₂ begins to form in significant amounts in the reactor product gas. SO₂ reacts irreversibly with most of the solvents typically used for H₂S and CO₂ absorption and would therefore poison the solvent, making periodic regeneration necessary. The volume of gas that must be treated by the second absorber is obviously much less than that treated by the first absorber, therefore adding a second stripper and keeping the two loops isolated significantly reduces the amount of solvent that is exposed to SO₂ (and also COS).
It was also apparent from an early stage that a rapid quench of the reactor products would be necessary to ensure that the more favorable high-temperature equilibrium composition was preserved. Examination of the quench conditions showed that they are similar to the conditions encountered in thermal cracking of ethane, therefore an arrangement of heat exchangers similar to that used in thermal cracking was introduced to provide heat-recovery and quench after the reactor. There are in fact several methods of accomplishing the quench, and these are discussed in more detail in Section 7.3.

Initially it was assumed that COS formed in the reactor would be removed by hydrolysis in the second absorber. This places a severe burden on the second absorber for reasons discussed in Section 7.1; a separate vessel was therefore added between the sulfur condenser and the second absorber to carry out hydrolysis of the COS.

The initial flow diagram of Fig. 6.1 was thus adapted to the flow diagram of Fig. 6.2, which forms the base-case design for the Berkeley Zero-Emissions Sulfur Process. This flow diagram is described in detail in the next section.

6.2 Process Description

The base-case flow diagram for the Berkeley Zero-Emissions Sulfur Process is shown in Fig. 6.2. This section gives a description of the main features of the base-case process. More detailed analyses of several parts of the flowsheet are given in Chapter 7, and these will be referred to where appropriate. A flowsheet mass balance showing compositions and flowrates of all streams, for a basis of 50 tonnes/day sulfur production, is given in Section 6.3.
Fig. 6.2 Base-Case Flowsheet for the Berkeley Zero-Emissions Sulfur Process
The first stage in the process is a standard absorber/stripper loop for recovering H₂S from the hydrocarbon gas. The "sour" fuel gas can be any H₂S-containing gas; e.g., refinery gas, natural gas or coal gas. The gas is contacted with a suitable solvent that absorbs all of the H₂S and the desired amount of CO₂ from the gas, leaving a treated fuel gas stream that is sulfur-free to the extent required by specifications. In the event that the fuel gas contains no CO₂, a make-up stream is introduced later in the process. The selection of solvent and design of the absorber to meet these criteria are discussed in Section 7.1; a typical solvent would be a solution of an ethanolamine in water, for example the flowsheet given in Section 6.3 uses a 2.0 kmol/m³ solution of diethanolamine (DEA).

The "rich" solution containing dissolved H₂S and CO₂ is heated in the first stripper, regenerating the solvent and producing a gas stream containing the desired proportion of H₂S and CO₂, saturated with water vapor. This gas is cooled to remove as much water as possible since H₂O adversely affects the reaction equilibrium, as discussed in Section 4.3.4. This cooling is normally accomplished by having a few extra plates at the top of the stripper column, with cold water circulating over them; the water is cooled in an external cooler, as shown in Fig. 6.2. If the cooler uses cooling water as coolant, then the gas temperature can be lowered to roughly 40 °C (or lower, depending on climate), which corresponds to a water vapor concentration of 7.4 mole % at 1 atm pressure. It is advantageous to reduce this water concentration, for reasons discussed in Chapter 4. The stripper may therefore be run at higher pressure than one atmosphere. The optimum ratio of H₂S to CO₂ in the reactor feed gas depends on a number of factors. Firstly, the reactor yield (moles S/mole of feed) is maximized when the feed gas is roughly 70 mole % H₂S, dry basis - - this minimizes the process recycle (Section 4.4). Increasing the amount of CO₂ in the reactor feed increases its heat capacity and hence the high-
temperature heat requirement of the process; however, increasing the amount of H₂S increases the amount of H₂S to be recycled, and hence the second stripper heat requirement (since the heat of reaction between H₂S and the solvent is greater than that between CO₂ and the solvent). The trade-off between these effects depends on the relative availability and cost of high- and low-temperature heat within the process, and is something that would be addressed at the detailed design stage. A typical feed composition might be expected to be roughly 60 mole % H₂S, dry basis, as used in the flowsheet of Section 6.3.

The gas mixture is then sent to the reactor section, which consists of the high-temperature furnace and associated heat exchangers. The object of the reactor section is to heat the gas and allow it to come to equilibrium at a high temperature, then quench it rapidly to a temperature at which the kinetics of the important reactions are very slow, so that these reactions do not have time to re-equilibrate at a lower temperature. There are several methods for achieving this quench and these are discussed in Section 7.3. The base-case for design is the quench-boiler arrangement shown in Fig. 6.2 and described in detail in Section 7.3.3. The arrangement of heat exchangers around the furnace is determined in part by the quench requirement and partly by heat-recovery needs. Process energy requirements and heat recovery are discussed in Section 7.4.

The thermodynamic analysis of Chapter 4 showed that the process performance is improved by running the furnace at higher temperatures. In practice this is limited by the availability of materials that will withstand the corrosive, sulfur-containing environment at high temperatures. The choice of materials for the furnace is discussed in Section 7.2: materials are identified that can withstand temperatures up to 1000 °C, however the furnace would probably
be kept at 950 °C to allow a margin of safety.

The gas leaving the furnace contains CO₂, H₂S, CO, H₂, COS, H₂O, elemental sulfur and traces of SO₂ (< 100 ppm if the furnace operates at 950 °C). Some of the reactions will have been quenched and will retain their high-temperature equilibrium composition, whereas others may have come to equilibrium at lower temperatures. This is discussed in Chapter 5 and Section 7.3. A typical composition of the gas after the quench is given in Section 6.3. This gas is then cooled to a temperature of 120 °C. At this temperature the vapor pressure of elemental sulfur is 0.04 mmHg, so the mole fraction of elemental sulfur is reduced to the order of 50 ppm, and 99.95 % of the sulfur is condensed and removed as liquid sulfur product.

The gas leaving the sulfur condenser contains a substantial fraction (roughly 2 mole %) of carbonyl sulfide, COS, which must be removed before the gas is sent to the second absorber/Stripper loop. Carbonyl sulfide is removed by hydrolysis in a hot, recirculating potassium carbonate solution in the hydrolyzer, giving H₂S and CO₂ as products. The design of the hydrolyzer is discussed in Section 7.1. The gas then passes to the second absorber/Stripper loop, which removes CO₂ and the remaining sulfur-containing species and leaves a gas consisting of carbon monoxide and hydrogen saturated with water vapor. Such gas mixtures are known as "synthesis gas" and can be used either as fuel or as chemical feedstock. The conditions in the second absorber are rather different from those in the first absorber, due to the high fraction of the gas that must be removed. The design of the second absorber/Stripper loop is discussed in Section 7.1.4.

It can be seen from Fig. 6.2 that the only effluent streams leaving the process are the
synthesis gas and liquid sulfur product streams. The water that is produced by the reaction is generally less than the amount lost by evaporation in the first absorber, and in practice it may be necessary to transfer some water from the second loop to the first loop, and also to introduce a small water make-up stream into the first loop. This will depend strongly on the water content of the sour gas. The only products are, therefore, liquid sulfur and the essentially sulfur-free synthesis gas; thus the process recovers both hydrogen and sulfur from the hydrogen sulfide and emits no sulfur-containing gases to the environment.

6.3 Process Flowsheet

The flowsheet for the Zero-Emissions Sulfur Process has been divided into three sections for ease of presentation. The first section consists of the first absorber/stripper loop and is shown in Figure 6.3. The second section is made up of the reactor, sulfur condenser and associated heat exchangers and is shown in Figure 6.4. The third section contains the hydrolyzer and second absorber/stripper loop and is shown in Figure 6.5. The flowsheet mass balance is given for 50 tonnes/day sulfur production (1 metric tonne is roughly the same as 1 long ton). All flows are in kmol/hr and compositions are in mole %, or parts-per-million (ppm) where appropriate. Several areas of particular engineering interest are discussed in more detail in Chapter 7. An economic analysis of this flowsheet is also given in Chapter 7.

Streams 11, 12 and 13 were eliminated as the result of a design modification. The assumptions that were made in developing the process flowsheet are given below.
First Absorption Section

The first absorption section is shown in Figure 6.3, and the stream data for this section for a plant producing 50 tonnes of sulfur per day are given in Table 6.1.

1. The "sour" hydrocarbon gas was assumed to contain 1 mole % CO₂, 1 mole % H₂S and 0 % H₂O. For absorber design the density of this gas was taken as that of methane. This gives the highest possible vapor flowrate and hence worst-case design for the first absorber (largest diameter). The pressure of this gas was assumed to be 10 bar.

2. The increase in solution temperature in the first absorber due to the heat of reaction was neglected. This increase is calculated to be roughly 5 °C, which may not greatly affect the solution loading, and in any case can be eliminated if necessary by cooling the solvent at an intermediate stage in the column.

3. The pressure of the first stripper was set at 2 bar to reduce the water content of the reactor feed gas. This would be optimized at the detailed design stage.

4. The absorber and stripper solution rates and loadings were found using data presented in Kohl and Riesenfeld (1985). The solvent composition was taken as 2.0 kmol/m³ diethanolamine (DEA) in water and the solution loadings were 0.1 moles CO₂/mole DEA and 0.35 moles H₂S/mole DEA. For DEA solution it is reasonable to assume that the solution leaving the stripper is essentially free of H₂S and CO₂ (Kohl and Riesenfeld, 1985), although this obviously depends on the number of stages in both columns and the steam rate in the stripper.
5. The stripper boil-up was calculated using the procedure recommended by Kohl and Riesenfeld (1985) and gives a molar ratio of steam to acid gas of 2:1, which should be ample for DEA solution.

6. The cooled stripper-off-gas is assumed to be saturated with water at 40 °C, 2 bar, i.e., contains roughly 3.7 mole % H₂O.

Table 6.1 Stream Flows for Figure 6.3

Basis: 50 tonnes S/day net production

<table>
<thead>
<tr>
<th>Stream No.</th>
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<th>2</th>
<th>3</th>
</tr>
</thead>
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<td>Temp. (°C)</td>
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<td>25</td>
<td>40</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Components</td>
<td>kmol/hr</td>
<td>mol %</td>
<td>kmol/hr</td>
</tr>
<tr>
<td>CO₂</td>
<td>65.8</td>
<td>1</td>
<td>46.8</td>
</tr>
<tr>
<td>H₂S</td>
<td>65.8</td>
<td>1</td>
<td>0.131</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
<td>48.2</td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>6444.4</td>
<td>98</td>
<td>6444.4</td>
</tr>
<tr>
<td>Solvent (DEA)</td>
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<td></td>
</tr>
<tr>
<td>TOTAL</td>
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<td>100</td>
<td>6540</td>
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Fig. 6.3 Flow Diagram for First Absorption Section
Table 6.1 (Continued)

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<th>5</th>
<th>6</th>
</tr>
</thead>
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<tr>
<td>Name</td>
<td>1st Absorber Bottoms</td>
<td>1st Stripper Feed</td>
<td>Stripper off-gas</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>40</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>10</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>Components</td>
<td>kmol/hr</td>
<td>mol %</td>
<td>kmol/hr</td>
</tr>
<tr>
<td>CO₂</td>
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<td>0.42</td>
<td>19.0</td>
</tr>
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<td>H₂S</td>
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<td>1.44</td>
<td>65.6</td>
</tr>
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<td>H₂O</td>
<td>4273.0</td>
<td>94.0</td>
<td>4273.0</td>
</tr>
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<td>Hydrocarbon</td>
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<td></td>
<td></td>
</tr>
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<td>Solvent (DEA)</td>
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<td>4.78</td>
<td>189.9</td>
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<tr>
<td>TOTAL</td>
<td>4547.6</td>
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<td>4547.6</td>
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</table>
Table 6.1 (Continued)

<table>
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<tr>
<th>Stream No.</th>
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<th>8</th>
<th>9</th>
<th>10</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>1st Stripper Boil-up</td>
<td>1st Stripper Bottoms</td>
<td>Cooled Soln</td>
<td>Cold Dry Feed Gas</td>
<td>Recycle Gas</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>100</td>
<td>90</td>
<td>50</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>2.1</td>
<td>10</td>
<td>10</td>
<td>1.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Components</td>
<td>kmol/hr</td>
<td>mol %</td>
<td>kmol/hr</td>
<td>mol %</td>
<td>kmol/hr</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>135.3</td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>202.9</td>
</tr>
<tr>
<td>H₂O</td>
<td>177.4</td>
<td>95.8</td>
<td>4321.3</td>
<td>95.8</td>
<td>4321.3</td>
</tr>
<tr>
<td>Hydrocarbon</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>Solvent (DEA)</td>
<td>7.89</td>
<td>4.21</td>
<td>189.9</td>
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<td>189.9</td>
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<td>TOTAL</td>
<td>185.3</td>
<td>100</td>
<td>4511.2</td>
<td>100</td>
<td>4511.2</td>
</tr>
</tbody>
</table>
Reactor Section

The reactor section is shown in Figure 6.4, and the stream data for this section for a plant producing 50 tonnes of sulfur per day are given in Table 6.2.

1. The highest temperature attained by the gas was taken as 950 °C and the quench was assumed to cool the gas to 650 °C. The interchanger was given a temperature approach of 50 °C to allow for the low heat-transfer coefficient expected for gas/gas heat transfer. The lower temperature in the interchanger was calculated to be 40 °C above the dew point of the gas, so as to prevent sulfur from condensing in the interchanger. Under certain circumstances the interchanger may not be required, in which case all the gas heating occurs in the furnace and all the cooling occurs in the quench boiler. This alternative configuration depends on materials costs and is discussed in Section 7.3.

2. The reactor feed was taken as 60/40 H₂S/CO₂, dry basis. The optimal reactor feed depends on several factors as discussed above, and would be determined at the detailed design stage.

3. The gas leaving the reactor was assumed to be at the 950 °C equilibrium composition. If catalysis is used it is possible that this may overestimate the COS mole fraction; however, this is a safe-side approximation.

4. The quench is assumed to occur in a waste-heat boiler, giving a quench rate of roughly 60,000 Ks⁻¹. At this quench rate the available kinetics data indicate that the reactions investigated
in Chapter 5 will be quenched completely, though the Claus reaction and water-gas-shift reaction may be able to re-equilibrate at a lower temperature, causing the SO$_2$ concentration to fall somewhat (see Sections 4.5 and 5.5). The SO$_2$ concentration is taken as half the maximum SO$_2$ concentration as a safe-side approximation, although in practice we expect the amount of SO$_2$ present in the cooled gas to be much lower. The water-gas-shift reaction is assumed to re-equilibrate instantaneously at temperatures above 450 °C.

5. The reactor was sized assuming the rate of H$_2$S decomposition given by the kinetics data for the catalyzed reaction found by Fukuda et al. (1978). The catalyst loading was taken as 8 wt % MoS$_2$ on γ-alumina (as used experimentally by Fukuda et al. — higher loadings may be achievable in practice). The packing density was taken as 700 kg/m$^3$ of packed bed, with bed voidage 0.4. Several reactor configurations were examined, and the optimum was found to be 4-inch packed tubes containing catalyst in both the heating and reactor sections. For a gas superficial velocity of 15 ms$^{-1}$ the length of tube required to achieve equilibrium conversion is 4.0 m, of which 2.5 m are required for heating the gas from 600 to 950 °C.

6. The total furnace duty was calculated from the high-temperature heat requirement and the stripper heat load, as described in Section 7.4.
Fig. 6.4 Flow Diagram for Reactor Section
Table 6.2 Stream Flows for Figure 6.4

Basis: 50 tonnes S/day net production

<table>
<thead>
<tr>
<th>Stream No.</th>
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<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
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<tbody>
<tr>
<td>Name</td>
<td>Cool Dry Feed Gas</td>
<td>Preheat Gas</td>
<td>Reactor Feed Gas</td>
<td>Reactor Effluent</td>
<td>Quench Gas</td>
</tr>
<tr>
<td>Temp. (°C)</td>
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<td>100</td>
<td>600</td>
<td>950</td>
<td>650</td>
</tr>
<tr>
<td>Pressure (bar)</td>
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<td>1.3</td>
<td>1.3</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Components</td>
<td>kmol/hr mol %</td>
<td>kmol/hr mol %</td>
<td>kmol/hr mol %</td>
<td>kmol/hr mol %</td>
<td>kmol/hr mol %</td>
</tr>
<tr>
<td>CO₂</td>
<td>135.3 38.5</td>
<td>135.3 38.5</td>
<td>135.3 38.5</td>
<td>84.4 22.0</td>
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<td>H₂S</td>
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<td>202.9 57.8</td>
<td>202.9 57.8</td>
<td>130.4 34.0</td>
<td>130.4 34.0</td>
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<tr>
<td>H₂O</td>
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<td>13.1 3.74</td>
<td>13.1 3.74</td>
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<td>43.8 11.4</td>
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<tr>
<td>H₂</td>
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<td>0.0789 205 ppm</td>
</tr>
<tr>
<td>S₂</td>
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<td>32.6 8.48</td>
<td>32.6 8.48</td>
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<td>6.92 1.80</td>
<td>6.92 1.80</td>
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<td>0.158 411 ppm</td>
<td>0.158 411 ppm</td>
<td>0.0789 205 ppm</td>
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<tr>
<td>CS₂</td>
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<td>TOTAL</td>
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<td>32</td>
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<td>----</td>
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</tr>
<tr>
<td>Name</td>
<td>Intercooler Gas</td>
<td>Condenser Gas</td>
<td>Sulfur Product</td>
<td>Cold Gas</td>
<td>Make-up CO₂</td>
</tr>
<tr>
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<td>120</td>
<td>120</td>
<td>25</td>
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<td>Pressure (bar)</td>
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<td>1.09</td>
<td>1.09</td>
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</tr>
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<td>kmol/hr</td>
<td>mol %</td>
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</tr>
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<td>110.1</td>
<td>28.7</td>
<td>110.1</td>
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<tr>
<td>H₂S</td>
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<td>33.9</td>
<td>130.4</td>
<td>33.9</td>
<td>130.4</td>
</tr>
<tr>
<td>H₂O</td>
<td>38.2</td>
<td>9.95</td>
<td>38.2</td>
<td>9.95</td>
<td>38.2</td>
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<td>4.71</td>
<td>18.1</td>
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<tr>
<td>H₂</td>
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<td>12.4</td>
<td>47.5</td>
<td>12.4</td>
<td>47.5</td>
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<tr>
<td>S₂</td>
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<td>8.48</td>
<td>32.6</td>
<td>8.48</td>
<td>32.54</td>
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<tr>
<td>COS</td>
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<td>6.92</td>
<td>1.80</td>
<td>6.92</td>
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<tr>
<td>SO₂</td>
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<td>205 ppm</td>
<td>0.079</td>
<td>205 ppm</td>
<td>0.079</td>
</tr>
<tr>
<td>CS₂</td>
<td>0.162</td>
<td>424 ppm</td>
<td>0.162</td>
<td>424 ppm</td>
<td>0.162</td>
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<tr>
<td>TOTAL</td>
<td>384.1</td>
<td>100</td>
<td>384.1</td>
<td>100</td>
<td>32.54</td>
</tr>
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</table>
Second Absorption Section

The second absorption section is shown in Figure 6.5, and the stream data for this section for a plant producing 50 tonnes of sulfur per day are given in Table 6.3.

1. The hydrolyzer was assumed to operate at 80 - 90 °C and to contain a recirculating solution of saturated solvent, as described in Section 7.1.1. The hydrolyzer was assumed to convert 99.9 % of the COS to CO₂ and H₂S and to absorb all of the CS₂, SO₂ and elemental sulfur remaining in the gas. The actual conversion of COS depends on the height of the hydrolyzer and the liquid flowrate and cannot be determined without more detailed research. The absorption of the minor sulfur-containing species causes degradation of the hydrolyzer solution, as discussed in Section 7.1; however, this is a very slow process.

2. The absorber and stripper solution rates and loadings were found using data presented in Kohl and Riesenfeld (1985). The solvent solution was taken as 2.0 kmol/m³ diethanolamine (DEA) in water and the solution loadings were 0.3 moles CO₂/mole DEA and 0.35 moles H₂S/mole DEA. Other assumptions regarding the performance of the second absorber/stripper loop were the same as for the first loop, with the exceptions noted below.

3. The increase in solution temperature for the second absorber is not negligible, due to the large amounts of gas absorbed. This increase is estimated to be roughly 15 °C. This is discussed in more detail in Section 7.1.

4. The second absorber design was based on the feed vapor flowrate. This gives a
somewhat larger column diameter than is necessary as 80% of the vapor is removed by absorption and most absorption occurs in the bottom few plates of the column; however, this is a safe-side approximation. The column height was calculated as the height required to absorb the CO₂ from the feed gas, i.e., assuming absorption of H₂S is rapid compared to that of CO₂.

5. If the stripper D7 is run at 2 bar and the absorber D6 runs at 1 bar then it will be necessary to place the pump J2 in line 25 instead of line 29. Running the stripper under higher pressure than the absorber is not a common practice; however, in this case it is necessary owing to the low pressures required in the reactor. This does not significantly affect the size of the pump.

6. The concentration of H₂S in the product gas was fixed at 20 ppm. This concentration is determined mainly by the stripper steam load. Increasing the stripper boil-up increases the removal of H₂S from the stripper solution, which reduces the H₂S concentration in the lean solution sent to the absorber and thereby reduces the H₂S fraction in the scrubbed gas. The H₂S concentration specified for the product gas will depend on the end-use of this gas. For a typical refinery fuel gas a concentration of 160 ppm is acceptable; if the gas is burned as fuel a substantial saving in the boil-up rate may therefore be possible. If, on the other hand, the product gas is sent to a hydrogen plant then it may be necessary to remove the H₂S to a lower level than 20 ppm, depending on the hydrogen plant requirements. The value of the product gas stream as synthesis gas would therefore be offset somewhat by the increase in costs due to increased steam demand in the second absorber/stripper loop. The concentration of 20 ppm chosen for the design basis corresponds to a boil-up rate of roughly one pound of steam per pound of acid gas, which is a typical industrial rate (Kohl and Riesenfeld, 1985).
Fig. 6.5 Flow Diagram for the Second Absorption Section
Table 6.3 Stream Flows for Figure 6.5

Basis: 50 tonnes S/day net production

<table>
<thead>
<tr>
<th>Stream No.</th>
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<td>22</td>
<td>23</td>
</tr>
<tr>
<td>Temp. (°C)</td>
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<th>mol %</th>
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<td>Stripper Feed</td>
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<td>Components</td>
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<td>kmol/hr</td>
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<tr>
<td>H₂</td>
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<tr>
<td>COS</td>
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<td></td>
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</tr>
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<td>Solvent (DEA)</td>
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<td>2nd Stripper Boil-up</td>
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<td>Stripper Bottoms</td>
<td>Cooled Solvent</td>
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<tr>
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<td>137.3</td>
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<td>95.1</td>
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<td>H₂</td>
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<td>95.7</td>
<td>8774.5</td>
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<td>CO</td>
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<td>9164.5</td>
<td>100</td>
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<td>H₂S</td>
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<td>4.25</td>
<td>390.1</td>
<td>4.25</td>
<td>390.1</td>
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<td>Solvent (DEA)</td>
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<td>TOTAL</td>
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<td>100</td>
<td>263.3</td>
<td>100</td>
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7. Process Evaluation

This chapter discusses some of the more important design aspects of the Zero-Emissions Sulfur Process. An approximate evaluation of the process economics and suggestions for further work are also included.

7.1 Gas Absorption

The base-case flowsheet for the Zero-Emissions Sulfur Process contains two absorber/stripper loops, the first recovering H₂S and CO₂ from the feed gas and the second removing H₂S and CO₂ from the product gas, for recycle to the reactor. In both cases the absorber must typically reduce the H₂S content to roughly 160 ppm if the sweetened gas is to be used as refinery fuel gas. (In some cases stricter limits must be met, depending on local legislation). The first absorber/stripper loop is identical to equipment currently used for acid-gas scrubbing, except that we seek to produce a gas stream containing the desired proportions of H₂S and CO₂ in the stripper off-gas. This can easily be achieved by using a solvent that absorbs H₂S rapidly and CO₂ more slowly, e.g., diethanolamine (DEA). The use of such solvents is well understood and design equations can be found in standard texts such as Kohl and Riesenfeld (1985). The second absorber/stripper loop is rather different, in that it must absorb approximately 75% of the gas fed to it (inlet CO₂ = 33.9 mole %, H₂S = 39.8 mole %) and must also be able to cope with the other sulfur-containing species present in the reactor quench gas, most notably COS (1.97 %) and SO₂ (< 200 ppm). This section describes strategies for achieving these goals.
7.1.1 COS Hydrolysis

COS is present in the gas leaving the sulfur condenser at levels much higher than normally encountered in acid-gas scrubbing (0.5 - 2 % c.f. 100 - 500 ppm in typical fuel gas). Even at lower levels COS would pose problems for absorber design for the following reasons:

1. COS causes degradation of the more commonly used (and cheaper) solvents such as monoethanolamine (MEA) and DEA (Kohl and Riesenfeld, 1985, p.36). This can be retarded somewhat by adding alkali to the solution (Berlie et al., 1965); however, the rate of solvent loss is still unacceptably high.

2. The kinetics of COS absorption are much slower than those of CO₂ (which are in turn slower than those of H₂S). Sharma (1964) found the rate of chemical reaction of a range of amine and alkanolamine solvents (including MEA, DEA and diisopropanolamine, DIPA) with COS to be roughly one-hundredth the rate of reaction with CO₂. Littel et al. (1992 a) extended this work to include other primary and secondary amines with similar results. Tertiary amines give somewhat better performance, COS being absorbed at the same rate as CO₂ in methyldiethanolamine (MDEA) solutions (Al-Ghawas and Sandall, 1991); however, the absorption of CO₂ by these solutions is not as rapid. The mechanism of solvation of CO₂ and COS in tertiary amines is different from that in primary and secondary amines. In the latter case the amine is able to react rapidly with dissolved CO₂, forming carbamate ions (thiocarbamate ions in the case of COS), which then undergo hydrolysis to bicarbonate (or bicarbonate and bisulfide). Tertiary amines are unable to form carbamate or thiocarbamate ions and consequently absorb CO₂ or COS more slowly as the rate of absorption is limited by the rate of the hydrolysis reaction.
The slower rate of reaction between $\text{CO}_2$ and tertiary amines increases the height of packing (or number of trays) required in the absorber, and the cost per mole of solvent is also much greater (Kohl and Riesenfeld, 1985). Al-Ghawas et al. (1989) describe the kinetics of COS absorption in MDEA as not being influenced by the hydrolysis of COS:

$$[\text{COS}]_{\text{soln}} + H_2O \rightarrow [\text{CO}_2]_{\text{soln}} + [H_2S]_{\text{soln}}$$  \hspace{1cm} (7.1)

Littel et al. (1992 b,c) dispute this and provide evidence that the rate-determining step for COS absorption in MDEA is the base-catalyzed hydrolysis reaction. This is in agreement with the work of Ernst et al. (1990), who proposed a two-stage mechanism for COS hydrolysis in tertiary amines, with base-catalyzed hydrolysis as the rate-determining step. Sharma and Danckwerts (1964) also suggest that the rate of COS hydrolysis is very low at 25 °C, however they base this statement on the work of Thompson et al. (1935) who carried out experiments in neutral solutions at 25 °C. Thompson et al. (1935) suggested the hydrolysis reaction was base-catalyzed, but did not report kinetic experiments in basic solutions. The hydrolysis rate constants discussed by Sharma and Danckwerts (1964) are therefore too low and the data of Littel et al. (1992 b) are to be preferred. COS absorption in alkanolamine solutions is also considerably improved by the addition of physical solvents to the chemical solvent. Hill (1976) improved absorption of COS in MDEA solutions by adding between 5 and 45 weight % sulfolane to the solution. Sykes (1976) achieved the same result for DIPA by adding up to 30 weight % of various sulfolanes. Various other chemicals have been found to act as homogenous catalysts for COS hydrolysis in alkanolamine solutions, and there are a number of patented processes based on these (Chen et al., 1984, Correll and Friedli, 1982). A good list of mixed solvent systems for promoting COS hydrolysis is given by Ernst and Chen (1988). Reilly et al. (1990) also describe hydrolysis catalysts.
Because of the difficulties described above it can be advantageous to remove the COS prior to the absorption stage. This would allow the use of a cheaper, more effective solvent such as MEA or DEA for the second absorber/stripper loop, with a consequent reduction in equipment size, fluid inventory and operating costs. Since both CO\(_2\) and H\(_2\)S should be removed from the product gas as completely as economically feasible, there is no need for a selective solvent to be used and DEA would be suitable for this loop.

Carbonyl sulfide can be removed from the gas by carrying out the hydrolysis reaction in a separate vessel (labelled "hydrolyzer" in Fig 6.2) between the sulfur condenser and the second absorber column. There are a number of possible strategies for performing the hydrolysis reaction:

i) COS and H\(_2\)O react to CO\(_2\) and H\(_2\)S in the vapor phase if contacted with suitable catalysts. George (1974b) found that basic sites promote the reaction. Chan and Dalla Lana (1978) describe hydrolysis using a promoted alumina catalyst, and the kinetics and mechanism for this reaction are given by Fiedorow et al. (1984). Other vapor-phase catalysts and processes are described by Yoshikawa et al. (1990), Nozue et al. (1985), Mori and Okada (1986) and Mori (1988). Vapor-phase reaction is not as satisfactory as reaction in solution, since the concentrations of both reagents and catalysts are much lower and the reactor volume required for the same conversion is therefore greater.

ii) Sykes (1976) proposed contacting the gas with a circulating solution containing DIPA and tetramethylene sulfone at 50 - 90 °C. The solvent would be allowed to become saturated with CO\(_2\) and H\(_2\)S, but at these temperatures the rates of absorption and
desorption are both high. COS is absorbed and hydrolyzed, and the CO₂ and H₂S thus produced are desorbed and passed on to an absorber column for selective absorption. Operating the absorber at higher temperature reduces the retention of acid gases in solution (although it increases both absorption and desorption rates), but also greatly increases the rate of hydrolysis and thus allows complete conversion of COS prior to the absorption stage.

iii) A similar, but hitherto untried, process would be to contact the gas with a hot potassium carbonate solution under essentially the same conditions described by Sykes (1976). Kohl and Riesenfeld (1985, p.230) report that better than 99 % removal of COS has been achieved using K₂CO₃ solutions at 85 °C, though they do not refer to a particular study and it is not clear how many stages were required. Dunlap and Galstaun (1982) state that COS bypasses hot K₂CO₃ solutions; however, they cite no experimental data to support this. Rousseau et al. (1987) studied the rate of COS absorption in 10 - 30 wt % K₂CO₃ and found high recoveries were attainable (up to 96 % under the conditions examined). The optimum solution concentration for COS removal was around 20 wt % K₂CO₃ (higher concentrations were better for CO₂ and H₂S removal) and the rate of COS removal depended primarily on temperature, indicating the importance of the hydrolysis reaction. Rousseau et al. (1987), studying scrubbing of coal gas, found no loss of solvent activity as a result of reaction with any of the coal gas constituents. Rib et al. (1983) also used K₂CO₃ solutions to scrub coal gas and found COS removals of roughly 30 - 40 % at 85 °C. Their apparatus was arranged to maximize selectivity of H₂S absorption over CO₂ absorption, therefore CO₂ (and hence COS) absorption would have been low.
It is possible that the rate of COS removal could be increased further by adding a physical solvent or alkanolamine to the solution. Rousseau et al. (1987) found that COS recovery increased from 72.7% to 91.7% when 5 wt% DEA was added to a 30 wt% K₂CO₃ solution (all other things being equal). Chaudhuri and Sharma (1989) found the rate of COS absorption into NaOH solution was enhanced by roughly a factor of 2 when an emulsified second phase of toluene or 2-propanol was present. Clearly, improving the absorption of COS will only increase the overall conversion under conditions where the COS concentration in aqueous solution is increased; however, this is worthy of further investigation. Other advantages of using hot K₂CO₃ solution are discussed below, as are process configurations and equipment design.

7.1.2 Removal of SO₂

Sulfur dioxide is present in the reactor quench gas at a level between 10 and 200 ppm. SO₂ reacts irreversibly with alkanolamines and must therefore be removed prior to the second absorber if solvent degradation is to be avoided. An advantage of using a hot potassium carbonate stage is that SO₂ reacts rapidly and irreversibly with carbonates forming potassium sulfite (K₂SO₃) (Kohl and Riesenfeld, 1985, p. 389). In the presence of H₂S, thiosulfate and other sulfoxy compounds will form. This would cause slow degradation of the K₂CO₃ solution, but would remove essentially all of the SO₂ and thereby protect the more expensive alkanolamine solution in the second absorber/stripper loop. It may be necessary to periodically replace or regenerate the K₂CO₃ solution; however, the time required for the solution concentration to fall significantly will depend on the inventory of hydrolyzer solution. For an SO₂ concentration of 200 ppm (the maximum expected) and a flowsheet basis of 50 tons of sulfur per day, K₂CO₃ is lost at a rate of 10.9 kg/hr.
An alternative, and rather effective, method of removing the SO₂ and preventing degradation of the hydrolyzer liquid is suggested by an experimental observation described in Section 5.6. It is well known that when H₂S and SO₂ are bubbled through water a milky solution is obtained, known as Wackenroder's liquid. This solution contains colloidal sulfur, hydrogen sulfide, thiosulfate, sulfite and polythionic acids (Yost and Russell, 1946). If the gas from the sulfur condenser were contacted with a recirculating hot water stream in a suitable vessel (which need not be very large due to the rapid rates of reaction), then significant removal of SO₂ would be achieved. The solution thereby formed is highly corrosive; however, it is easily disposed of by injection at a suitable point upstream of the sulfur condenser of the ZESP or into the combustor of a sulfuric acid plant, so there would be no emissions liability. The solution could therefore be replaced regularly with fresh water and the degradation rate of the more expensive hydrolyzer solution would be much reduced. Adoption of such a scheme would depend on whether the extra capital cost for a small packed vessel and circulation pump was justified by the improved performance of the hydrolyzer. This would be determined at the detailed design stage.

7.1.3 Process Configuration and Equipment

The base case flowsheet (Fig. 6.2) shows the hydrolyzer as a separate column between the sulfur condenser and the second absorber. In practice it may be possible to combine the hydrolyzer and the second absorber inside the same column, depending on the number of stages required.

The hydrolyzer must provide sufficient stages to allow complete conversion of the COS to CO₂ and H₂S. Water must be provided to compensate for the H₂O lost from the solution by...
the hydrolysis reaction; however, since the gas from the sulfur condenser contains 11% H₂O this water can be provided by condensation from the gas. If the hydrolyzer feed contains 2% COS, cooling the gas to 44 °C will provide sufficient water to maintain a constant concentration of the K₂CO₃ solution. The gas must be further cooled to 20 °C or less before entering the second absorber, and this can be done by contacting the gas with chilled water in a separate set of stages. The best arrangement is therefore to place the gas-cooling stages above the hydrolysis stages and reduce the water content of the vapor to 7.4% (saturated at 1 bar, 40 °C). A portion of the water thus removed from the gas can be bled to the hydrolysis stages to maintain carbonate solution concentration, as shown in Fig. 7.1. Surplus water from this system could be used as make-up in the first absorber/ stripper loop.

Figure 7.1 Carbonyl Sulfide Hydrolyzer
7.1.4 Design of the Second Absorber/Stripper Loop

The second absorber operates under conditions not normally encountered in gas cleaning. The feed to this absorber contains roughly 40 mole % \( \text{H}_2\text{S} \) and 34 mole % \( \text{CO}_2 \), both of which must be removed to low levels. The molar flowrate of the gas therefore decreases by roughly 80 % through the column.

In practice most of the \( \text{H}_2\text{S} \) is absorbed very rapidly, typically in the first few feet of packing. The height of the column is therefore determined by the number of stages required to remove the \( \text{CO}_2 \) to the desired level. In the case where the product gas is to be sent to a shift reactor for conversion to hydrogen, a high recovery of \( \text{CO}_2 \) is not necessary as the \( \text{CO}_2 \) will be absorbed after the shift reaction and may then be recycled to the ZESP reactor feed (via stream 32 in Fig. 6.2). In the case where the product gas is used as a fuel, the presence of \( \text{CO}_2 \) in the gas lowers the heating value, but otherwise is not harmful. There is therefore considerable scope for optimizing the design of the second absorber, depending on the product gas requirements. For the purposes of this study it was assumed that the product gas contains only 1 mole % \( \text{CO}_2 \). This is a safe-side approximation that imposes the most stringent conditions that might be expected for the absorber.

The column diameter was calculated based on the total inlet gas flow, \textit{i.e.}, including \( \text{H}_2\text{S} \), and was found to be 70 inches. The method of calculation was taken from Kohl and Riesenfeld (1985) and involved predicting the flooding limit using the correlation of Eckert (1970). The reduction in diameters allowed if \( \text{H}_2\text{S} \) is not included in the flow is small (8 inches). The number of transfer units required to reduce the \( \text{CO}_2 \) vapor fraction from 34 % to 1 % is roughly 3.5.
The height of a transfer unit is roughly 10 ft at the top of the column and 29 ft at the bottom. An average value of 20 ft was therefore assumed as an approximation, giving a total height of 80 ft (allowing for disengagement spaces, distributors, etc.). This probably overestimates the height required, as most of both the CO₂ and the H₂S are absorbed in the lowest few feet of packing.

Because of the large amounts of acid gas absorbed and high solution loadings, the heat of reaction causes the temperature of the solution to increase by roughly 15 °C. This temperature rise has an adverse effect on the sorbent properties of the solution and therefore should be prevented if possible. The heat of reaction can be removed by circulating a part of the absorber solution through a cooling loop and returning it to the lower stages of the column. Other strategies are also possible, and this is something that would be addressed at the detailed design stage.

The design of the second stripper was straightforward and followed the procedure recommended by Kohl and Riesenfeld (1985).

7.2 Materials Selection

The materials of construction used for most of the ZESP will be selected based on experience of what works well in similar processes. Absorber/stripper units are common in refineries, sulfur condensers are found on all Claus plants and vessels containing hot potassium carbonate solutions (similar to the hydrolyzer) have been tested on a coal gasification plant (Rib et al., 1983), so materials for these units can easily be identified. A more difficult selection
problem is what material to use for the construction of the furnace and quench tubes. These tubes must withstand high temperatures and extremely corrosive gases and should also have high thermal conductivity. The cost of the material from which the tubes are manufactured may be a significant factor in the overall process economics (see Section 7.5); however, because of the tough requirements imposed by the process, materials performance may be more important than cost in selection.

In practice the selection of materials must involve experimental trials, possibly in a pilot-plant that allows test sections of different materials to be exposed to the exact process conditions. For meaningful results the exposure time must be several thousand hours, although some preliminary selection may be made by exposing coupons of the material to process gases for shorter times. Such detailed analysis is beyond the scope of this work. This section discusses the requirements for furnace-tube and quencher materials and evaluates some materials that may be suitable candidates.

7.2.1 Process Requirements

The gas that enters the high-temperature furnace at roughly 600 °C contains a 60/40 mixture of CO\textsubscript{2} and H\textsubscript{2}S, dry basis, saturated with water at some temperature between 10 and 40 °C. (For example, if the water saturation temperature is 40 °C, the gas composition is 38.5 % CO\textsubscript{2}, 57.8 % H\textsubscript{2}S, and 3.7 % H\textsubscript{2}O). The gas is heated and undergoes reaction as it passes through the furnace tubes, the catalyst being contained inside the tubes, as described in Chapter 6. When the gas leaves the furnace it is at 950 °C and contains significant amounts of CO, H\textsubscript{2}O, H\textsubscript{2}, S\textsubscript{2} and COS in addition to unreacted CO\textsubscript{2} and H\textsubscript{2}S and small amounts of SO\textsubscript{2} and
CS$_2$ (a typical composition is given in Section 6.3). This atmosphere is of the type described by metallurgists as a "reducing, mixed-gas" environment, though we can note that it is only very mildly reducing. On their outer side the tubes are exposed to hot combustion gases formed from the burning of furnace fuel, and this may be described as an oxidizing environment. The furnace tube material must therefore be resistant to both the oxidizing and the reducing, sulfur-containing environments at temperatures up to 1000 °C.

In the case of the quench boiler the gas entering is the same as that leaving the furnace. This gas is cooled to 650 °C, but maintains roughly the same composition, due to the quench (see Chapter 5 and Section 7.3). For the best heat-transfer properties the gas would be sent to the shellside of the boiler and the tubes would contain the boiling water. This gives a higher heat-transfer coefficient and allows the water to be boiled under higher pressure for the same tube wall thickness (see Section 7.3). A disadvantage of this arrangement is that the shell must also be made from material that withstands the hot, corrosive gas; therefore a trade-off must be made at the detailed design stage.

For both furnace and quench boiler tubes it is important that the tubes should not provide an appreciable resistance to heat transfer. The size of the furnace is partly determined by the length of tubing required to heat the gas, and the size of the quencher and quench rate achievable are also affected by the tube thermal conductivity. For practical purposes, however, the thermal resistance of the tubes is only important if the tube material selected is non-metallic.
7.2.2 Materials Properties

An excellent account of materials corrosion in high-temperature environments and the selection of materials for these environments is given by Lai (1990). In particular, Chapter 7.4 of Lai’s book addresses the selection of materials for reducing, mixed-gas applications such as the furnace and quencher of the ZESP. A few of Lai’s comments that will be of use in the specification of materials of construction for the ZESP are reproduced below.

In general high temperature alloys rely on the formation of oxide scales, particularly chromium oxide, Cr$_2$O$_3$, to resist both oxidation and sulfidation. Materials that resist sulfidation therefore usually have good oxidation resistance properties and the oxidizing environment on the outside of the furnace tubes will not cause additional corrosion problems. Most high-temperature alloys are Fe-, Co- or Ni-based, with chromium added to improve the corrosion resistance. The sulfidation rate is strongly dependent on the chromium content and increases as the Cr fraction is reduced. A good rule of thumb is that the chromium fraction should not be less than 25 %. Sulfidation resistance can also be increased by adding small amounts of titanium, silicon and aluminum, especially in conjunction with a high Cr fraction, although the amounts of Si and Al that can be added are constrained by fabrication difficulties (use of cast parts reduces this problem). In general high-cobalt alloys are better than Fe or Ni; most high-Ni alloys undergo rapid catastrophic failure, although some may give satisfactory performance, due to the presence of Cr, Ti, etc.

The poor performance of Ni is related to the sulfidation mechanism, which is known as breakaway corrosion. Initially the metal surface is covered by a strong chromium oxide scale.
Alloying elements (Fe, Ni, etc.) diffuse through this scale and form external sulfides. These sulfides are then able to form metal-metal sulfide eutectics that melt, giving liquid slags that cause the chromium oxide scale to break up, resulting in catastrophic sulfidation attack. The eutectic Ni-Ni$_3$S$_2$ melts at 635 °C, therefore Ni is particularly prone to this method of corrosion. Other eutectic melting temperatures are 880 °C for Co-Co$_4$S$_3$ and 985 °C for Fe-FeS. It is believed that the presence of Ti, Si or Al in the alloy reduces the rates of diffusion through the oxide scale and hence retards corrosion.

The dependence of corrosion on the oxide scale means that the sulfidation resistance of the alloy depends on both the partial pressure of oxygen and that of sulfur. For the atmospheres encountered at high temperature in the ZESP the oxygen partial pressure is not sufficient to maintain a stable oxide film, therefore the alloy has a limited life determined by the rate at which breakaway corrosion occurs. It is thus important that the material selected should have a high resistance to this type of corrosion. Some materials that might be suitable are described in the next section.

7.2.3 Suitable Materials

The materials that have been evaluated fall into three categories:

1. Materials that we expect to give satisfactory performance.

2. Materials whose performance may be satisfactory and which therefore should be tested under process conditions.
3. Materials that might be thought of as obvious candidates, but are in fact unsuitable.

The alloys have been rated on the basis of published data, chiefly from Lai (1990) and the manufacturers brochures. The data used were for mixed-gas, sulfur-containing, reducing environments; however, no data are available for the exact gas compositions encountered in the ZESP and the rankings are therefore necessarily approximate. The materials of the first and second categories should be subjected to tests as described above before final selection is made. Alloy compositions (in wt %) are given in Table 7.1 (Lai, 1990), together with approximate cost data for materials in the first and second categories.

The costs are given in $/ft for 1-inch schedule 40 tubing based on an order of 1000 ft. Schedule 40 tubing is quite thick; however, a considerable corrosion allowance would probably be given in designing the furnace. A large corrosion allowance is not necessary for the quencher, as the tube-wall temperature will be considerably lowered by the presence of the coolant. Incoloy 801 is not currently manufactured in 1-inch tubes, therefore the price was approximated from the price of 4-inch stock by multiplying by the ratio of the weights. Costs are based on prices quoted by manufacturers and may be subject to change depending on order size, etc.
7.2.3.1 Satisfactory Performance Expected

**Haynes HR 160** (Haynes International, Inc.)

This is a Ni-Co-Cr-Si alloy developed specifically for high-temperature sulfur-containing environments. Sulfidation resistance is excellent compared with stainless steels, Incoloy 800H, and the other Haynes alloys listed below, and oxidation resistance is also very good. Strength compares favorably with other high-temperature alloys (10,000 hour rupture stress is greater than 12 MPa at 980 °C) and thermal expansion is lower than 304 stainless, Inconel 601 or Incoloy 800H. Wear resistance is not high, but since no flowing solids are encountered in our system this is not expected to cause difficulties.

**RA 85H** (Rolled Alloys, Inc.)

This is a modified austenitic steel alloy containing high Cr, Al, Si and C and low Ni, developed for high strength and sulfidation resistance. RA 85H has been applied successfully in sulfur-containing atmospheres at 1100 °C. Its strength is considerably better than 310 stainless steel at high temperatures where the prime mechanism of deformation is creep-rupture. The average stress to rupture in 100,000 hours (11 years) is 500 psi (3.4 MPa), which is considerably higher than the stresses encountered in the ZESP furnace tubes, though not as good as HR 160. The 10,000 hour rupture stress is 6.2 MPa at 980 °C. The low Ni content and high Si and Al improve sulfidation resistance.
### Table 7.1 Composition and Cost Data for Materials Suitable for Furnace Construction

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cost $/ft for 1&quot; 40s tube</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Mo</th>
<th>W</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR 160</td>
<td>43.22</td>
<td>0.05</td>
<td>28</td>
<td>Bal</td>
<td>29</td>
<td>1.5</td>
<td></td>
<td></td>
<td>Si 2.75</td>
</tr>
<tr>
<td>RA 85H</td>
<td>20.02</td>
<td>0.2</td>
<td>18.5</td>
<td>14.5</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haynes 25</td>
<td>78.68</td>
<td>0.1</td>
<td>20</td>
<td>10</td>
<td>Bal</td>
<td>3.0*</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haynes 188</td>
<td>66.41</td>
<td>0.1</td>
<td>22</td>
<td>22</td>
<td>Bal</td>
<td>3.0*</td>
<td>14</td>
<td></td>
<td>La 0.04</td>
</tr>
<tr>
<td>Haynes 556</td>
<td>37.09</td>
<td>0.1</td>
<td>22</td>
<td>20</td>
<td>18</td>
<td>Bal</td>
<td>3.0</td>
<td>2.5</td>
<td>Ta 0.6, N 0.2, Zr, La</td>
</tr>
<tr>
<td>Incoloy 801</td>
<td>11.88*</td>
<td>0.1*</td>
<td>19-22</td>
<td>30-34</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td>Ti 0.75-1.5, Mn 1.5*</td>
</tr>
<tr>
<td>Haynes 6B</td>
<td>1.2</td>
<td>30.0</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td>1.5*</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Multimet N155</td>
<td>0.08</td>
<td>0.1</td>
<td>21</td>
<td>20</td>
<td>20</td>
<td>Bal</td>
<td>3.0</td>
<td>2.5</td>
<td>Cb+Ta 1.0, N 0.15</td>
</tr>
<tr>
<td>Incoloy 800H</td>
<td>0.1*</td>
<td>23</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td>14.4</td>
<td></td>
<td>Al 0.4, Ti 0.4</td>
</tr>
<tr>
<td>Inconel 601</td>
<td>0.2*</td>
<td>22-24</td>
<td>12-15</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RA 309</td>
<td>0.25*</td>
<td>24-26</td>
<td>19-22</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Si 1.2</td>
</tr>
<tr>
<td>RA 310</td>
<td>0.05</td>
<td>19</td>
<td>35</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RA 330</td>
<td>0.05</td>
<td>25</td>
<td>Bal</td>
<td></td>
<td>3.0</td>
<td>18</td>
<td>3.0</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>RA 333</td>
<td>0.05</td>
<td>25</td>
<td>Bal</td>
<td></td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RA 446</td>
<td>0.20*</td>
<td>23-27</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>N 0.25*</td>
</tr>
<tr>
<td>HA</td>
<td>0.2*</td>
<td>8-10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HH</td>
<td>0.5*</td>
<td>24-28</td>
<td>11-14</td>
<td>Bal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* - maximum
‡ - scaled from cost of 4-inch tube
7.2.3.2 Possible, But Less Satisfactory Candidates

**Haynes #25** (Haynes International, Inc.)

A Co-Ni-Cr-W alloy with high Co (51%), Cr, and W. Good oxidation and sulfidation properties (second only to HR 160 among Haynes alloys). High temperature strength is excellent due to the high Co fraction (alloys containing a higher Co fraction than this have poor fabrication qualities).

**Haynes #188** (Haynes International, Inc.)

A Co-Ni-Cr-W alloy with lower Co than #25 (roughly 40%) and low manganese. Good for oxidizing environments. Sulfidation in mixed-gas, reducing environments is slightly worse than #25, but better than Incoloy 800H or Haynes #556. Strength properties are slightly worse than #25.

**Haynes #556** (Haynes International, Inc.)

A Fe-Ni-Cr-Co alloy. Strength is not as good as #188, but sulfidation resistance is better in coal gas at high temperatures (though worse at intermediate temperatures, 700 - 800 °C).

**Incoloy 801** (Inco Alloys, Inc.)

High Ni, High Cr iron alloy modified from the common alloy Incoloy 800 by addition of a high Ti fraction. High Ti gives better strength properties and sulfidation resistance.
7.2.3.3 Unsuitable Materials

**Haynes #6B** - 57 wt% cobalt alloy with excellent sulfidation resistance (best of all materials listed), but poor formability and welding properties. Not available in tube stock.

**Multimet N155** - A Fe-Ni-Cr-Co alloy, predecessor to Haynes #556. Resists sulfidation slightly better than #556 in coal gas atmospheres and performs as well as #188 at high temperatures, though not as strong. Not available in tube stock.

**Incoloy 800H** - High Ni and Mn content causes strong susceptibility to breakaway corrosion.

**Inconel 601** - Poor sulfidation resistance in mixed-gas, reducing environments, low strength above 800°C.

**RA 309 and RA 310** - poor resistance to breakaway corrosion, poor creep properties at high temperatures.

**RA 330 and RA 333** - high Ni content gives high susceptibility to breakaway corrosion.

**RA 446** - high chrome ferritic alloy, low strength at high temperatures, but excellent sulfidation resistance. Not available in tube stock.

**HA and HH** - Fe-based casting alloys with high sulfidation resistance, usually used for magnets, tools and cutters. Not available in tube stock.
Zirconia - Zirconia (ZrO₂) is a ceramic material and has good high temperature strength and sulfidation properties, but can only be manufactured in 12-inch long tubes. Joining these tubes would impose severe fabrication difficulties. The thermal conductivity of this material is also low.

7.2.3.4 Lined Tubes

Another possibility that might be considered is the use of tubes containing a thin lining of material that resists attack by the corrosive gas. If the surface layer is thin enough the lining need not cause too great a reduction in the tube thermal conductivity. Linings of molybdenum, silicon or quartz would effectively protect the metal; however, fabrication difficulties would probably make this option more expensive than use of a suitable alloy.

7.3 Process Heat Recovery and Quench Operation

This section discusses energy use in the Zero-Emissions Sulfur Process and strategies for quenching the reaction products. The details of process heat integration cannot be determined at this stage; however, some preliminary conclusions can be drawn.

7.3.1 Process Energy Use

The process contains two main heat sinks, these being the high-temperature heat required to heat the reaction gases in the furnace and the somewhat lower-temperature heat required by the two stripper reboilers. There is therefore considerable scope for recovering heat from the
furnace gases and using this heat in the strippers. It is, however, impossible to recover all of the heat from the reactor gas. Some heat must be used to provide the enthalpy of reaction for the endothermic reactions (which outweighs that produced by the exothermic reactions) and some sensible heat is also lost when the gas enters the hydrolyzer. The net reactor heat consumption is therefore the enthalpy of stream 19 in Fig. 6.2 minus the enthalpy of stream 14. It is important to distinguish between this and the furnace heat duty. The net reactor heat consumption is primarily determined by the amount of heat needed to achieve a given conversion and is a function of the reactor inlet and outlet concentrations. The furnace heat duty depends on the proportion of the gas heating that is carried out in the furnace (as opposed to the interchanger or other equipment), and also the amount of steam produced in the furnace.

In some cases it may be economical to carry out all of the gas heating in the furnace and then cool the gas against boiling water in the quencher, E6. In this case the interchanger, E5, is removed from the process and extra duty is placed on the furnace and quencher. These vessels both have greater temperature driving forces (log mean temperature differences) than the interchanger, therefore there would be some saving in total area. It will be seen in the next section, however, that the cost of the furnace is much greater than the cost of the interchanger (Section 7.4). Removing the interchanger at the expense of increasing the furnace cost could therefore increase the overall process cost. An energy balance was calculated for the flowsheet given in Section 6.3. The heat loads estimated are shown in Table 7.7.

It can be seen that the stripper heat loads are much greater than the reactor heat requirement; however, these loads are somewhat inaccurate, due to the uncertainties in the design of the second absorber/stripper loop described above and in Chapter 6. The stripper duty
depends on both the amount of CO₂ and H₂S that is recovered and the required concentrations of CO₂ and H₂S in the clean gas. The stripper boil-up (pounds of H₂O per pound acid gas) is determined mainly by the H₂S concentration specified for the clean gas (see Section 6.3). The solvent flowrate is determined by the amount of material to be absorbed and equilibrium properties of the solvent. There is therefore scope for reducing the stripper heat loads if we can either increase the H₂S fraction in the clean gas, or else reduce the amount of CO₂ recycled (by increasing the H₂S fraction in the feed or bringing in a CO₂ make-up stream). Conversely, the process can be operated to give a very low H₂S fraction in the clean gas (less than 4 ppm); however, this will substantially increase the stripper steam requirement.

Table 7.2 Process Heat Requirements

Basis: 50 tons per day of Sulfur

(Stripper loads calculated assuming 20 ppm H₂S in clean gas)

<table>
<thead>
<tr>
<th>Duty</th>
<th>Heat Required (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor</td>
<td>1.92</td>
</tr>
<tr>
<td>First Stripper</td>
<td>2.42</td>
</tr>
<tr>
<td>Second Stripper</td>
<td>6.69</td>
</tr>
</tbody>
</table>

A further possibility for the process is to use the product gas stream as a part of the fuel for the furnace. This gas stream contains 66 mole % H₂ and 25 mole % CO and has a heating value (LHV) of roughly 10240 Btu/lb (55.4 kcal/mole). If all of this stream is used as fuel in the combustor we can produce roughly 4.6 MW, i.e., 42 % of the process heat requirement,
which considerably reduces process running costs. In some cases (see next section) the process would be run without the first absorber loop, in which case the product gas can provide 53% of the process heat. It should also be noted that the process has not yet been optimized and that more substantial energy savings may be possible at the detailed design stage.

7.3.2 Quench Operation

A key feature of the Zero-Emissions Sulfur Process is the quench following the high-temperature reactor. The gases leaving the reactor must be cooled rapidly to prevent the formation of byproduct COS, as discussed in Chapter 5. Slow cooling results in excessive COS formation, which not only increases the duty of the hydrolyzer and second absorber/stripper loop, but also increases the H₂S/CO₂ recycle, thereby considerably reducing process efficiency. The rate of cooling can be expressed as a quench rate in degrees-centigrade-per-second (or Ks⁻¹) and the effect of this quench rate on experimental yield was described in Chapter 5.

The temperature to which the gas must be quenched depends on the flow velocity of the gas and spatial arrangement of the process equipment; however, it has been determined experimentally that for gas velocities greater than 1 ms⁻¹ cooling to a temperature of 750 °C is sufficient. Experiments also showed that a quench rate of roughly 1000 Ks⁻¹ is sufficient to prevent re-equilibration of the H₂S-decomposition and COS-forming reactions (Chapter 5).

This section describes three alternative methods of performing the quench:

1. By injection of a water spray into the gas.
2. By cooling in a waste-heat boiler.

3. By heat-exchange to the reactor feed gas.

The quench rates achievable by each method are calculated and other factors important in selecting between the different methods are discussed. For purposes of comparison the quench rate from 950 to 600 °C was calculated. The gas was taken as having the composition given by chemical equilibrium at 900 °C and shown in Table 7.3. The heat capacity of this gas mixture averaged 1.21 J/g K over the temperature range of interest (using data from Perry and Green, 1985), therefore the cooling duty is 423.5 kJ/kg. Where necessary the gas flowrate was taken as 24.5 kg/s, which corresponds to a 250 tonne/day sulfur production basis, although the basis is unimportant for comparison between schemes.

<table>
<thead>
<tr>
<th>Species</th>
<th>CO₂</th>
<th>H₂S</th>
<th>H₂O</th>
<th>H₂</th>
<th>CO</th>
<th>S₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole Fraction</td>
<td>0.342</td>
<td>0.285</td>
<td>0.179</td>
<td>0.038</td>
<td>0.091</td>
<td>0.064</td>
</tr>
</tbody>
</table>

COS was counted as part of the CO₂ fraction

7.3.2.1 Spray Cooling

This method achieves cooling of the gas by spraying water droplets into it. The droplets evaporate rapidly due to the high interfacial area and large temperature difference between the gas and the liquid water. The droplet sizes typically range from 20 to 250 μm, the mass average
being roughly 100 μm. Particles between 220 and 250 μm constitute only 1% of the water mass (Arena, 1973). The quench rates achievable were determined assuming that the rate-limiting step is heat transfer to the drop, and depend on the droplet size, as shown in Table 7.4. The value of 56,000 Ks⁻¹ for 100 μm droplets may be taken as a reasonable average.

Table 7.4 Average Quench Rate from 950 to 600 °C for Spray Cooling
for Different Water Droplet Sizes

<table>
<thead>
<tr>
<th>Droplet size (μm)</th>
<th>250</th>
<th>200</th>
<th>150</th>
<th>100</th>
<th>75</th>
<th>50</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quench Rate (Ks⁻¹)</td>
<td>8900</td>
<td>1.4x10⁴</td>
<td>2.5x10⁴</td>
<td>5.6x10⁴</td>
<td>9.9x10⁴</td>
<td>2.2x10⁵</td>
<td>8.9x10⁵</td>
</tr>
</tbody>
</table>

In reality the quench rates achievable may not be as large as those calculated, since mixing effects will also play a role. The area around the droplet will become cooled below the bulk temperature of the gas and effects due to the presence of other droplets may also be non-negligible.

An overall energy balance also shows that to cool the gas from 950 °C to 600 °C it is necessary to add 0.117 kg H₂O/kg gas if the water is initially at 20 °C. This would increase the H₂O mole fraction from 18 mole % to 33 mole %, neglecting the effect of re-equilibration of any of the gas-phase reactions. This dilution of the gas stream somewhat reduces the sulfur recovery in the sulfur condenser and also increases the net reactor heat consumption by increasing the flow (and hence enthalpy) of stream 19.
7.3.2.2 Cooling in a Waste-Heat Boiler

In this method the gas is cooled in a counter-current heat-exchanger that uses boiling water as coolant. The steam thus generated may be used elsewhere in the process, or, if the steam is raised at sufficient pressure it may be fed to a steam turbine and used to generate electric power. In order to maximize the overall heat-transfer coefficient (and hence quench rate) the gas would be assigned to the shell side and the liquid to the tubes, although this increases the cost of the unit as described in Section 7.2. (If the gas is assigned to the tubes the heat-transfer properties are slightly worse, but the residence time also decreases, so the quench rate is much the same). The quench rate can be found from the gas temperature change divided by the gas-side residence time. To maximize the quench rate this residence time must be kept low, therefore a shell and tube arrangement is preferred to a furnace-box arrangement. Other heat-exchanger configurations (welded-plate, etc.) are not considered, since these would incur severe fabrication problems given the nature of the materials of construction that must be used.

The overall heat-transfer coefficient is strongly dependent on the flow properties and internal layout of the exchanger, therefore rather than developing several detailed designs the quench rate was calculated for a suitable range of overall heat-transfer coefficients. Sinnott (1983) recommends a range of 20 to 300 W/m²K for waste-heat boilers. If an extended-surface heat-exchanger is used then a value of 400 W/m²K is recommended by EPRI (Larson and Williams, 1987); however, it is unlikely that an extended-surface heat exchanger could be fabricated from materials that would withstand the high-temperature corrosive gas, so this is not a realistic option.
The residence time for the gas was taken as the volume of the shell, minus the volume of the tubes, divided by the gas flowrate. This neglects the volume occupied by baffles, blanked tubes and tie-rods, as well as baffle leakage and dead spaces, so the residence time calculated is a safe-side approximation. Only standard 1:1 heat-exchanger configurations were considered. Five lengths (8, 10, 12, 16 and 20 ft) and two tube diameters (1-inch and 3/4-inch) were compared in order to determine the shell diameter and volume occupied by the gas in each case, before selecting the smallest volume for calculation of the residence time. Shell diameters for standard tube-sheet counts were taken from Perry and Green (1985, p. 11-13 to 11-15). In all cases the smallest shell diameter was for a triangular-pitch tube arrangement. The results are summarized in Table 7.5.

<table>
<thead>
<tr>
<th>Overall Heat-transfer Coefficient (W/m²K)</th>
<th>Area Required (m²)</th>
<th>Optimum Tube Diameter (inch)</th>
<th>Optimum Tube Length (ft)</th>
<th>Quench Rate (Ks⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1027</td>
<td>3/4</td>
<td>20</td>
<td>5150</td>
</tr>
<tr>
<td>300</td>
<td>68.5</td>
<td>3/4</td>
<td>8</td>
<td>61,940</td>
</tr>
</tbody>
</table>

It should be noted that these are the average quench rates through the boiler and that the rate of gas cooling at the inlet is much greater than the average rate due to the greater temperature difference between the incoming gas and the coolant. Higher quench rates than those quoted will therefore be achieved in the critical high-temperature region. The water evaporation
temperature was taken as 250°C, which allows generation of steam at 40 bar, suitable for power generation. A higher quench rate could be achieved by using cooler water, but in view of the high quench rates achievable this does not appear to be necessary.

7.3.2.3 Heat-exchange to the Reactor Feed Gas

The third option is to cool the gas using the reactor feed as coolant. In this case the interchanger serves as the quencher and there is no need for a separate vessel to carry out the quench. This method allows direct recovery of the heat from the reactor gases (rather than indirect recovery in the form of steam); however, the gas-to-gas heat-transfer coefficients are low and the quench rates are therefore the lowest attained by any of the three methods.

The gas mass flowrates are identical and their heat capacities may be taken as being approximately the same, therefore the temperature difference between the streams is roughly constant. If the hot gas is quenched from 950 °C to 600 °C against cold gas coming in at 200 °C then the temperature difference is 400°C, which imposes a large thermal gradient on the tube walls, but helps compensate for the low overall heat-transfer coefficient.

In this case the hot gas is assigned to the tube-side, since the heat-transfer properties are not affected strongly by which gas is shell- or tube-side. Placing the hot gas tube-side increases the range of materials suitable for shell manufacture and increases the quench rate, since the tube-side residence time is lower than that for the shell side.

A range of heat-transfer coefficients were again considered. Sinnott (1983) suggests a
range of 10 to 50 W/m²K for gas-gas heat exchangers, although we may note that we expect the lower end of this range to be more realistic as the gas is at low pressure. The results are shown in Table 7.6.

Table 7.6 Quench Rates Achievable in a Gas-Gas Exchanger

<table>
<thead>
<tr>
<th>Overall Heat-transfer Coefficient (W/m²K)</th>
<th>Area Required (m²)</th>
<th>Quench Rate (Ks⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2594</td>
<td>2083</td>
</tr>
<tr>
<td>50</td>
<td>519</td>
<td>10,420</td>
</tr>
</tbody>
</table>

7.3.2.4 Selection of Quench Method

The range of quench rates achievable by each method is summarized in Table 7.7. As noted above, the more rapid the quench, the less byproduct COS is formed; however, economic considerations must also play a part in determining which method to use in practice. All of these methods give higher quench rates than were used experimentally.

The equipment costs for spray cooling are low, since no heat-exchanger is required, and the quench rates achievable are high, but there are many drawbacks with this method. Spray cooling does not permit recovery of the heat from the gas, and therefore increases process energy consumption. A substantial amount of water (0.117 kg/kg gas) is added to the process gas, which may cause byproduct formation (particularly SO₂), increases the amount of effluent water to be
treated, and reduces the recovery of sulfur in the sulfur condenser. Successful operation of a spray quench relies upon the formation of small droplets, and corrosion due to the process gases could make this difficult to achieve. For these reasons this method is not recommended.

**Table 7.7 Quench Rates Achievable by Different Methods**

<table>
<thead>
<tr>
<th>Quench Method</th>
<th>Quench Rates Achievable (Ks⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray Cooling</td>
<td>9,000 - 100,000</td>
</tr>
<tr>
<td>Cooling in a waste-heat boiler</td>
<td>5,000 - 62,000</td>
</tr>
<tr>
<td>Cooling in a gas-gas exchanger</td>
<td>2,000 - 10,000</td>
</tr>
</tbody>
</table>

The choice between the other two methods is more complicated and requires consideration of energy recovery and economics as well as quench properties. The waste-heat boiler is the most capital-intensive option since it requires an extra heat-exchanger, although it enables us to reach quench rates almost as high as spray cooling and also recover the heat from the gas in the form of steam. The gas-gas exchanger option requires one less exchanger (though of greater area) and recovers heat at a higher temperature, but has a less effective quench. The amount of heat recovered by quenching in the gas-gas interchanger can be increased if the temperature approach between the two gases is reduced; however, this is at the cost of greater area and lower quench rate, and it can be seen from Table 7.6 that the areas required for this unit are already large. Although the gas-gas quench recovers heat at a higher temperature this would only be advantageous if the heat thereby recovered could reduce the furnace heating requirement, since the stripper heat is required at much lower temperatures. Another important consideration is that
the quench boiler will have lower tube-wall temperatures than the interchanger. It may therefore be possible to use a cheaper material of construction for this unit, in which case the boiler option may be cheaper (and in some cases the interchanger may even be eliminated entirely, as discussed above). Final selection between these two methods will therefore be made on the basis of detailed design calculations that are beyond the scope of this work.
7.4 Process Economics

The economics of the Zero-Emissions Sulfur Process were evaluated for two cases, corresponding to different possible markets for the process. The first case is for a stand-alone plant producing 50 tons of sulfur per day, such as might be installed at a natural-gas well-head or other production facility. The second case is for a plant that produces 250 tons of sulfur per day, which would be suitable for installation in a large oil refinery. In the second case the first absorber/stripper loop is omitted from the process as desulfurization and acid-gas removal are normally carried out as part of other refinery processes and it is not necessary to duplicate the equipment. Case I would be suitable for treating 125 Mscf/day of a typical natural gas containing 1 mole % H$_2$S. Case II would be suitable for a refinery processing 200,000 bbl/day of a typical crude containing 1 wt % sulfur.

Costs for process equipment were calculated using data presented in Peters and Timmerhaus (1981). Installation factors were found using the procedure recommended by George et al. (1988). All costs are scaled to July 1992 using the CE (Chemical Engineering) Plant Cost Indices. Utility availability and costs are shown in Table 7.8, and the plant operating rate was taken as 8330 hours per year (95 %). It should be noted that the cost/Btu for low-pressure steam is somewhat lower than the cost/Btu of fuel. This is because it is common industrial practice to raise steam at high pressure and then expand down to lower pressures in a steam turbine thereby generating electricity. (In some cases the steam is raised using heat recovered from the exhaust gas of a gas turbine engine, in which case the electricity production is even greater). The cost/Btu of the low-pressure steam is therefore reduced to account for the credit obtained for this electricity. Detailed breakdowns of the cost estimates are given in
Appendix II.C, the discussion that follows highlights key considerations and compares the costs of the Zero-Emissions Sulfur Process with those of the existing technology (the Claus process).

It is important to note that these costs are based on very approximate designs. No attempts were made to optimize the process, and most process equipment was designed for a worst-case size (i.e., a substantial overdesign was incorporated to allow for process uncertainties). In general, the cost given should therefore overestimate the actual cost; however, this cannot be determined for certain until a more detailed design is performed.

Table 7.8 Utility Availability and Costs

<table>
<thead>
<tr>
<th>Utility</th>
<th>Cost</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Gas</td>
<td>2.00</td>
<td>$/10^3 scf</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.07</td>
<td>$/kW-hr</td>
</tr>
<tr>
<td>Steam (75 psia, saturated)</td>
<td>1.71</td>
<td>$/10^3 lb</td>
</tr>
<tr>
<td>Cooling Tower Water</td>
<td>0.10</td>
<td>$/10^3 gal</td>
</tr>
</tbody>
</table>

7.4.1 Case Studies

Case I: "Stand-alone" Plant - 50 tonnes of Sulfur per Day

This plant would be configured to operate independent of other site facilities, for
example, at a production well-head. The direct fixed capital (DFC) costs for the process are
given in Table 7.9 and operating costs are given in Table 7.10. The DFC cost for a Claus plant
and Tail Gas Unit to achieve the same sulfur recovery was estimated from Lynn et al. (1987) to
be $6.06 million in July 1992 prices. The operating costs for the Claus plant are roughly $325,000 per year, i.e., $162,000/year cheaper than the ZESP, which would offset the initial
capital advantage over a period of 11 years on a simple rate of return comparison. It must be
remembered, however, that the capital cost for the ZESP may be significantly overestimated for
reasons discussed below.

The main assumptions of this analysis are described below:

1. The most significant capital costs are incurred in the furnace reactor. The furnace
installed cost makes up 45% of the DFC cost, with roughly half of the furnace cost
coming from the cost of the reactor tubes.

The furnace was sized assuming the catalyzed rate of H$_2$S decomposition given
by Fukuda et al. (1978) and assuming the same catalyst loading as was used
experimentally by Fukuda et al. In practice, higher loadings may be possible; however,
catalyst degradation may also be important.

The cost for the furnace was taken as the cost of the tubes required for the
reactor plus the cost of a furnace required to meet the total heat duty (not just the high-
temperature duty). This makes allowance for uncertainties in the fabrication costs of the
furnace. The furnace tubes were taken as 4-inch Incoloy 801 (the most widely available
Table 7.9 Direct Fixed Capital Costs for 50-ton/day Sulfur Plant

<table>
<thead>
<tr>
<th>Section</th>
<th>Installed Cost, July 1992 ($ thousands)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>First Absorption Section</strong></td>
<td></td>
</tr>
<tr>
<td>Vessels</td>
<td>185</td>
</tr>
<tr>
<td>Heat Exchangers</td>
<td>324</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td>586</td>
</tr>
<tr>
<td><strong>Reactor Section</strong></td>
<td></td>
</tr>
<tr>
<td>Furnace Reactor</td>
<td>1,893</td>
</tr>
<tr>
<td>Heat Exchangers</td>
<td>674</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td>2,603</td>
</tr>
<tr>
<td><strong>Second Absorption Section</strong></td>
<td></td>
</tr>
<tr>
<td>Vessels</td>
<td>358</td>
</tr>
<tr>
<td>Heat Exchangers</td>
<td>662</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td>1,061</td>
</tr>
<tr>
<td><strong>Total Direct Fixed Capital Cost</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4,250</td>
</tr>
</tbody>
</table>
of the suitable materials) with 0.2-inch wall thickness. This gives a large corrosion allowance, and once again it may be possible to reduce costs when more design data become available. The bare-module cost for the furnace was found by this method to be $823 thousand. If, however, it were necessary to use a more expensive material to achieve this wall thickness then the cost would be greater. For example, with tubes made from RA 85H, the furnace bare-module cost is $1.1 million, giving a DFC plant cost of $4.9 million, i.e., an increase of 16% in total DFC cost. If thicker tube walls were needed this would also increase the capital cost; however, this cannot be determined until materials tests have been performed.

2. The major process operating cost is the cost of the furnace fuel (75% of the total operating costs). This was calculated assuming that the process must generate all the steam needed for the strippers, in addition to supplying the heat necessary for the
reaction. It was assumed that a part of this heat requirement would be met by burning the product gas as fuel in the combustor, since for the stand-alone plant the product gas has no other value.

The amount of heat required is mainly determined by the stripper heat loads, as described in the previous section. There is therefore considerable scope for reducing process operating costs by optimization of the two absorber/stripper loops. If the stripper duty could be cut by 20% the operating cost would be reduced to $385,000 annually, in which case the simple payback time for the Claus process to break even with the ZESP would be 30 years.

It should be noted that the difference in operating costs between the Zero-Emissions Sulfur Process and the Claus process is almost entirely due to the greater requirement for low-temperature heat to run the ZESP strippers. Producing this heat by burning fuel to raise low-pressure steam (as assumed) is a rather uneconomical way of meeting this demand. If low-pressure steam is available from elsewhere then the energy cost is significantly reduced and the ZESP operating cost becomes lower than that of the Claus process (see Case II), although it is best not to assume this for a "stand-alone" plant. Another alternative would be to burn the extra fuel beyond that needed for the reactor in a combined-cycle cogeneration plant, thereby providing the low-pressure steam and a substantial credit for the electricity produced. Either of these options make the ZESP operating cost less than that of the Claus plant, in which case the Zero-Emissions Sulfur Process is favorable in both capital and operating cost.
Other assumptions of the economic analysis are given in Appendix II.C. It should be noted, however, that all other equipment and operating costs are minor compared to the two discussed above, and that the uncertainty in these two is high enough to make detailed analyses of the other costs of questionable value.

Case II: "Refinery" Plant - 250 tonnes of Sulfur per Day

This plant would be configured to operate as part of a large, integrated fuel-processing facility, for example, a large oil refinery. In a typical oil refinery several processes will have desulfurization stages, therefore H₂S is recovered from the fuel at several locations and then sent to a single sulfur-recovery plant. The first absorber/stripper loop is therefore unnecessary as this equipment is duplicated elsewhere. Further capital and operating cost savings are described below.

The DFC costs for a 250-ton/day sulfur plant are given in Table 7.11 and operating costs are given in Table 7.12. The DFC cost for a Claus plant and Tail-gas Unit for the same duty is estimated as $15.9 million (adapted from Lynn et al., 1987). The annual operating cost for the Claus process is $1.47 million, which in this case is greater than the operating cost of the Zero-Emissions Sulfur Process. The Zero-Emissions Sulfur Process therefore not only has an initial capital cost one-third cheaper than the Claus process, but also has lower operating costs and therefore appears to be favorable under all circumstances. This advantage compared to Case I can be seen to come mainly from the removal of the first absorber/stripper loop and the substitution of low-pressure steam for furnace fuel in the operating costs (see below). It must be noted, however, that the costs for the Claus plant and SCOT tail-gas unit were adapted from
Table 7.11 Direct Fixed Capital Costs for 250-ton/day Sulfur Plant

<table>
<thead>
<tr>
<th></th>
<th>Installed Cost, July 1992 ($ thousands)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reactor Section</strong></td>
<td></td>
</tr>
<tr>
<td>Furnace Reactor</td>
<td>5,757</td>
</tr>
<tr>
<td>Heat Exchangers</td>
<td>1,772</td>
</tr>
<tr>
<td>Subtotal</td>
<td>7,623</td>
</tr>
<tr>
<td><strong>Second Absorption Section</strong></td>
<td></td>
</tr>
<tr>
<td>Vessels</td>
<td>957</td>
</tr>
<tr>
<td>Heat Exchangers</td>
<td>1,737</td>
</tr>
<tr>
<td>Subtotal</td>
<td>2,802</td>
</tr>
<tr>
<td><strong>Total Direct Fixed Capital Cost</strong></td>
<td>10,425</td>
</tr>
</tbody>
</table>

data presented by Lynn et al. (1987) and therefore contain certain assumptions regarding the degree of process integration of these plants. There will be considerable variation in the operating costs from one site to another, depending on the degree of process integration, relative costs and availability of low pressure steam, hydrogen, etc. The absolute difference between the operating costs of the two processes may therefore vary quite considerably from site to site, and should strictly be evaluated on a site-by-site basis. The results presented merely indicate that the operating cost for the ZESP decreases relative to that of the Claus process as the opportunities
for integration with other processes are increased. The difference between this case and Case I shows that the ZESP is particularly suitable for integration with other processes, especially those that produce low-grade heat.

Table 7.12 Annual Operating Costs for 250-ton/day Sulfur Plant

<table>
<thead>
<tr>
<th>Utility</th>
<th>Usage</th>
<th>Annual Cost ($ thousands)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Consumption</td>
<td>0 MW</td>
<td>0</td>
</tr>
<tr>
<td>Electricity</td>
<td>56 kW</td>
<td>33</td>
</tr>
<tr>
<td>Cooling Water</td>
<td>6404 gal/min</td>
<td>320</td>
</tr>
<tr>
<td>Steam</td>
<td>71,501 lb/hr</td>
<td>1,018</td>
</tr>
<tr>
<td>Total Annual Operating Cost</td>
<td></td>
<td>1,371</td>
</tr>
</tbody>
</table>

The furnace design assumptions were the same as for Case I, except that in this case it is not necessary for the furnace to raise the steam required for the stripper, so the furnace heating duty is reduced to the high-temperature heating duty (9.60 MW). In this case the heating value of the product gas is 20 MW, which is more than sufficient to meet the reduced furnace duty so no extra fuel is required.

Under certain circumstances it might be more economic to send the product gas to a shift reactor to produce hydrogen (depending on the site hydrogen requirements). In such cases there would be a credit for the product gas and the annual operating cost would be somewhat reduced.
The process operating cost was calculated assuming all the product gas is burned within the plant and the balance of the heat requirement is brought in as low-pressure steam. This can be seen to be a worst-case scenario equivalent to assuming that the product gas has no value other than as fuel. All other assumptions were the same as for Case I.

If the process product gas is used to generate hydrogen then a further saving may be possible for Case II by integrating the process with a hydrogen plant. In this case it is not necessary to remove CO₂ from the product gas to such a high degree, as the hydrogen plant contains a CO₂-removal stage after the shift reactor. (Care must be taken, however, to ensure that we do not send so much CO₂ to the hydrogen plant that the shift reactor conversion is adversely affected). This allows a saving in both the capital and operating costs of the second absorber/stripper loop. The extra CO₂ required to make up for that lost from the recycle would be introduced into the process as a make-up stream (stream 32 in Fig. 6.2), which could be purchased back from the hydrogen plant. The advisability of such a scheme would depend on the process savings and relative values of CO₂ and H₂, and therefore would be determined on a site-by-site basis.

7.4.2 Other Advantages of the Zero-Emissions Sulfur Process

In addition to the economic advantages listed above, the Berkeley Zero-Emissions Sulfur Process also has several operability advantages over the Claus process.

Firstly, the Claus process requires very tight control of the air-to-H₂S ratio to achieve an exact stoichiometric ratio of 2 H₂S to 1 SO₂ in the reactor sequence. If this ratio is upset slightly
then the unconverted H$_2$S or SO$_2$ is passed on to the tail-gas unit, creating considerable difficulties. For the ZESP the CO$_2$ to H$_2$S ratio is not critical, owing to the rather broad maximum in the process yield described in Section 4.4. The Zero-Emissions Sulfur Process is therefore much more robust and requires much less sophisticated control.

A similar problem is caused for the Claus process if the incoming H$_2$S stream is contaminated by hydrocarbon material. This is often the case if low-temperature, high-pressure absorption is used, due to condensation of organics in the absorber solution and subsequent vaporization in the stripper. If hydrocarbon material is present in the Claus process feed it consumes some of the oxygen from the air feed, making control of the H$_2$S-to-SO$_2$ ratio more difficult. Obviously fluctuations in the amount of hydrocarbon material present exacerbate this problem. For the Zero-Emissions Sulfur Process any organic material sent to the furnace will react with CO$_2$, forming carbon monoxide and hydrogen, and will end up as part of the product gas. This does not significantly affect the Zero-Emissions Sulfur Process (except to slightly improve the quality of the product gas).

A third advantage of the Zero-Emissions Sulfur Process is its scalability. The Claus process is not economically attractive below a certain size (roughly 25 to 50 tons of sulfur per day), due to the multistage reactor/condenser system. The Zero-Emissions Sulfur Process can easily be scaled down to 400 kg S/day, at which point the smallest column (the first stripper) would have a diameter of 4 inches. Such a plant could process roughly 1 million scf per day of a typical natural gas containing 1 mole % H$_2$S and would cost roughly $250,000 (estimated using the six-tenths rule). It is even possible that such a small plant could be designed to fit into a portable module (since the process contains no large machine drives). This would allow re-use
of the same plant at more than one well-head location as reserves decline and would facilitate use offshore, etc.

7.5 Assessment of Additional Work Required

This dissertation has described the development of the Zero-Emissions Sulfur Process from the experimental discovery that was its inspiration through analysis of the important chemistry to an initial process design. It is therefore appropriate that we should end by discussing the future work that must be done before the process can be implemented industrially. From the nature of the project it was inevitable that some areas requiring detailed analysis or extensive investment would be passed over in the interest of presenting as complete a version of the broad picture as possible, given the funds available. If sufficient interest is generated by this study then attention can be turned to these subjects.

The most important research needed from the standpoint of process development is the construction of a pilot plant to allow testing of furnace reactor materials. The uncertainty in the reactor cost is the most significant gap in our knowledge of process performance, and the material of construction for the reactor can only be selected properly once tests have been performed under process conditions. Once the reactor design is more certain it will be possible to carry out more detailed optimization of process conditions, since many possible methods of optimization (changing feed composition, removing the interchanger, etc.) will affect the reactor size and thus cannot be evaluated until the reactor material is known.

Development of better catalysts and supports, as described in Section 5.5.3, is also
important for process reactor design. If the catalyst performance can be improved, by increasing catalyst loading or otherwise, then the reactor size can be significantly reduced, giving a major saving in process capital cost. A more fundamental analysis of the reaction chemistry, as suggested in Sections 5.4.6 and 5.5.3, may also help improve catalyst and reactor design.

Another novel area of the design that has not been tried previously is the hydrolyzer containing a hot, recirculating potassium carbonate solution. Similar schemes were discussed in Section 7.1.1; however, it will be necessary to test this idea, firstly on a laboratory scale to evaluate the necessary design parameters, then on a pilot-plant scale to investigate the effect of trace components of the gas such as CS\textsubscript{2} and SO\textsubscript{2}. If SO\textsubscript{2} is to be removed using a "Wackenroder Column" as described in Section 7.1.2, then this should also be tested. Detailed design and optimization of the absorber/stripper loops (in particular the second loop) is not advisable until sufficient information on reactor costs and performance has been obtained to allow overall process optimization, \textit{i.e.}, after pilot-plant trials have been made. When such an analysis is performed methods for increasing solution loadings in both loops (for example, addition of a physical solvent, choice of chemical solvent, etc.) should be given careful consideration, as solution loading has a profound impact upon process operating costs.

The cost of building a pilot plant and of carrying out the other studies listed above is expected to be a significant investment; however, it is hoped that the benefits described in the previous section will justify the expenditure.
8. Conclusion

A process for the recovery of elemental sulfur from acid gases containing hydrogen sulfide has been developed, based on the experimental observation that elemental sulfur is formed when mixtures of hydrogen sulfide and carbon dioxide are heated to high temperatures and cooled rapidly.

The fraction of elemental sulfur formed at chemical equilibrium is favored by low pressures and temperatures in the range 800 °C to 1000 °C. Below this range large amounts of carbonyl sulfide, COS, are formed and above this range significant amounts of sulfur dioxide, SO₂, are formed. Both of these species impose operating difficulties on any sulfur-recovery process based on this chemistry. The presence of water vapor in the CO₂/H₂S mixture also slightly decreases the fraction of elemental sulfur formed at equilibrium.

The reaction was investigated experimentally and was found to occur via the thermal decomposition of H₂S, with the reaction equilibrium shifted by the rapid equilibration of the water-gas-shift reaction. Thermal decomposition of H₂S is therefore the rate-limiting step for H₂S conversion. The main byproduct formed is carbonyl sulfide, which is formed by a second-order reaction between H₂S and CO₂ that is somewhat similar to the water-gas-shift reaction. This reaction becomes significant at lower temperatures relative to the H₂S-decomposition reaction, but is less favored at high temperatures. Formation of byproduct COS on cooling can be prevented by quenching the gas rapidly to a low temperature at which the kinetics of the COS-forming reactions are slow enough to prevent re-equilibration within processing timescales. It was found experimentally that quenching to 650 °C at a quench rate of 1000 K/s was sufficient.
to prevent excess COS formation under the conditions studied. A computer model was developed using the chemistry described above, and this model gave good prediction of the experimental results and could be used for reactor design.

The reactor performance can be considerably improved by applying a catalyst for \( \text{H}_2\text{S} \) decomposition, for example, molybdenum disulfide, MoS\(_2\). Molybdenum disulfide exhibited a strong catalytic effect at all temperatures investigated (up to 900 °C) and did not appear to undergo deactivation during 24 hours exposure. Methods of improving catalyst fabrication, loading, etc. should be addressed as the subject of future work.

A process was designed based on this chemistry, and is as follows. Hydrogen sulfide is separated from the acid gas (e.g. refinery gas, coal gas, natural gas, etc.) by absorption into a suitable solvent in an absorber column. Carbon dioxide (which frequently accompanies \( \text{H}_2\text{S} \) in acid gases) is also removed at this stage. A gas stream containing only CO\(_2\) and \( \text{H}_2\text{S} \) can then be regenerated from the solvent in a second column known as a stripper. The mixture of \( \text{H}_2\text{S} \) and CO\(_2\) is reacted at high temperature to form water vapor, carbon monoxide, hydrogen and elemental sulfur and then quenched rapidly to preserve the high-temperature equilibrium composition. The sulfur is condensed from the gas stream at 120 °C and sent to storage. The remaining gases are treated to remove byproduct species such as SO\(_2\) and COS, and are then sent to a second absorber/stripper system to remove unreacted \( \text{H}_2\text{S} \) and CO\(_2\), for recycle to the reactor. By using this recycle we ensure that sulfur leaves the process only in the product stream of elemental sulfur. The final product gas contains primarily CO and \( \text{H}_2 \) plus small residuals of \( \text{H}_2\text{S} \) and CO\(_2\), and is valuable either as a fuel or as a chemical feedstock. The fraction of \( \text{H}_2\text{S} \) remaining in this stream is determined by the flow of steam to the second stripper and may be
controlled to a very low level, depending on process requirements and economic factors.

This process can be used to recover sulfur from any gas stream and can therefore be used in oil refineries, coal gasification plants or natural gas sweetening plants. The process is considerably cheaper to build than the existing technology, whilst the operating costs are comparable if sources of low temperature steam are available (for example, from a cogeneration plant or from elsewhere in the chemical site). A further advantage over the Claus Process is that the chemical (or fuel) value of the hydrogen from the $\text{H}_2\text{S}$ is recovered in a product gas stream that can be sold to generate extra income. The process also has several operability advantages over the Claus process and is easily scaled down to a relatively small size. In addition to these economic benefits this process produces negligible emissions of sulfur containing gases, and will therefore contribute to eliminating the problem of acid rain.
NOMENCLATURE FOR PART II

GC  Gas chromatograph
DEA  diethanolamine
MEA  monoethanolamine
SCOT  Shell Claus Off-Gas Treatment (process)
TEA  triethanolamine
ZESP  Zero-Emissions Sulfur Process

a        correlation constant for temperature profiles
b        correlation constant for temperature profiles
C_i     concentration of species i
C_{total}  total concentration of the gas phase
e_r     measure of the root-mean-square error between the kinetic model and the experimental data
F_s     standard flowrate used experimentally (2.935 mls⁻¹)
k        rate constant
k_1     first-order, non-catalytic, H_2S thermal decomposition rate constant
k_2     rate constant for non-catalytic thermal-recombination reaction between H_2 and S_2
k_{sg,f}  forward rate constant for the sulfur-gas-shift reaction
k_{sg,r}  reverse rate constant for the sulfur-gas-shift reaction
k_{sw}   rate constant determined by Schecker and Wagner (1969) for the non-catalytic thermal decomposition of COS
K_{sg}   equilibrium constant for the sulfur-gas-shift reaction
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>property evaluated under the conditions of the n\textsuperscript{th} interval</td>
</tr>
<tr>
<td>N</td>
<td>number of data points</td>
</tr>
<tr>
<td>P</td>
<td>total pressure</td>
</tr>
<tr>
<td>P\textsubscript{i}</td>
<td>partial pressure of species i</td>
</tr>
<tr>
<td>r</td>
<td>ratio between experimental conversion and that predicted by the model for the same conditions</td>
</tr>
<tr>
<td>R</td>
<td>ideal gas constant</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>Δt</td>
<td>residence time</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>T\textsubscript{gas, outer}</td>
<td>temperature of gas in reactor outer tube</td>
</tr>
<tr>
<td>T\textsubscript{inner}</td>
<td>temperature measured in reactor inner tube</td>
</tr>
<tr>
<td>T\textsubscript{set}</td>
<td>furnace set-point temperature</td>
</tr>
<tr>
<td>T\textsubscript{thermowell}</td>
<td>temperature measured in reactor thermowell</td>
</tr>
<tr>
<td>ΔT</td>
<td>temperature difference</td>
</tr>
<tr>
<td>x</td>
<td>distance from reactor inner tube entry</td>
</tr>
<tr>
<td>X\textsubscript{e}</td>
<td>experimental conversion</td>
</tr>
<tr>
<td>X\textsubscript{m}</td>
<td>conversion predicted by the model</td>
</tr>
</tbody>
</table>
REFERENCES FOR PART II


George, Z.M. Kinetics of Cobalt-Molybdate-Catalyzed Reactions of \( \text{SO}_2 \) with \( \text{H}_2\text{S} \) and \( \text{COS} \) and the Hydrolysis of \( \text{COS} \). \textit{J. Catal.} 1974a, 32, 261-271.


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Appendices
Appendix I.A  Apparatus Supplement

This Appendix contains a piping and instrument diagram of the apparatus used in Part I (Fig. I.A.1) and instructions on the operation of this apparatus for future users.

Referring to Fig. I.A.1, the initial state of the reactor is purged and vented, with SV113 open and all other valves closed. Before heating it is necessary to purge the reactor with CO₂. To prevent any possible emission of H₂S from the apparatus close SV113 and open SV114 and SV115. Open SV106 and SV110 and adjust the CO₂ flow using CV106 and FI106. After 10 minutes close SV110 and open SV111 — this purges the hot end of the reactor. After ten more minutes the initial purge is complete. The sample may now be loaded and left in the cool end of the reactor while the furnace heats. While the furnace is heating the experimental flow may be established by opening SV108 and the appropriate feed isolation and control valves. The furnace requires roughly two hours to reach thermal equilibrium.

The sample is loaded into the reactor by sliding the inner tube into the outer tube through the threaded fitting. (Be careful that the sample tube doesn’t collide with the thermowell as it is inserted). The sample tube requires less than one minute to reach thermal steady state. When the system is ready to be exposed to process gas close SV110, SV106 and SV108 and open SV107. The reactor and sample are now exposed to the process gas mixture. In some cases (e.g. sintering experiments) it may be advantageous to fill the reactor with process gas before inserting the sample into the high-temperature zone.

After the required exposure time the sample is removed from the furnace by withdrawing
Fig. I.A.1 Apparatus Piping and Instrumentation Diagram
the sample tube through the threaded joint. The sample should be allowed to cool under the process gas, then the process gas is switched back to the scrubbers by opening SV108 and closing SV107. The reactor is next purged by opening SV106 and SV111, followed by closing SV111 and opening SV110. After purging is complete, SV115, SV110, SV111 and SV106 must be closed before SV113 may be opened and the reactor vented. The cold-end stopper may now be opened and the old sample may be replaced with a fresh sample. This procedure is repeated as often as necessary.

At the end of a day's experiments the flow measurement section is purged with \( N_2 \). Close SV107, SV115, SV109 and all feed isolation valves except that of \( N_2 \). Open all feed control valves. With \( N_2 \) regulator outlet pressure set at 100 psi, establish a full flow of nitrogen, then open and close SV108 repeatedly. Closing SV108 causes the apparatus to be pressurized with \( N_2 \) and when the valve is opened the gas empties from all the flowmeters and control valves. Repeating the procedure considerably dilutes the residual gas in the flow measurement and control section.
### Appendix I.B Source and Purity of Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Source</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Mattheson Gas Products, Inc.</td>
<td>99.8 % (N₂, O₂, CH₄)</td>
</tr>
<tr>
<td>H₂S</td>
<td>Mattheson Gas Products, Inc.</td>
<td>99.5 %</td>
</tr>
<tr>
<td>CO</td>
<td>Mattheson Gas Products, Inc.</td>
<td>99.5 % (N₂, O₂, CO₂, CH₄)</td>
</tr>
<tr>
<td>N₂</td>
<td>A.L. Welding, Inc.</td>
<td>99.7 %</td>
</tr>
<tr>
<td>H₂</td>
<td>A.L. Welding, Inc.</td>
<td>99.99 %</td>
</tr>
</tbody>
</table>
Appendix II.A Kinetic Model Computer Code

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variables from data file or used in calculating temperature/time profile

implicit real*8 (a-h,o-z)
character*14 INFILE, OUTFILE, EXPNAME
dimension X(40), T(40), TABS(40), TAVE(40), VINT(40)
dimension TINT(40), RUNT(40)
real FLOW, FCARB, FWAT, FSULF, PRESS, QRATE, TMAX, TQ
real TTMAX, TLOW
integer IMAX, N, NN

variables used for rate and equilibrium constants

double precision KFOR(40), KREV(40), KWGS(40), KCLAU5(40)
double precision KCOS(40), KCOSR(40), KCOSB(40), KSNW(40)

c variables used for mass balances (C tot is in mole/cm3)

double precision PHS(40), PH(40), PS(40), CONV(40)
double precision NCARB(40), NCO(40), NWAT(40), NH(40)
double precision NS(40), NSO(40), NHS(40), NTOT(40)
double precision NCOS(40), CTOT(40)
double precision HPREV, SOPREV, TESTA, TESTB, ALPHA
double precision BETA, GAMMA, DELTA, BECOS, GACOS

246
KIN1 = 3
KIN = 5
KOUT = 8
IMAX = 38

read file names from data file furnace.dat

Open (unit=KIN1, file='furnace.dat', status='old')
read (KIN1, 10) INFILE
read (KIN1, 10) OUTFILE
Format (A14)
close(KIN1)

read in the temperature profile

open (unit=KOUT, file=OUTFILE, status='old')
open (unit=KIN, file=INFILE, status='old')
read (KIN,15) EXPNAME
Format (A14)
read (KIN,*) FLOW, FCARB, FWAT, FSULF, PRESS

do 20 i=1,IMAX
    read(KIN,*) X(I), T(I)
20    continue

write initial data to output file

write (KOUT,*) 'Conditions of experiment ', EXPNAME
write (KOUT,*) 'F/Fs = ', FLOW
write (KOUT,*) 'Feed composition'
write (KOUT,30) 'CO2 = ', FCARB, 'H2O = ', FWAT, 'H2S = ', FSULF
Format (A8, F6.3, A8, F6.3, A8, F6.3)
write (KOUT,35) PRESS
35 Format ('Pressure = ',1x, F6.3,2x,'atm')
convert temperatures to Kelvin

do 40 i=1,IMAX
   TABS(I) = T(I) + 273.2
40 continue

calculate average interval temperatures

TABS(IMAX+1) = 523
do 50 i=1,IMAX
   TAVE(I) = (TABS(I)+TABS(I+1))/2
50 continue

calculate the velocity and time spent in each interval

do 60 i=1,IMAX
   if (X(I) .GE. X(I+1)) then
      VINT(I) = 66.4E-6*FLOW*TAVE(I)
   elseif (X(I) .LT. X(I+1)) then
      VINT(I) = 0.001676*FLOW*TAVE(I)
   endif
   TINT(I) = (ABS(X(I+1)-X(I)))*0.01*NINT(I)
   CTOT(I) = PRESS*0.012904/TAVE(I)
60 continue

calculate the total run time and quench rate

RUNT(1) = 0.
do 70 i=1,IMAX-1
   RUNT(I+1) = RUNT(I) + TINT(I)
70 continue

do 80 i=1,IMAX
   if (T(I) .GT. T(I-1)) then
      TMAX = T(I)
      TTMAX = RUNT(I)
80 continue
else
    continue
endif

80  continue

   do 90 i=1,IMAX
      if (T(I) .GT. 600 .AND. T(I+1) .LE. 600) then
         TLOW = T(I+1)
         TQ = RUNT(I) - TTMAX
      else
         continue
      endif
   continue

90  continue

   QRATE = (TMAX - TLOW)/TQ

   c
   c write out answers for temperature profile and quench
   c

   write (KOUT,100) 'X', 'T', 'T ave', 'v (m/s)', 't int (s)', 'run t (s)'
   100 Format(A9,1x,A9,1x,A9,1x,A9,1x,A9,1x,A9)
   do 110 i=1,IMAX
      write (KOUT,105) X(I), T(I), TAVE(I), VINT(I), TINT (I), RUNT (I)
   105 Format(F6.1,4x,F6.1,4x,F6.1,4x,F8.6,2x,F8.6,2x,F8.5)
   continue

   write (KOUT,112) TMAX
   write (KOUT,114) TLOW
   write (KOUT,116) TQ
   write (KOUT,118) QRATE
   112 Format(' Quench from',3x,F6.1,1x,'C')
   114 Format(' to',12x,F6.1,1x,'C')
   116 Format(' in',6x,F12.6,1x,'s')
   118 Format(' Quench rate',3x,F6.1,1x,'K/s')

   c
   c calculate the kinetic and equilibrium constants for each interval
   c

   do 120 i=1,IMAX
      KFOR(I) = 2.46000e6*dexp(-20406/TAVE(I))
      KREV(I) = KFOR(I)/(274.2*dexp(-10930/TAVE(I)))
      KWGS(I) = 0.63981 - 0.00278*TAVE(I) + 2.85537e-6*(TAVE(I))**2
      KCLAUS(I) = 14.17716 - 0.04105*TAVE(I) + 3.00e-5*(TAVE(I))**2
   continue

249
DELTA = -1.413 - (1.075*dlog(TAVE(I))) + (10960/TAVE(I)) + (17770/(TAVE(I)**2))
KCOS(I) = 0.4347*dexp(-2917/TAVE(I))
KCOSB(I) = CTOT(I)*2.40e4*(dexp(-4000/TAVE(I)))
KCOSR(I) = KCOSB(I)/KCOS(I)
KSNW(I) = 1.905e12*(PRESS/TAVE(I))*(dexp(-30712/TAVE(I)))

continue

set the initial mass balance

NHS(1) = FSULF
NH(1) = 0.
NS(1) = 0.
NCARB(1) = FCARB
NCO(1) = 0.
NWAT(1) = FWAT
NCOS(1) = 0.
NSO(1) = 0.
NTOT(1) = FSULF+FCARB+FWAT
PHS(1) = FSULF*PRESS
PS(1) = 0.
PH(1) = 0.

d this is the top of the outer loop that solves each zone in series

do 500 i=1,IMAX-1

correct the interval time to allow for the change in the number of moles due to reaction

t TINT(I) = TINT(I)/NTOT(I)

calculate pH2S for the next stage

BETA = (KREV(I)*PH(I)*SQRT(PS(I))) + (KCOSR(I)*NWAT(I)*NCOS(I))
GAMMA = dexp(-(KFOR(I) + KCOSB(I)*NCARB(I))/TINT(I))
PHS(I+1) = PHS(I)*GAMMA + BETA*(1-GAMMA)/(KFOR(I) + KCOSB(I)*NCARB(I))
convert from partial pressure to No. of moles (n)

\[ \text{NHS}(I+1) = \frac{\text{PHS}(I+1) \times \text{NTOT}(I)}{\text{PRESS}} \]

find number of moles of COS

\[
\text{if} \ (\text{NWAT}(I) \leq 1e-15) \ \text{then} \\
\quad \text{BECOS} = \text{KCOSB}(I) \times \text{NHS}(I) \times \text{NCARB}(I) \\
\quad \text{NCOS}(I+1) = \text{NCOS}(I) + \text{BECOS} \times \text{TINT}(I)
\]

\[
\text{elseif} \ (\text{NWAT}(I) > 1e-15) \ \text{then} \\
\quad \text{BECOS} = \text{KCOSB}(I) \times \text{NHS}(I) \times \text{NCARB}(I) \\
\quad \text{GACOS} = \text{dexp}(-(\text{KCOSR}(I) \times \text{NWAT}(I) + \text{KSNW}(I)) \times \text{TINT}(I)) \\
\quad \text{NCOS}(I+1) = \text{NCOS}(I) \times \text{GACOS} \\
\quad \quad + \text{BECOS} \times (1-\text{GACOS}) / (\text{KCOSR}(I) \times \text{NWAT}(I) + \text{KSNW}(I))
\]

get an initial guess of pH2O and initialize the loop parameters

\[
\text{NWAT}(I+1) = \text{FWAT} + \text{FSULF} - \text{NHS}(I+1) - \text{NH}(I) \\
\text{NTOT}(I+1) = \text{NTOT}(I) \\
\text{NH}(I+1) = \text{NH}(I) \\
\text{NSO}(I+1) = \text{NSO}(I)
\]

\[
\text{if} \ (\text{NS}(I) \gt 1e-6) \ \text{then} \\
\quad \text{NS}(I+1) = \text{NS}(I)
\]

\[
\text{else} \\
\quad \text{NS}(I+1) = (\text{FSULF} - (\text{NHS}(I) + \text{NCOS}(I))) / 2
\]

\[
\text{N} = 0
\]

this is the top of the outer loop (for H2/H2O)

\[
N = N+1 \\
\text{ALPHA} = \text{KCLAUS}(I) \times \text{SQRT}(\text{NTOT}(I+1)/\text{PRESS}) \times (\text{NHS}(I+1)/\text{NWAT}(I+1))^{**2}
\]

initialize parameters for inner loop

\[
\text{NN} = 0
\]
this is the inner iteration loop solving for S2 and SO2

300  
NN = NN + 1  
SOPREV = NSO(I+1)  
if (NS(I+1) .LE. 0.000000000000 .AND. I .GT. 10) then  
    write(KOUT,*) 'S went negative at stage', I  
    NS(I+1) = 1.000000e-10  
    go to 550  
elseif (NS(I+1) .LE. 0.000000000000 .AND. I .LE. 10) then  
    NS(I+1) = 0.000000e-10  
    NSO(I+1) = 0.000000e-10  
    go to 350  
endif  
NSO(I+1) = (NS(I+1)**1.5)/ALPHA  
NS(I+1) = (NS(I+1) + FSULF - NHS(I+1) - NCOS(I+1) - NSO(I+1))/3  
NTOT(I+1) = 1 + NSO(I+1) + NS(I+1)  
TESTA = 1 - (SOPREV/NSO(I+1))

test convergence for inner loop

c

if (ABS(TESTA) .LE. 1e-6) then  
    go to 350  
elseif (NN .GT. 100) then  
    write(KOUT,*) 'S loop failed in 100 iterations at stage', I  
    go to 550  
else  
    go to 300  
endif

c
perform remaining mass balances

c
350  
HPREV = NH(I+1)  
NCARB(I+1) = FCARB - NSO(I+1) - (NCOS(I+1) + NWAT(I+1))/2  
NCO(I+1) = FCARB - NCARB(I+1) - NCOS(I+1)  
NH(I+1) = NCQ(I+1)*NWAT(I+1)/(NCARB(I+1)*KWGS(I))  
NWAT(I+1) = FWAT + FSULF - NHS(I+1) - NH(I+1)  
TESTB = 1 - (HPREV/NH(I+1))

test convergence of outer loop

c
if (ABS(TESTB) .LE. 1e-6) then
  go to 400
elseif (N .GT. 100) then
  write(KOUT,*) 'H loop failed in 100 iterations at stage', I
  go to 550
else
  go to 200
endif

c
this is the end of the loop, now convert n to p
c
400  PH(I+1) = NH(I+1)*PRESS/NTOT(I+1)
    PS(I+1) = NS(I+1)*PRESS/NTOT(I+1)
500  continue
c
calculate the conversion
c
550  do 600 i=1,IMAX
       CONV(I) = 1 - (NHS(I)/FSULF)
600  continue
c
cwrite out the answers
c
write(KOUT,*) 'Mole Fractions at Each Stage'
write(KOUT,610) 'x', 'T', 'H2O', 'H2', 'H2S', 'S2', 'COS', 'Conv'
610  Format(a6,1x,a6,1x,a10,1x,a10,1x,a10,1x,a10,1x,a10,1x,a10)
    do 700 i=1,IMAX
       write(KOUT,650) X(I), T(I), (NWAT(I)/NTOT(I)), (NH(I)/NTOT(I)),
                      (NHS(I)/NTOT(I)), (NS(I)/NTOT(I)), (NCOS(I)/NTOT(I)), CONV(I)
650  Format(f6.1,1x,f6.1,1x,e10.3,1x,e10.3,1x,e10.3,1x,e10.3,1x,e10.3)
    700  continue

c
write(KOUT,*) 'x', 'T', 'CO2', 'CO', 'SO2'
710  Format(a6,1x,a6,1x,a10,1x,a10,1x,a10)
    do 800 i+1,IMAX
write(KOUT,750) X(I), T(I), NCARB(I)/NTOT(I), NCO(I)/NTOT(I)
               NSO(I)/NTOT(I)
1
750 Format(f6.1,1x,f6.1,1x,e10.3,1x,e10.3,1x,e10.3)
800 continue
950 close(KIN)
close(KOUT)

END
Appendix II.B Error Analysis Supplement

This appendix gives additional details on the methods used to calculate the error in the experimental measurements. Discussion of these and other sources of error is given in Section 5.4.5.

Calculation of Errors

Errors were assessed numerically for those experiments that were most susceptible to the error in question. In general, these were the experiments carried out at low temperatures, low flowrates and low H₂S concentrations. In some cases the same experimental random error could affect the predicted conversion in several ways, for example, the error in the flowmeter readings affected the total flowrate, the feed concentration and the interpretation of the G.C. results. This was accounted for by determining the conditions that gave the maximum deviation in the conversion calculated and hence assessing the maximum error by comparing this value with the value originally calculated. Random errors were assessed in the standard way, i.e., by taking repeat measurements.

Gas Chromatograph Data Analysis

To minimize the effect of errors in the G.C. integration procedure the G.C. results were analyzed by dividing the smaller peak areas by the area for CO₂ (the largest peak). The ratios thus obtained could then be compared with calibrated ratios. For most experiments roughly 10 G.C. samples were taken at steady state, and some estimate of the random error can therefore
be found from the standard error between repeated measurements. The errors in the ratios were:

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Average (%)</th>
<th>Worst Case (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S/CO₂</td>
<td>1.55</td>
<td>1.99</td>
</tr>
<tr>
<td>CO/CO₂</td>
<td>5.5</td>
<td>9.4</td>
</tr>
<tr>
<td>COS/CO₂</td>
<td>23.2</td>
<td>37.0</td>
</tr>
</tbody>
</table>

However, the method of taking ratios (and the high CO₂ concentrations used) effectively screened out the error in the CO and COS concentrations, so that the error in the predicted CO₂ concentration was less than 0.3 %. Consequently, only the H₂S measurement error was passed on to the conversion.
Appendix II.C Detailed Cost Breakdowns

Cost Breakdown for 50 tonnes of Sulfur per day:

<table>
<thead>
<tr>
<th>Equipment Item</th>
<th>No.</th>
<th>Bare module cost ($1000)</th>
<th>Installation factor</th>
<th>Installed Cost ($1000)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MAIN ITEMS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R1 Furnace</td>
<td>1</td>
<td>823</td>
<td>2.3</td>
<td>1,893</td>
</tr>
<tr>
<td>D1 1st Absorber</td>
<td>1</td>
<td></td>
<td></td>
<td>116</td>
</tr>
<tr>
<td>D2 1st Stripper</td>
<td>1</td>
<td></td>
<td></td>
<td>69</td>
</tr>
<tr>
<td>D4 Sulfur Separator</td>
<td>1</td>
<td>6</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>D5 Hydrolyzer</td>
<td>1</td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
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Total Installed Cost (D.F.C.) 4,250

257
Cost Breakdown for 250 tonnes of Sulfur per day:

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<th>Equipment Item</th>
<th>No. of items</th>
<th>Bare module cost ($1000) (July 1992)</th>
<th>Installation factor</th>
<th>Installed Cost ($1000)</th>
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</tbody>
</table>

Total Installed Cost (D.F.C.) 10,425

The same installation factors were used as for the 50 tonnes/day plant, which causes the costs to be overestimated slightly.