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CaO INTERACTION IN THE STAGED COMBUSTION OF COAL

Final Report

By
Arthur Levy
Earl L. Merryman
Bruce W. Rising

December 19, 1983

Work Performed Under Contract No. AC22-80PC30301

Battelle Columbus Laboratories
Columbus, Ohio

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FINAL REPORT

Contract No. DE-AC22-80PC-30301
Battelle Project No. G7663

on

**CaO INTERACTION IN THE
STAGED COMBUSTION OF COAL**

to

U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY
TECHNOLOGY CENTER

December 19, 1983

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Arthur Levy, Earl L. Merryman and Bruce W. Rising

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REPORT SUMMARY

The LIMB (limestone injection multi-stage burner) process offers special potential for reducing NO_x and SO_x by at least 50 percent in coal combustion. This is to be accomplished by adding limestone with fuel and/or air in a low NO_x burner. This program has been directed to defining the chemistry and kinetics necessary to optimize sulfur capture in LIMB combustion. More specifically, this program has attempted to clarify the role of calcium sulfide in LIMB chemistry. When limestone is added in a staged burner, there is a strong possibility that under certain circumstances CaS is produced in the reducing (fuel-rich) zone of the burner. Since CaS is more stable than CaSO_4 , this affords the opportunity to (1) operate the burner at a higher temperature, 2200-2500 F, (2) pass the CaS rapidly through the high temperature zone (before dissociation), and (3) complete the combustion in a lean (air-rich) region where the sulfur is finally retained in CaSO_4 . For these reasons this program has concentrated on the high temperature chemistry and kinetics of CaS.

To achieve the program objective, the program was divided into three tasks. These involved (1) a study of CaS formation, (2) a brief examination of CaS oxidation, and (3) a laboratory examination of the combustion of coal in the presence of CaO under first stage, fuel-rich conditions.

In the most general sense, the study has shown that the formation of CaS in the reducing zones of the burner may be restricted by competing kinetics and thermodynamics. The addition of lime in LIMB

will require special care to optimize the ability to capture sulfur. The basis for this generalized conclusion is summarized below.

Task I - CaS Formation

CaS formation has been examined relative to its generation from pyrites and organic sulfur. In the absence of oxygen in the reaction between CaO and pyrite, up to 12 percent of the total sulfur can appear as SO₂. At a fixed Ca/S ratio increasing the temperature from 550 to 1100 C increased S₂ and SO₂ formation. Most of the sulfur is retained in the solid residue as FeS or pyrrhotites; the maximum CaS observed was 38 weight percent. Short reaction time experiments (1-2 seconds) suggest very little CaS production.

In experiments where the pyrite was dissociated prior to reacting with CaO (S₂ + CaO system) CaS production was more definite. Sulfur retention was markedly enhanced in the presence of carbon.

Kinetic experiments for reactions of H₂S or COS with CaO using a microdifferential reactor technique yield only CaS (no SO₂), and first order rate constants are in agreement with other studies using a TGA technique. Activation energies for the gas-solid reaction are low. Rate calculations based on these kinetic data suggest that CaS formation in the second or less available in a LIMB is very low. This raises important questions as to the best means for optimizing the LIMB process.

Task II - CaS Oxidation

A brief examination of the oxidation of CaS suggests that the oxidation may occur via different reaction paths. This is reflected in some reactions showing a gain and others a loss in weight. Conversion of CaS to CaSO₄ occurs with some loss of sulfur as SO₂ during oxidation. Exposure of CaS to oxygen at 1100 C for over one minute using the micro-differential reactor technique produced mainly sulfate in the solid,

with some loss of volatile sulfur species; exposure less than one minute left unreacted sulfide with some loss of volatile sulfur species.

Task III - CaS in Coal Flames

A methane-coal burner system was devised for the purpose of examining CaS formation in fuel-rich coal combustion zones. In this system CaO-impregnated coal was fed into the pre- and post-flame environments of a stoichiometric-to-slightly lean methane flame. The coal combustion products had residence times of 0.4-1 second in this environment and were analyzed for sulfur in the solids and gases. In this environment a definite correlation, similar to Freund's, exists between sulfur retention and carbon burnout, i.e., sulfur retention varied inversely with carbon burnout. In all the firings at residence times >300 msec less than one-third of the sulfur retained was identified as sulfide. At longer residence times most all of the sulfur retained was as sulfate, with only a minor amount as sulfide. More detailed examination of this system shows that CO₂ (from the methane flame) can react with CaS in the 1-2 seconds provided in the post-combustion zone. CO retards this reaction.

In general sulfur retention in these fuel-rich firings was limited to less than 35 percent sulfur retention at residence times above 500 msecs, suggesting that a LIMB-type capture process could be kinetically limited.

CaO-impregnated coal was also subjected to first-stage (fuel-rich) high temperature reactions without the methane flame combustion product environment. Under these conditions sulfur retention at 2100 F reached 70-80 percent; carbon burnout under this condition was 50-65 percent. Sulfur retention increased in these experiments with increased temperature, increased Ca/S ratio, and increased F/A ratio. It is not clear in these experiments how much of the sulfur was retained as sulfide or sulfate.

These last experiments, which approach more closely to the LIMB process, raise a series of important questions. Although our

results suggest that CaS formation may be kinetically limited in its formation in pyrite-CaO systems as well as H₂S- or COS-CaO systems, our results also show enhanced retention of sulfur when carbon (or coal or charcoal) is incorporated in the system. It is not clear from our current work to what extent sulfide and sulfate tie up the sulfur. Relating our current results to some of the early burnt lime chemistry of Turkdogen in his blast furnace studies suggests critical equilibria among CaO-CaS-CaSO₄. Relating our current results to the work we recently conducted for EPA on limestone-coal pellets for retention of sulfur in stoker combustion suggests that the source of the sulfur in coal may also be important relative to its influence on the efficiency of the LIMB process in pulverized coal firing or the efficiency of a limestone-coal pellet in stoker firing. In this situation our results suggest that CaO is more efficient in retaining organically-bound sulfur relative to the pyritic sulfur in a coal.

It is on the basis of these results in relation to those of other studies that we think that the chemistry of sulfide-sulfate processes in staged coal combustion require rather detailed examination if the LIMB process is to be optimized effectively. Suggestions for future work include (1) consideration of the apparent contradictions in H₂S-CaO versus H₂S-CaCO₃ kinetics, (2) examination of CaS-CaSO₄ equilibria in fuel-rich flame environments, and (3) examination of the effects of organic/pyritic sulfur ratios in coals on sulfur retention.

FINAL REPORT
on
CaO INTERACTIONS IN THE STAGED
COMBUSTION OF COAL

INTRODUCTION

The need for reliable and economic methods for reducing sulfur dioxide emission levels in the combustion of high sulfur coals is a formidable problem. The problem is further exacerbated by the fact that coal combustion generates sulfur oxides and nitrogen oxides and these sulfur oxide and nitrogen oxide emissions both contribute to current concerns of acid rain.

Technology is available to control the emissions of SO_x and NO_x by various post combustion treatment procedures such as flue gas treatment for SO_x the ammonia treatments, thermal DeNO_x and selective catalytic reduction for NO_x . In recent years, attention has focused on in-situ combustion techniques for controlling SO_2 and NO_x . These techniques incorporate the use of lime or limestone to tie up the SO_2 , and staged combustion to convert much of the fuel-bound nitrogen to free nitrogen. Most recently, attention has been directed to the combined in-situ control of SO_2 and NO_x via the Limestone Injection Multiple Burner (LIMB) program. In essence, this program aims to develop a coal burner which (1) keeps NO_x at a minimum by staging the fuel and air in the burner and (2) keeps the SO_2 at a minimum by introducing limestone at the optimum conditions where temperatures are low enough to retain the SO_2 as sulfate.

The capture of sulfur in a LIMB-type burner involves CaO-sulfur chemistry under both reducing and oxidizing conditions. This DOE

study is directed to analyzing the chemistry of sulfur capture in the above situation. The program reported here was initiated September 23, 1980, and culminated August 22, 1983.

OBJECTIVE

The program was aimed at defining the chemistry and combustion kinetics necessary to optimize sulfur capture with the ultimate applications of reducing the SO_2 and NO_x in the staged firing of pulverized coal. The specific objective of the program was to define the conditions for CaS formation when coal and limestone are present in the reducing environment of a fuel-rich first stage of a two-stage burner process.

Project Scope

In line with the introductory statements, sulfur capture chemistry in a LIMB-type burner calls for combining CaO first under rich and then under lean conditions with the sulfur species from coal*. This program has directed its attention to fuel-rich (first stage) conditions where coal and limestone might be added simultaneously. In accord with this situation, the program was separated into three tasks:

- (1) A study of CaS production.
- (2) A study of CaS oxidation
- (3) A staged combustion study of coal and CaO-treated coals.

This report is arranged in the same fashion. First, however, a brief technical discussion of CaO-sulfur chemistry, as it relates to this study, is presented.

* G. P. Carver, M. P. Heap, D. W. Pershing, D. P. Rees, and D. M. Zallen, Low Emissions Process and Burner, U.S. Patent 4,381,718 (May 3, 1983).

TECHNICAL BACKGROUND

LIMB technology encompasses the incorporation of limestone additions to low NO_x burner technology. Schematically the LIMB technology is illustrated in the EPA diagram of Figure 1 to which is added some of the fuel nitrogen- and fuel-sulfur chemistry which takes place in various regions of LIMB.

NO_x control is achieved in the fuel-rich zones of the burner. Fuel NO, i.e., via fuel bound nitrogen, is produced by two routes, the volatile NO and the char NO routes. In the devolatilization process the nitrogen constituents are converted to NO and N_2 via

The nitrogen in the char goes through a similar sequence

Sulfur-capture chemistry in LIMB may be more complex. First off, devolatilization of sulfur species is not as well defined as for the nitrogen species. As indicated in the figure, organic sulfur devolatilizes mainly as H_2S and COS, is partially oxidized to SO_2 , and presumably is partially converted to CaS in the fuel-rich zone. Pyritic sulfur is converted to H_2S via the dissociation of pyrite and the reactions of sulfur vapor with organic volatiles. Ultimately, any CaS is oxidized to CaSO_4 in the lean regions of the burner or furnace.

The mechanism by which sulfur capture occurs in a staged burner, i.e., the limestone injection multistage burner (LIMB), is generally accepted as occurring through CaS and CaSO_4 formation. This may be an accepted, but not a necessarily proven, mechanism. In this section, we touch on the background chemistry which comes into play in this process; in the program we have attempted to establish this chemistry in the laboratory.

FIGURE 1. STAGED COMBUSTION AND ASSOCIATED RICH AND LEAN S-N CHEMISTRY

FIGURE 2. MODES OF SULFUR IN A REDUCING ENVIRONMENT(1)

CaO-Sulfur Chemistry

Sulfur Release

In an oxidizing atmosphere sulfur release ultimately ends up as SO_2 (with some 1-3 percent of the sulfur as SO_3). Hence in-situ sulfur capture under standard oxidizing conditions involves principally SO_2 -CaO chemistry.

Sulfur release in a reducing atmosphere is not straightforward. Figure 2 from Attar's work in coal chemistry presents a useful description⁽¹⁾. As Attar points out, sulfur release can follow three paths. Path a, the left path in the figure, shows that the pyritic sulfur in coal will be released by two paths (only one is shown in the figure). At about 800 C most of the sulfur in coal is volatilized and the pyrite is dissociated

Hydrogen released from the coal at these temperatures will also reduce the pyrite to iron sulfide as shown in Figure 2.

At these temperatures, H_2S is evolved from coal, which in turn reacts with the basic ash minerals, path b the central path in the figure, to form mineral sulfides, CaS , FeS , MgS , etc. In path c, the right-hand path, the organic matrix in the coal structure tends to collapse at temperatures over 850 C, sealing off part of the pore structure in the coal. H_2S and hydrogen are also evolved at this time.

It is apparent from this picture that the reaction sequences in a LIMB, staged firing of coal there will be regions of sulfide formation and of sulfate formation.

The above comments notwithstanding a clear picture of sulfur release processes in coal is lacking. Solomon, in studies of the devolatilization of coal, observed a consistent buildup of sulfur in the volatiles relative to the original coal⁽²⁾. The sulfur content of the volatiles, predominately H_2S , was twice the sulfur content of the

original coal. Solomon also noted that the coal was more rapidly depleted of the organic sulfur than of the pyritic sulfur.

CaO-Sulfur Chemistry

A broad spectrum of the many reactions that may occur in a limestone-sulfur capture process are depicted in Figure 3.⁽³⁾ This analysis by Hsieh et al. shows how complex the chemistry can become in a coal system. The principal reactions which govern the sulfur capture process are:

Reducing*

Oxidizing

Equivalent reactions with CaCO_3 are not shown here; the carbonate is rapidly broken down to CaO early in the combustion process and the chemistry follows the CaO reaction shown. Using 1400K (2060 F) as a point of reference, the free energies per mole of CaS or of CaSO_4 show that CaS is more stable at temperatures above 2100 F.

* In these discussions inorganic sulfur in coal is considered in terms of pyrite, FeS_2 . Organic sulfur is shown here as H_2S . It must be recognized that this strongly oversimplifies the coal chemistry. One should include COS , CS_2 , and other organo-sulfur products. For the most part, however, the H_2S chemistry is sufficient to depict the role of organic sulfur in coal combustion.

FIGURE 3. THE TEMPERATURE RANGES OF THE REACTIONS⁽³⁾

Figures 4 and 5 show, respectively, equilibrium plots for H_2S and a nomograph for CaSO_4 . Using 4 percent H_2O as a point of reference in Figure 4, one notes that the pressure of H_2S can be maintained below 200 ppm at 1150 C (2100 F). Figure 5 shows the importance of temperature and excess air in maintaining the stability of CaSO_4 . Thus if the excess air is below 15 percent, SO_2 levels will be above 300 ppm at 2100 F.

Sulfur-Retention Fuel-Rich Systems

Sulfur retention in fuel-rich systems implies in large part the conversion of pyritic and organic (fuel-bound) sulfur to sulfides. Two basic investigations of sulfur retention by calcium are those by Skopov et al⁽⁵⁾ and by Brothers and Crandlemire⁽⁶⁾. Skopov et al ran a TGA/DTA analysis. Figures 6 and 7 summarize their observations. The DTA/DTG results show the stepwise formation of CaS , its decrease and the formation of an adduct $\text{FeS}\cdot\text{CaO}$. The curves also show the dissociation of pyrite and the slow conversion of pyrrhotites to sulfide. The pressure curves in Figure 7 show the formation of SO_2 following the release of free sulfur vapor. More will be said about this reaction system in the discussions of our experiments later in this report.

Brothers and Crandlemire's recent study on the pyrolysis of coal-lime mixtures was carried out under temperature in a quartz boat. Their results appear to satisfy the following chemistry.

FIGURE 4. H₂S EQUILIBRIA FOR EQUATION 3⁽⁴⁾

FIGURE 5. CaO-CaSO₄ NOMAGRAM

FIGURE 6. DTA/DTG FOR CaO-PYRITE⁽⁵⁾

FIGURE 7. GAS EVOLUTION FROM CaO-PYRITE⁽⁵⁾

Their studies showed that under these pyrolytic conditions some 80 percent of the pyritic sulfur and about 50 percent of the organic sulfur in bituminous coal was retained as calcium sulfide.

In another recent study, Schrodtt et al have examined the effects of iron oxides on the sulfur chemistry in coal ashes⁽⁷⁾. Their experiments were carried out in packed beds with gas passed through the bed. Their desulfurization studies with H_2S and Fe_2O_3 showed a significant conversion to Fe_3O_4 with the eventual formation of FeS . Migration of the iron to the particle surfaces enhanced the reaction rate and the sulfur capacity of the ash. This conclusion is in accord with some of Battelle's limestone-coal pellet combustion on stoker beds.⁽⁸⁾

In all the studies pertaining to sulfur retention under fuel-rich conditions the rate of sulfidation becomes important if one is to develop a practical process. Freund has developed kinetic data for the H_2S - CaO reaction using drop-tube type experiments⁽⁹⁾ whereby stones containing calcium and magnesium were dropped through a stream of H_2S at constant temperature. From a practical sense the results were not encouraging in that the absorption of H_2S was slow relative to the desurfacing of the sorbent.

Freund and Lyon have also extended this examination to the retention of sulfur in calcium oxide impregnated coals⁽¹⁰⁾. Their results which show a correlation between sulfur retention and fuel-stoichiometry are discussed later in this report relative to our own studies.

Kim, Feldman et al have also examined sulfur retention with a calcium oxide-treated coal⁽¹¹⁾. In this instance, the coal was impregnated into the coal structure via an aqueous slurry. In fixed-bed experiments the CaO -impregnated coal is taken through a gasification (reduction) stage, followed by a combustion (oxidizing) stage. A comparison of Figures 8a and 8b from their paper shows that the H_2S level is markedly reduced in the experiments with treated coal. Most of the H_2S released (2.18 percent, Figure 8a) is converted to CaS (75.7 percent S in the ash, Figure 8b) in the gasification of treated coal; only a very small fraction of this sulfide was converted to H_2S and/or SO_2 ,

FIGURE 8. FIXED BED GASIFICATION OF COAL
 (a) untreated
 (b) treated (BTC) coal

less than 0.02 percent, in the combustion stage with the addition of air and steam.

In summary, evidence is presented in the literature for the formulation of CaS under fuel-rich combustion. Under sufficiently rich conditions and with sufficient reaction time, sulfur in coal can be converted to calcium sulfide. The questions to be determined in the program at hand concern how fast and how much CaS is produced in a LIMB environment, i.e., are the kinetics and the thermodynamics favorable for LIMB-type burners?

TASK 1A. CHEMISTRY OF CAS FORMATION

Objective

The objective of Task 1 was to develop kinetic data on the rate of CaS formation for the express purpose of modeling the type of reactions taking place between calcium and sulfur compounds during the combustion of coal, particularly as they might occur in oxygen-deficient LIMB first stage environments. These studies focused primarily on reactions taking place in fixed beds in which different bed mixtures were exposed to various temperatures and gas-phase compositions.

Experimental: CaO-Solid Mixtures Reaction

Procedure

The procedure employed for examining CaS formation for pyrite-time reactions involved passing a stream of nitrogen over a boat containing a mixture of CaO and FeS₂ or over two boats in series where the pyrite was in the upstream boat and the CaO was downstream. The boats were in a tubular furnace where temperatures were controlled between 550 and 1100 C. The gas stream was monitored for sulfur species, mainly S₂

and SO_2 . The beds were analyzed for sulfide and sulfate. Figure 9 outlines the experimental layout.

FIGURE 9. EXPERIMENTAL SETUP

Reactants

The bed materials used in this phase of Task 1 were CaO-FeS_2 , CaO-sulfur , and $\text{CaO-FeS}_2\text{-charcoal}$ mixture. The mixtures were made from finely pulverized material and were thoroughly mixed by hand and rotation (several hours) prior to their use. The final mixtures contained Ca/S mole ratios in the range 0.50 to 3.0.

The CaO used in this study was a 98.8 percent purity Baker Reagent Grade material, 100 percent less than 325 mesh (44 micron). The CaO was checked for carbonate content by heating to 970°C for 10 minutes. The weight loss at temperature was 1.5 percent indicating negligible carbonate present.

Three different purities of pyrites were used in the experiments as indicated below.

Sample	Percent						
	Fe	S	C	H	N	O	H ₂ O
A. Pyrite "A"(a)	39.9	40.7	5.10	0.69	0.8	3.4	--
B. Pyrite (-325 mesh)(b)	43.9	51.6	0	0	0	--	0.14
C. Pyrite (-200 mesh)(b)	42.6	50.2	0	0	0	--	0.19

- (a) Crude sample obtained from Rico, Colorado Sample contained 1.3 percent organic sulfur.
 (b) Samples from C. E. Minerals, King of Prussia, Pennsylvania.

The different pyrites contained 76.2, 95.5, and 92.8 percent by weight FeS₂ for samples A, B, and C, respectively. The -200 mesh pyrite was used in most of the runs of this study.

The charcoal was heat-treated in nitrogen at 500 C prior to use to remove low temperature volatiles. The resulting charcoal had the following weight percent composition:

<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>Moisture</u>	<u>Ash and Oxygen (By difference)</u>
91.6	0.6	2.6	0.15	0.22	4.83

The charcoal contributed only a very small amount of sulfur compared to the total sulfur from the pyrite.

Reactor

A 1 to 1-1/4 inch O.D. x 24-inch long quartz tube placed in the core of a high resistance furnace was used as a reaction chamber.

Samples (about 1 gram) were placed in the entrance to the reactor via a tapered ground glass joint. Alundum and stainless steel boats were used to contain the samples in most of the runs. Results of preliminary runs with quartz boats suggested that the mixtures reacted with the quartz at times. The stainless steel boats were made of 0.001 in. foil to minimize heat sink effects in the short-term sample exposure studies. The samples were weighed before and after reaction to the nearest 0.5 mg except for some of the earlier experiments in which samples were weighed to the nearest 0.01 grams.

The sample and reactor were thoroughly flushed with nitrogen prior to inserting the sample into the hot reaction zone. Zone temperatures from 550 to 1100 C were used in this study.

An inert gas or gas mixture was passed over the sample during each run. Gas velocities ranged from 1 to 5 cm/sec at room temperature. Most of the samples were reacted at temperature in an inert environment of 99.995 percent pure nitrogen. Other environments used included N₂-O₂ (air), N₂-H₂O (saturated 25 C), Ar-CO (10 percent CO), and Ar-CO₂ (12 percent CO₂). Argon was used as a diluent with the CO and CO₂ to facilitate mass spectrometric analysis; the mass spectrometer was used in some of the earlier CaO-FeS₂ runs and some later runs containing charcoal.

Platinum/Pt 10 percent Rh and chromel-alumel thermocouples were used to measure the furnace and sample temperatures. In some instances, the thermocouples were placed in direct contact with the sample container. In most runs, the thermocouple was on the outside of the reactor implanted in an indentation in the reactor wall just above the sample container. Both procedures gave essentially the same temperature readings.

Instrumentation and Analytical Procedures

Generally, the exit gases from the reactor were passed through one or two cold traps depending on the SO₂ analytical procedure. The first trap was used to collect the condensible vapors, mainly sulfur.

The second trap, when used, was connected in series with the first trap and contained hydrogen peroxide (H_2O_2) to trap the SO_2 . When the second trap was not used, the exit gases, with condensibles removed, were directed to a Faristor or to a mass spectrometer for SO_2 analysis. Indication of the presence of H_2S was obtained by examining the Faristor data and the SO_2 -peroxide data since the former responds to H_2S but the peroxide oxidation does not.

Elemental sulfur released from the pyrite was collected in a cooled, quartz wool filter in the first trap. In most cases, the filter was weighed to determine the amount of sulfur deposited. In a few instances, the sulfur and filter were heated in an oxygen stream to several hundred degrees centigrade and the gases passed over hot platinum to ensure complete oxidation of the sulfur oxide(s) to sulfate. Whether the sulfur was weighed or oxidized to SO_2 and/or SO_3 , the data generally showed low sulfur values. Indications were that some of the sulfur failed to deposit in the quartz wool filter.

At the completion of a run, the sample was removed from the reactor and cooled to room temperature and weighed. The peroxide samples were titrated with barium perchlorate (using a Thorin indicator) to give the sulfate content of the solution. The sulfate value was then converted to an equivalent value of SO_2 collected.

Results

The reactions that were examined included:

- Reaction of CaO and FeS_2 in nitrogen in the time-temperature range of 5 to 15 minutes and 575 to 1100 C;
 $\text{Ca/S} = 0.5, 1.0$ and 3.0
- Reaction of CaO and FeS_2 in nitrogen in the time-temperature range of 1 to 130 seconds and 750 to 1100 C;
 $\text{Ca/S} = 0.5, 1.0$, and 3.0
- Reaction of CaO -pyrite-charcoal mixtures in the presence of N_2 , $\text{N}_2\text{-O}_2$, $\text{N}_2\text{-H}_2\text{O}$, Ar-CO , and Ar-CO_2
- Sequential reaction of CaO with sulfur vapors generated from FeS_2

- Reaction of CaO-S_2 and CaO-S_2 -charcoal mixtures in nitrogen
- The thermal stability of pyrite was also examined in the 575 to 1100 C range.

The results of these studies are presented below primarily in relation to the volatile products emitted from the reactions. Selected samples were analyzed by X-ray diffraction and by wet chemical techniques to determine the solid products formed in the reactions.

CaO-FeS₂ Reactions

Two sets of experiments were carried out with the CaO-pyrite mixtures. One set of experiments involved long-term exposures (5 to 15 minutes) primarily to determine the chemistry of the reaction, while the other set involved short-term exposure, mainly to determine the rates of the processes.

Long-Term Exposure. The experimental data are summarized in Table 1 where they are grouped in series according to temperature. The last three columns in the table present the results relative to the sulfur emitted and retained.

The two major volatile products observed from the reacting mixtures were elemental sulfur and sulfur oxides. The percent sulfur converted to SO_2 shown in the third from last column in the table was calculated from hydrogen peroxide data and would include any sulfur oxide oxidized in the peroxide. The major oxide was observed to be SO_2 ; SO_3 would not be expected in the absence of oxygen, while the other oxides, S_2O and SO , are less stable than SO_2 and would likely decompose or disproportionate.⁽¹²⁾

The percent sulfur retained in the solid (last column in the table) was calculated assuming the total sample weight loss was due solely to the volatile products observed from the reactions, that is, to the release of elemental sulfur and the formation of SO_x (determined from peroxide data). This assumption seems justified since the only

TABLE 1. REACTION OF CaO WITH FeS₂

Run	Ca/S	Temp, °C	Run Time (Min)	Sample Wt. Mg.		Wt. Loss	Percent of Total Sulfur in Sample		
				Total	Sulfur	Mg/Gram	Converted To		
						Initial Sulfur In Sample	SO ₂	Elemental Sulfur	Retained in Solid
Series I									
1	0.50	575	20	995	342	102	2.08	6.08	91.8
Series II									
2	0.50	750	22.5	1000	344	378	3.70	30.4	65.9
3	0.50	750	21	1000	344	378	4.15	29.5	66.4
4	0.50	750	10	1050	361	499	6.04	37.8	56.2
5	0.50	750	10	1000	351	399	2.39	35.1	62.5
6	1.0	750	15	1000	265	438	3.85	36.1	60.1
7	1.0	750	25	1000	265	340	3.70	26.6	69.7
8	1.0	750	5	1000	265	264	3.77	18.9	77.4
9	1.0	750	9	1000	265	415	4.95	31.6	63.4
10	1.0	750	11	1000	268	168	3.11	10.6	86.3
11	1.0	750	10	1010	270	315	3.65	24.5	71.8
Series III									
12	0.50	970	20	1000	344	291	6.92	21.5	71.6
13	0.50	970	15.5	1000	344	517	8.10	35.5	56.4
14	1.0	970	15	1000	265	396	5.58	28.4	66.0
15	3.0	970	10	1000	159	188	6.39	6.00	87.6
16	3.0	970	10	1000	160	250	8.52	7.89	83.6
Series IV									
17	0.50	1100	5	1000	344	610	11.5	39.3	49.1
18	1.0	1100	8	999	264	475	12.1	23.3	64.6
19	3.0	1100	9	1002	160	324	7.16	18.1	74.7
20	3.0	1100	9	1001	160	289	7.70	13.5	78.8

components that could be released from the mixtures i.e., sulfur, SO_x , and O_2 , showed negligible release of oxygen (as O_2) from the samples, suggesting the oxygen is tied up as SO_x . The calculated sulfur retention values shown in the table would be on the low side if other volatile oxygen-bearing compounds had been formed and were not detected. The percent sulfur (S_2) formed (next to last column) was determined from the total sample weight loss minus the weight of SO_2 formed.

Data from the continuous monitoring of SO_2 during these studies, and from the short exposure time studies presented in the next section, indicated that the CaO-pyrite reaction, in terms of SO_2 formation and sample weight loss, was essentially complete within the first minute of reaction. Data from each run in the long-term exposure studies therefore represents the final state of the reaction at a given temperature, independent of time. The data in Table 1 are summarized in a bar-graph form in Figure 10. All of the data in the figure are from CaO-pyrite mixtures using the -200 mesh pyrite 92.8 percent pure. Values from duplicate runs are averaged. Runs made with -325 mesh pyrite appeared to retain more sulfur, while samples out-gassed prior to reaction generally gave lower sulfur retention values as seen in comparing similar runs in Table 1.

It is evident from Figure 10 that SO_2 levels are fairly low at all temperatures and Ca/S ratios studied, not exceeding 12 percent of the total sulfur in the sample in any run. However, it was found from studies of pyrite decomposition that about 2-1/2 percent of the sulfur in the pyrite could be converted to SO_2 in an atmosphere of nitrogen regardless of temperature in the range of 575 to 1100 C (dashed line in Figure 10). This appears to be due to an impurity in the pyrite. Thus, the SO_2 produced from reaction with CaO may be as much as 2-1/2 percent lower than that shown in the figure for each run.

In comparing the sulfur retention and elemental sulfur (S_2) data in Figure 10 at the different temperatures, it is evident that increasing the temperature at any given Ca/S ratio decreased the retention of sulfur in the solid and increased the amount of elemental sulfur and SO_2 emitted. The one exception is the elemental sulfur at

FIGURE 10. FORMATION AND RETENTION OF SULFUR SPECIES IN CaO-PYRITE MIXTURES

1100 C. At $\text{Ca/S} = 1.0$ the sulfur retention and elemental sulfur values varied by only a few percentage points in the temperature range 750 to 1100 C. This was noticeably less variation than at Ca/S ratios of 0.5 and 3.0 as seen in the figure.

Comparing the data at a given temperature, one sees that the sulfur retention increased noticeably with increasing Ca/S ratio along with a corresponding decrease in elemental sulfur and in most cases in SO_2 also. At the highest temperature studied, 1100 C (approaching fuel-rich stage combustion temperatures), doubling the calcium content of the mixture (Ca/S increased from 0.5 to 1.0) increased the sulfur retention by about 16 percentage points while a subsequent tripling of the calcium content (Ca/S from 1.0 to 3.0) increased the sulfur retention by another 10 percentage points. It is evident from the data, however, that the effectiveness of the calcium in retaining the sulfur, while increasing with the Ca/S ratio, appears to be approaching an asymptotic value. The results suggest that a Ca/S ratio somewhere between 1 and 3 may be most practical for capturing sulfur. Certainly the lower temperatures are more favorable for sulfur retention, but the time-temperature limitations in combustion will have to be considered in optimizing the capture process.

Short-Term Exposure. Data from the reaction of CaO with FeS_2 in nitrogen in time intervals up to 130 seconds are plotted in Figures 11, 12, and 13. Data from the longer time exposures of Table 1 are also included in the plots. At Ca/S mole ratios of 0.5 and 1.0, the long-term exposure data appear to fall in line fairly well with the short-term data (Figures 11 and 12). However, at $\text{Ca/S} = 3.0$ (Figure 13), the long- and short-term data are noticeably out of line. An explanation for this inconsistency is not evident.

Temperature effects are apparent in the data. As expected the samples lost weight more rapidly as the temperature was increased from 750 to 1100 C. The samples approached a constant weight after several seconds reaction time. As shown in the figures, the final weights at each Ca/S ratio were different at each different temperature, suggesting formation of temperature-dependent products.

FIGURE 11. WEIGHT LOSS IN CaO-PYRITE EXPERIMENTS-Ca/S = 0.5

FIGURE 12. WEIGHT LOSS IN CaO-PYRITE EXPERIMENTS-Ca/S = 1.0

FIGURE 13. WEIGHT LOSS IN CaO-PYRITE EXPERIMENTS-Ca/S = 3.0

At no time in any of the runs did the sample weight loss exceed the weight of sulfur in the unreacted sample. The maximum observed weight loss was about 60 percent of the sulfur weight in the sample (1100 C run, Figure 11). In all of the runs but this one, the weight loss was 50 percent or less of the sulfur weight in the sample, with the highest values occurring at the highest temperature, i.e. 1100 C. One can account for the 50 percent weight loss via the decomposition of the pyrite

Values less than 50 percent can arise from the formation of different pyrrhotite compounds; this is discussed later.

It is apparent from these observations that 50 percent or more of the sulfur was retained in the samples, except for the one run which retained 40 percent sulfur.

Sulfur Compounds Retained in Solids. Several samples were analyzed from the long- and short-term exposure runs using X-ray diffraction and wet chemical methods.

Qualitative X-Ray Analyses. Two of the exposed solid samples examined by X-ray analyses were taken from Runs 11 and 12 (Table 1). The compounds present and the estimated relative pattern strength are tabulated below.

<u>Sample</u>	<u>Temperature, C</u>	<u>Compound</u>	<u>Pattern Strength</u>
Run 11 Ca/S = 0.5	750	CaO	100
		CaS	70
		Fe ₇ S ₈	20
		-Fe ₂ O ₃	9
		FeS ₂	6
Run 12 Ca/S = 0.5	970	CaS	100
		Unknown (FeS-CaO)?	88
		Fe ₉ S ₁₀	44

The sample exposed at 750 C contained unreacted CaO and a trace of unreacted pyrite. The major products of reaction at 750 C were CaS and a pyrrhotite Fe₇S₈. A small amount of iron oxide was also observed at 750 C. At 970 C, the exposed sample showed no CaO or pyrite remaining. The major products formed at the higher temperature were CaS, an unknown compound, and a pyrrhotite Fe₉S₁₀. The unknown compound produced a very strong peak but could not be identified in the X-ray Powder Diffraction File.

Although the X-ray data are only quantitative, it appears that the reaction at 970 C produced primarily CaS and a fewer number of compounds overall than did the reaction at 750 C.

Quantitative X-ray Data - General Observations. Six samples were selected for quantitative analysis by X-ray diffraction (XRD) to determine the major solid products. These samples are products from reactions of CaO and FeS₂ at a Ca/S mole ratio of 1.0. The XRD data from the six exposed samples are summarized in Table 2.

The X-ray data show a general increase of calcium sulfide content with increasing temperature in the 750 to 1100 C range (at long exposure time, 8 minutes or more, Samples 1, 2, and 3). At constant temperature, (1100 C), the calcium sulfide concentration in the sample increased with increasing reaction time, as seen in Samples 3, 4, and 5. Unreacted CaO was present in the sample at low temperature, 750 C, and at the higher temperatures (970 and 1100 C) if charcoal was present, Sample 6, or if the exposure time was short (15 seconds or less, Samples 4 and 5). CaO was completely consumed at 970 C and at 1100 C if the reaction time was extended to several minutes as seen in Samples 2 and 3. High temperature and long residence time appear essential for significant conversion of CaO to CaS.

Several of the samples in Table 2 show the formation of an unidentified compound at 2.35A. This unknown presumably contains significant quantities of calcium and iron, particularly Samples 2 and 3, since the X-ray data show insufficient quantities of these elements for a material balance. The complex was not observed at 750 C, Sample 1, or at the 4-second reaction time at 1100 C, Sample 5, or in the presence of charcoal. Temperature, time, and carbon content of the sample appear to be important parameters in determining the extent of formation of the complex.

The X-ray data also show possible formation of CaSO₄ at the lower temperatures and longer reaction times and at 1100 C at short exposure times. The data suggest that CaSO₄ may be an intermediate or an equilibrium product in the reaction at 1100 C.

Pyrrhotites and small amounts of unreacted pyrite (more in Sample 5) are also evident in all samples, except Sample 6 which contained charcoal. The pyrrhotites appear to decrease in concentration with increasing temperature at the longer exposure times as, for

TABLE 2. X-RAY DIFFRACTION DATA FROM THE REACTION OF FeS_2 WITH CaO

Sample No.	Run Conditions, Temp°C/Time, Min	Compound	Pattern Strength	Percent by Wt. in Sample
1	750/25	CaO	100	33 ± 3
		CaS	41	10.5 ± 2
		Pyrrhotite Fe_7S_8	7	
		FeS_2	5	6 ± 1
		Possible CaSO_4	8	
2	970/15	CaS	100	19.5 ± 2
		Unknown (2.35 Å)	14	
		FeS_2	13	10 ± 2
		Pyrrhotite Fe_9S_{10}	5	
		Possible CaSO_4	8	
		Quartz	4	
3	1100/8	CaS	100	33 ± 2
		Unknown (2.35 Å)	22	
		Possible FeS_6	6	
		Pyrrhotite $\text{Fe}_{11}\text{S}_{12}$	2	
		Quartz	3	
4	1100/0.25	CaS	100	11 ± 1
		CaO	28	10 ± 1
		Probable CaSO_4	15	
		Pyrrhotite Fe_7S_8	12	
		Possible FeS_2	4	~ 2
		Unknown (2.35 Å)	2	
		Quartz	13	
5	1100/0.667	CaO	100	24 ± 2
		FeS_2	26	22 ± 2
		Pyrrhotite Fe_9S_{10}	22	
		CaS	21	4 ± 1
		Quartz	15	
		Possible CaSO_4	3	
6**	1100/10	CaS	100	37.5 ± 3
		CaO	14	8.5 ± 1
		Fe	14	
		Quartz	6	

** CaO/FeS_2 75 wt/o, charcoal 25 w/o.

example, in Samples 2 and 3, and decrease with increasing time at constant temperature, Samples 4 and 5, indicating thermal instability of the pyrrhotites at the temperatures used.

The X-ray analysis of Sample 6 indicates that the presence of charcoal in the sample altered the amount and type of solid products formed in the CaO-FeS_2 reaction as seen in comparing the products of Sample 6 with those of Sample 3. The charcoal appeared to retard the formation of the unknown compound and may even enhance CaS formation slightly.

Calcium and Iron Material Balance. Quantitative analyses of the CaS , CaO , and FeS_2 in each reacted sample was made by XRD. The results are presented in Table 3 as moles of calcium and iron in the reacted sample. These values are compared to the original moles of calcium and iron in the unreacted sample and are reported as a percentage in the last column of the table.

TABLE 3. QUANTITATIVE X-RAY DATA ON CALCIUM AND IRON COMPOUNDS

Sample No.	Moles				Percent of Total Moles (Reacted/Unreacted)	
	Ca		Fe		Ca	Fe
	Reacted	Unreacted	Reacted	Unreacted		
1	0.0068	0.0082	0.00046	0.0041	81.4	11.2
2	0.0024	0.0082	0.00076	0.0041	29.3	18.5
3	0.0040	0.0082	--	0.0041	48.8	--
4	0.0021	0.0056	--	0.0028	36.8	--
5	0.0029	0.0052	0.00112	0.0026	56.4	43.1
6	0.0029	0.0033	Fe only	0.0016	88.4	--

The lack of quantitative data on the pyrrhotites, CaSO_4 and unknown compounds in the samples, in most cases, prevents an accurate determination of material balance. It does appear from the Table 3 data, however, that within the error of the XRD method, a calcium balance is obtained in Sample 6, and also in Sample 1 if the reported CaSO_4 in that sample is taken into account. These samples did not contain the unknown compound which probably accounts for the satisfactory material balance observed. It thus appears that much of the calcium is tied up as CaSO_4 and/or the unknown compound in Samples 2, 3, and 4. The X-ray data cannot account for all of the calcium in Sample 5 since the CaO and CaS present here account for only 56.4 percent of the total calcium and no unidentified compound is reported. These results may be providing a clue to equilibria that can exist among CaO , CaS , and CaSO_4 . This is discussed further at the end of this report.

Similarly, much of the iron in each of the six samples appeared to be associated with the unknown compound and/or pyrrhotites, except Sample 6 which contained charcoal and apparently resulted in the formation of elemental iron. Also, the X-ray data cannot account for all of the iron present in some of the samples, as, for example, Samples 1 and 6. In an effort to fill in some of the analytical gaps from the X-ray analyses, selected samples were analyzed further by wet-chemical methods.

Wet-Chemical Analyses.* Four of the six samples analyzed by XRD were also examined by various wet-chemical methods to determine the Ca^{++} , Fe^x , sulfide and total sulfur content of each sample. Only the acid soluble Ca^{++} and Fe^x in each sample were determined. The data are presented in Table 4.

* Late in this program the authors came upon the work of Brothers and Starzomski⁽¹³⁾ which offers a potential quantitative method for analyzing for CaS in the presence of FeS . They report that a 10 g $\text{MgCl}_2/100$ g H_2O solution will dissolve CaS quantitatively and preferentially to FeS .

TABLE 4. CHEMICAL ANALYSES OF REACTED CaO-FeS_2 SAMPLES

Sample No.	Reaction Temp °C	Wt. Percent, Reacted Samples						
		Ca		Fe		Total Sulfur		Total Sulfide
		Meas.	Calc.	Meas.	Calc.	Meas.	Calc.*	Measured
1	750	35.3	36.3	24.6	25.3	20.5	19.2	5.21
2	970	34.4	36.9	26.4	25.7	22.3	21.2	16.0
3	1100	40.9	37.8	16.9	26.3	29.2	24.6	26.5
6	1100	28.0	30.3	15.5	21.1	20.1	23.3	23.8

* Taking into account the measured loss of elemental sulfur during sample reaction.

The data in Columns 3 and 4 in the table show that, within experimental error, all of the calcium in each of the four samples was present and accounted for in the acid solution. Likewise, in Columns 5 and 6, it is seen that all or nearly all of the iron in Samples 1 and 2 was detected in the acid solutions. Samples 3 and 6 on the other hand indicate some insoluble iron remaining in these samples. In the case of Sample 6, this may be the elemental iron observed in that sample as indicated from the X-ray data. The X-ray data from Sample 3 do not suggest an insoluble iron compound (although pyrite is not very soluble in dilute acid solution).

The total sulfur and sulfide values of each sample are shown in the last three columns of Table 4. The calculated total sulfur values in the next to last column were determined from the initial calculated weight of sulfur in the original sample minus the measured

weight of sulfur (as S_2 and sulfur in SO_2) evolved from the sample during reaction. The measured and calculated total sulfur values are in fair-to-good agreement in each sample.

The data show that all of the sulfur in the high temperature samples, Samples 3 and 6, is present as sulfide, and most of the sulfur in Sample 2, 970 C, was a sulfide. The low temperature sample at 750 C, however, contained much less sulfide. Overall, the results are in qualitative agreement with the X-ray data in that the XRD analyses showed only sulfide-type compounds in Samples 3 and 6, while sulfate, in addition to sulfides, were detected in Samples 1 and 2.

Rate Data

Rate data were obtained from the $CaO-FeS_2$ runs in terms of (1) the global reaction (sample weight loss), (2) SO_2 formation and (3) CaS formation. An activation energy was determined for the weight loss process.

Global Reaction - Sample Weight Loss. In the $CaO-FeS_2$ study, sample weight loss occurred as a result of evolution of volatile from the mixtures. Weight loss rates therefore represent rates of production of volatile from the samples. Experimental evidence indicates the volatiles to be primarily S_2 and SO_2 , although small quantities of other volatiles may also be present. Thus, weight loss rates represent primarily rates at which sulfur-bearing species were evolved from the sample, and therefore give some indication of sulfur retention potential of the mixtures.

The rate at which each sample lost weight during the first 5 to 10 seconds of reaction was determined for each run. The data are tabulated below.

Ca/S	Rate, Gram/Gram Sulfur-sec. $\times 10^2$		
	750 C	970 C	1100 C
0.5	0.66 (0.010)	2.5 (0.039)	--
1.0	0.74 (0.012)	2.3 (0.036)	4.1 (0.064)
3.0	1.2 (0.019)	2.5 (0.039)	4.4 (0.064)

The numbers in parentheses represent the moles of volatiles emitted per gram of sulfur in the sample per second, based on the emission of S_2 and SO_2 only from the mixtures. As seen from the SO_2 rates in the next section, most of the sulfur emitted per unit time appears to be S_2 , which probably reflects the different reaction paths in the mechanisms leading to S_2 and SO_2 formation.

For these short residence time studies, the rates were determined after a few seconds heat up to allow equilibration of sample and furnace temperatures. Significant reaction did not occur until around 550 C and therefore the sample heat-up time interval is essentially from 550 to the desired temperatures. Bare thermocouples indicated a maximum temperature rise of about 450 C per second at 970 C, uncorrected for radiation. Heat rates would be slower for the sample mixtures and would depend on furnace temperature, quantity and geometry of the sample, but temperatures should equilibrate within a few seconds and the reported rates should be fairly representative of the temperature.

The tabulated rate data suggest that the rate of sample weight loss nearly triples in going from 750 to 970 C and nearly doubles in increasing the temperature from 970 to 1100 C. The rate values, particularly at the two higher temperatures, appear to be independent of the calcium content of the sample, suggesting that the reaction process is zero order. If, then, one assumes that the weight loss process is zero order, the rate expression becomes simply,

$$R = k.$$

An Arrhenius plot of $\log k$ vs $1/T$ for these data (Figure 14) yields an activation energy of 14.3 Kcal/mole for the reaction process. Details of the reaction process are discussed later.

SO₂ Rate of Formation. The rate of SO₂ release from the solids was estimated from the SO₂ concentration versus time curves obtained from the continuous monitoring SO₂ detector. Typical concentration versus time curves for SO₂ release at 750 and 970 C are shown in Figure 15. Most of the SO₂ was formed from the solids within the first 30 seconds of reaction. Peak concentrations of well over 30,000 ppm were frequently observed. This high concentration caused saturation of the detector resulting in the flat region shown in the figure. Although high ppm SO₂ values were observed from the solids, this represents only a small fraction of the total sulfur in the sample as seen in the data in Table 1.

The maximum rate of SO₂ formation was taken from the slope of concentration versus time curves and is reported below as moles/sec per gram sulfur in sample at reaction temperatures.

<u>Runs</u>	<u>Ca/S</u>	<u>Pyrite Mesh</u>	<u>Temperature</u>	<u>SO₂, Moles/Gram Sulfur in Sample - sec</u>
15	1.0	-200	970 C	2.9×10^{-6}
14, 16	1.0	-200	750 C	5.9×10^{-7}
17	1.0	-325	750 C	1.2×10^{-6}

The rate of SO₂ evolution increased by a factor of 5 in increasing the temperature from 750 to 970 C. Decreasing the pyrite particle size from -200 mesh to -325 mesh appeared to more than double the rate of SO₂ formation. Overall however, the rates of SO₂ evolution are very low, suggesting that the weight loss is mainly S₂ vapors. Using the zero order kinetics discussed earlier it is noted that the SO₂ data and the weight loss data yield the same activation energy, further supporting the argument that S₂ vapors are directly tied to the weight loss.

Rate of CaS Formation. Using the X-ray data of Table 2, the formation of CaS at 1100 C was examined as a function of time. The data

FIGURE 14. ARRHENIUS PLOT OF THE CaO-PYRITE REACTION IN THE 750 to 1100 C RANGE

FIGURE 15. SO_2 RELEASE RATES

for Samples 3, 4, and 5 are plotted in Figure 16 showing the fraction of CaO converted to CaS (i.e., $\frac{\text{moles of CaS produced}}{\text{moles of CaO in original sample}}$) as a function of time using a $\log_{10} t$ abscissa. As seen from the plot, which is strictly empirical, the data approximate very closely to a straight line at least from $t = 3$ seconds on.

Applying a least square treatment to the data points for the straight line produces the following equation (valid for $t > 3$ sec),

$$F = 0.205 \log_{10} t - 0.0640, \quad (I)$$

where

F = fraction of CaO converted to CaS

t = time in seconds.

Differentiating Equation I with respect to time gives

$$\frac{dF}{dt} = \frac{0.0890}{t} \quad (II)$$

FIGURE 16. CaS CONVERSION RATES

Equation II shows that the increase in the moles of CaS per mole of CaO per unit time is inversely proportional to the time at $t > 3$ sec. Thus, the maximum rate of CaS formation in the time interval $3 < t < \infty$ occurs at the start of the time interval and continues to decrease as the reaction proceeds.

The main observation from the results presented here is that, at 1100 C and in the time interval typically encountered in combustion units for high-temperature reactions, i.e., 2 seconds or so, little CaS is formed from the pyrite-CaO reaction, at least in the absence of oxygen. However, combustion temperatures are generally higher than 1100 C, more like 1400 C or more, and this coupled with the presence of sub-stoichiometric levels of oxygen in fuel-rich staging could significantly improve CaS formation. In any event, in the absence of oxygen, the Task 1 results from the CaO-FeS₂ reaction up to 1100 C indicate that, for short time intervals, a major portion of the sulfur is tied up as FeS and/or pyrrhotites rather than CaS.

CaO-FeS₂-Charcoal Reaction, Effects of O₂, H₂O, CO and CO₂

A series of runs was carried out in which charcoal was added to the CaO-FeS₂ mixtures to determine its effect on the sulfur retention process. Runs made with the crude pyrite (Sample A) are included here since this material contained measurable amounts of carbon and hydrogen. Most of the runs in this series were made with the more pure 92.8 percent pyrite. The effects of different gas constituents on sulfur retention was also examined in these runs.

Charcoal was added to the CaO-FeS₂ mixtures to determine the effect of a coal-like environment on sulfur retention. The mixtures were reacted at 1100 C for 10 minutes in an atmosphere of nitrogen and in atmospheres of N₂-O₂ (air), N₂-H₂O (saturated at 25 C), CO-Ar (10 percent CO), and CO₂-Ar (12 percent CO₂). The Ca/S mole ratio was maintained at 1.0. Data from the runs are presented in Table 5.

TABLE 5. SULFUR RETENTION IN THE CaO-FeS₂-C SYSTEM
T = 1100 C, t = 10 minutes

Run	Atmosphere	Initial Sample Wt. (mg)		Wt. Loss Mg/Gram Sulfur	Percent of Total Sulfur Sample		
		Total	Sulfur		As SO ₂	As S ₂	Retained*
1	N ₂	412	35.5	749	0.70	3.1	96
2	N ₂	522	135	644	0.87	0.45	98
3	N ₂ -O ₂	875	226	1099	40.5	1.28	58
4	N ₂ -H ₂ O	778	201	1111	1.92	0.00	98
5	CO-Ar	532	137	820	1.28	0.00	98
6	CO ₂ -Ar	742	192	1208	1.70	0.00	98

* Approximate values.

The reaction mixture contained 25 percent by weight charcoal in all runs except Run 1 where the charcoal was 75 percent by weight. The most striking observation from these data is that in all runs except Run 3 the addition of charcoal resulted in greatly reduced amounts of SO₂ and elemental sulfur released from the mixtures compared to a CaO-pyrite mixture only. Relative to the non-carbon mixture the reduction amounted to nearly an order of magnitude for each volatile sulfur component.

The addition of H₂O, CO, or CO₂ to the gas stream had little effect on the amount of volatile sulfur products formed. The amount of SO₂ appeared to increase slightly while the quantity of sulfur evolved decreased to zero (within weighing error) in the presence of these components. The addition of oxygen to the gas mixture (Run 3), on the other hand, greatly increased the production of SO₂, as would be expected in a sulfur-laden environment.

The sample weight loss column in the above tabulation indicates that the sample lost weight even though most of the sulfur was apparently retained in the solid (except for Run 3). The weight loss in

each sample is attributed to release of high temperature volatiles in the charcoal and to the formation of CO, and possibly H₂S, COS, and H₂O in the interaction of charcoal with CaO and FeS₂. A measurable quantity of H₂S and/or COS, possibly 9 percent or more of the total sulfur, was produced in the reaction but the predominant sulfide was not determined.

Crude Pyrite Run. Sample weight loss data obtained from the reaction of CaO with the crude pyrite are tabulated below. The data are plotted in Figure 17 as function of the reaction temperature. As seen in the figure, the sample weight loss increased linearly with increasing temperature over the 555 to 1080 C range covered.

Run	Temp, C	Run Time, min.	Sample wt, mg		SO ₂ Evolved, grams	S-Converted, percent
			Initial Sulfur	Weight Loss		
1	970	30	730	330	0.1560	10.7
2	555	40	499	95	0.0583	5.8
3	575	20	472	100	--	--
4	750	25	698	220	--	--
5	1080	12	551	290	--	--

FIGURE 17. SAMPLE WEIGHT LOSS IN CaO-FeS₂ REACTION

The weight loss in each case involved primarily the release of elemental sulfur and the generation of sulfur oxide(s). (The crude pyrite contained some carbon and hydrogen but this was assumed to stay with the solids in the absence of oxygen.) The elemental sulfur was identified in part from the color of the deposit (yellow to off-white) and from the oxidation of the deposit in air over platinum to produce sulfate in hydrogen peroxide solution. The sulfur oxide(s) was identified on the mass spectrometer as primarily SO_2 . Other oxides such as S_2O or SO may also have been present, but as mentioned earlier, these species are relatively unstable and likely converted to S_2 and/or SO_2 .

Data for Run 1 at 970 C, show about 10.7 percent of the total sulfur in the original sample was converted to SO_2 and that about 47 percent of the total weight loss was due to the formation of SO_2 . This leaves some 53 percent of the weight loss due to the release of elemental sulfur, or 24 percent of the total original sulfur in the mixture released as elemental sulfur. The combined loss of original sulfur in the mixture totals 35 percent, indicating about 65 percent of the sulfur stayed with the solid phase at 970 C using the impure pyrite at $\text{Ca/S} = 0.65$. Also, about 53 percent of the oxygen remained with the solid phase based on the amount of SO_2 evolved. Oxygen available from impurities in the sample could alter this value.

At 555 C, Run 2, the total sample weight loss was much less, totaling 0.095 grams compared to 0.33 grams at 970 C. Accordingly, only 6 percent of the total sulfur in the original sample was converted to SO_2 . However, at 555 C, the fraction of the sample weight loss due to SO_x formation was higher than at 970 C, totaling 62 percent, leaving 38 percent of the weight loss due to elemental sulfur. Thus, a larger fraction of the volatiles was SO_2 at the lower temperature. In all, about 13 percent of the original sulfur in the sample was lost as SO_2 and elemental sulfur at 555 C. Also, about 81 percent of the oxygen remained with the solids.

Run 3 was a duplicate of Run 2 although the temperature was slightly higher in Run 3. The weight loss for this run was slightly higher as would be expected from the increase in temperature. The SO_2

evolved from Run 3 was followed mass spectrometrically to determine an approximate time-concentration relationship for the SO_2 emission process. The mass spectrometer data indicated a rather slow SO_2 formation process at this low temperature, taking several minutes for most of the SO_2 to be produced.

The amount of SO_2 evolved at 750 to 1080 C, Runs 4 and 5 was not determined, but interpolating the data at 555 and 970 C to include the 750 and 1080 C values suggests about 77 percent of the sulfur stays with the solids at 750 C and 60 percent at 1080 C. The presence of carbon in the crude pyrite- CaO samples did not appear to alter the amount of SO_2 evolved as did the charcoal in the earlier runs. This is probably due to the much lower carbon/sulfur ratio in the crude pyrite ($\text{C/S} = 0.33$) compared to the CaO-FeS-charcoal samples ($\text{C/S}=2.4$). The SO_2 emission and sulfur retention data with the crude pyrite are more in line with the CaO-FeS_2 data of Table 1.

Reaction of CaO with Sulfur Vapor

The formation of relatively large quantities of elemental sulfur in the volatile products from the reaction of CaO with FeS_2 observed in earlier experiments suggested that the pyrite was first decomposing to release sulfur and the sulfur vapor was then reacting with the CaO . To explore this further, experiments were conducted in which elemental sulfur was first generated from the pyrite and then allowed to pass over CaO . Further exploration of the CaO-sulfur reaction was also made using well mixed powders of CaO and elemental sulfur. Effects of carbon on the reaction were also briefly examined.

Sequential Reaction of CaO with Sulfur Generated from FeS_2

Two runs were made in which CaO and pyrite were heated to 1100 C in the reactor in a sequential type arrangement wherein CaO and pyrite were placed in separate boats in the reaction chamber. The pyrite

(-200 mesh) was placed upstream of the CaO so that sulfur vapors generated from the FeS_2 would pass over the finely powdered CaO. Nitrogen was used as the carrier gas. Data from the runs are tabulated below.

Run	Temp., C	Run Time, min	Initial Sample Wt. mg			Wt. Change, mg		Percent Sulfur in Original Sample		
			Total		Sulfur	Pyrite	CaO	to SO_2	to S_2	Retained
			Pyrite	CaO	(Pyrite)					
1	1100	15	1000	500	495	-290	0.00	10.8	36.0	--
2	1100	15	1500	1000	743	-365	+ 80	11.8	25.6	43.7

Data from both runs indicate reaction with the CaO is taking place at 1100 C as evidenced by the conversion of 11 to 12 percent of the total sulfur to SO_2 .

The pyrite sample weight loss in Run 1 was high for pyrrhotite formation and likely indicates some loss of sample or a weighing error. Sample weight loss in Run 2 was consistent with FeS or pyrrhotite formation. The CaO sample in Run 2 gained weight as would be expected if sulfur were reacting with the powder. This sample was analyzed for sulfide and total sulfur content. The results presented later showed only CaS formation in the CaO sample. The CaO sample in Run 1, on the other hand, showed no weight gain even though nearly as much SO_2 was produced in this run as in Run 2. This further implies probable weighing errors in Run 1.

The formation of SO_2 and CaS in the reaction of sulfur vapors with CaO enhances the earlier postulation that sulfur released from the pyrite is responsible for the reaction with CaO in CaO-pyrite mixture.

CaO - Elemental Sulfur Reactions

Mixtures of CaO and elemental sulfur powder were heated to 1100 C in the reactor in a atmosphere of nitrogen to determine the reaction products of these mixtures. The data are tabulated below.

Run	Ca/S	Temp., C	Run Time, min	Initial Sample		Wt. Loss mg/gram Sulfur	Percent of Total Sulfur in Sample		
				Total	Sulfur		to SO ₂	to S ₂	Retained
1	1.0	1100	18	749	272	967	6.6	83.5	9.9
2	3.0	1100	9	551	88	1009	14.2	72.6	13.2

As observed in the sequential reaction and with the earlier CaO-pyrite mixtures, the CaO-S₂ mixtures evolved primarily SO₂ and elemental sulfur. However, much more elemental sulfur was evolved in the above runs on a percentage basis simply because of the high volatility of sulfur and of the absence of pyrite in the CaO-S₂ mixtures. Iron in the CaO-pyrite mixtures can account for a major part of the sulfur retention as pyrrhotites and FeS.

Similarly, at 1100 C, more sulfur was retained in the sample at Ca/S ratio of 3.0 (Run 2) than at 1.0 (Run 1) as was also observed in the CaO-pyrite mixture. Also, the calculated values of 9.9 percent sulfur retention for Ca/S = 1.0 is close to the 9.5 percent value calculated from the CaO-pyrite mixture at Ca/S = 1.0 and 1100 C after subtracting out the sulfur retained by the pyrrhotite (assuming the formula FeS_{1.10}). Using the same procedure at Ca/S = 3.0, the sulfur retention values are 13.2 and 19.4 percent respectively. The 13.2 percent value is low due to the loss of some of the sample in that run and is likely more closely in agreement with 19.4 percent value. Overall the results substantiate a CaO-S₂ reaction in the CaO-pyrite mixtures.

CaO-Elemental Sulfur-Carbon Reaction

Two runs were made at 1100 C to examine the effect of carbon on the CaO-S₂ reaction. The Ca/S ratio in each run was 1.0. One run contained 25 percent by weight CaO-S₂, the other run 50 percent CaO-S₂; the remainder was charcoal. The data are presented below.

Run	Carbon/S	Ca/S	Temp., C	Run Time, min	Initial Sample Wt. mg		Wt Loss mg/gram Sulfur	Percent of Total Sulfur in Sample		
					Total	Sulfur		to SO ₂	to S ₂	Retained
1	20.2	1.0	1100	9	558	50.6	1134	0.38	5-10	90
2	6.7	1.0	1100	20	481	87.5	1333	0.57	35-40	60

Very little SO₂ formation was observed in either of the runs. However, qualitatively CO, H₂S, and/or COS were observed in both runs. The evolution of these gases probably accounted for the excessive sample weight losses; the lack of quantitative data for these gases made it difficult to determine accurately the sulfur losses and retention in the samples. The SO₂ data, on the other hand, are considered reliable. The sulfur emitted as S₂ and the sulfur retained in the solids were thus calculated from the weighed sulfur deposits and from the difference between the weighed sulfur deposit and the amount of sulfur in the original sample respectively. Based on this procedure, the addition of carbon appears to have enhanced the retention of sulfur in the mixtures compared to the CaO-S₂ mixture at Ca/S = 1.0 and 1100 C. The higher the carbon/S ratio, the more retention of sulfur.

Analyses of Solids:

CaO - Elemental Sulfur Reaction

Three of the solid samples obtained in these studies were analyzed for sulfide content by a wet chemistry method in which the sulfide was released as H₂S and oxidized to SO₂. Each of the samples were also analyzed for total sulfur (by combustion) and calcium content (by atomic absorption). The data at 1100 C are presented below.

No.	Sample Description	Weight Percent				Percent Sulfur Retained
		Sulfur		Ca	Moisture	
		Total	Sulfide			
1	Sequential Reaction (CaO + pyrite Run 2)	14.8	15.0	66.0	0.73	44.4
2	CaO-Sulfur Reaction (Ca/S=3.0, Run 2)	5.4	5.6	67.0	0.2	28.9
3	CaO-Sulfur-C Mixture* (Ca/S=1.0 Run 2)	18.1	10.0	31.6	1.25	75.3

Each of the samples from the sequential and CaO-S₂ reactions, Samples 1 and 2, showed only calcium sulfide present. The last column in the tabulation shows the percent sulfur retained in the sample based on the sample analysis. Samples 1 and 2 showed less than 50 percent sulfur retention, in agreement with earlier calculated values (see tabulations pages 41 and 42). The earlier calculated sulfur retention for Sample 1 was 43.7 percent in excellent agreement with above analysis at 44.4 percent above. For Sample 2, the earlier calculated value was 13.2 percent compared to 28.9 percent above. However, as mentioned earlier the calculated value was apparently low and the above analytical data tends to confirm this. It appears in comparing the above sulfur retention values with those from the CaO-FeS₂ reaction, Table 1, that the sulfur from the FeS₂ was more effective in reacting with CaO than is elemental sulfur mixed with the CaO. No doubt in the latter case, a lot of the sulfur escaped before it was hot enough to react with the CaO, thus causing lower sulfur retention values.

Data from Sample 3 in which carbon was added to the CaO-S₂ sample indicates a more complex reaction process taking place in this mixture. The sulfide and total sulfur data suggest that both sulfides and sulfates are formed in this reaction, with the sulfides somewhat in excess. Calculations showed that much more sulfur was retained in the solid phase in Sample 3, which contained carbon, than in Sample 2 which had no carbon (75.3 percent vs 28.9 percent respectively). The data are in qualitative agreement with earlier results which showed higher retention of sulfur in the presence of carbon.

Thermal Decomposition of Pyrite

Data from earlier runs, especially the sequential reaction runs with CaO and pyrite, suggested that some SO₂ came from the pyrite mixture itself. Table 6 summarizes pyrite pyrolyses in an atmosphere of nitrogen in the 575 to 1100 C range.

The small quantities of SO₂ produced in these experiments indicate the presence of some oxygen impurity in the pyrite samples. Where the pyrite was more pure, Runs 3 and 14, less SO₂ was emitted.

Out-gassing the sample prior to reaction does not appear to affect the amount of SO₂ released from the pyrite, although CaO-pyrite mixtures were affected by out-gassing as mentioned earlier. The release of SO₂, although small, would be added to the total SO₂ evolved in the CaO-pyrite reaction and should be taken into account.

The time-weight loss data shown in Table 6 for pyrite samples at 750 C indicates that several seconds are required to release the sulfur from the pyrite. At 970 C, however, much less time is required, but still more than 5 seconds were needed. It should be remembered, however, that a few seconds were needed to bring the sample to the desired temperature. It therefore seems likely that a pyrite particle actually at 970 C or higher would thermally decompose in a fraction of a second to form sulfur; at 750 C or lower, the release of sulfur may take a few seconds. This could be detrimental to sulfur capture in fast reacting systems, but at 750 C and lower, the temperature would be too low for pulverized coal combustion processes.

Plotting the weight loss data in Table 6 at 750 C gives a rate of sample weight loss of 1.27×10^{-2} gram/gram sulfur-sec in sample. This is approximately 1.8 times faster than the rates observed at 750 C for weight loss in the CaO-pyrite mixtures at CaS = 0.5 and 1.0 and about the same as that observed at Ca/S = 3.0 (Figure 13). Rates should be expected to be slower in the CaO-pyrite mixtures due to reaction of sulfur with CaO in the mixtures. The results agree with the postulated reaction sequence of FeS₂ releasing sulfur and the sulfur reacting with the CaO.

TABLE 6. THERMAL DECOMPOSITION OF PYRITE

Run No.	Run Time, min	Temp., C	Sample Purity, percent	Weight Loss Grams Per Gram Sulfur in Sample	Percent Original Sulfur Oxidized to SO ₂
1	10	575	92.8	0.169	2.6
2	10	750	"	0.469	3.3
3	10	750	99.9	0.322	1.1
4	5/6	750	92.8	0.392	--
5	1/2	"	"	0.288	--
6	1/3	"	"	0.205	--
7	1/6	"	"	0.198	--
8*	6	970	"	--	2.2
9	1/2	970	"	.602	--
10	1/12	970	"	0.308	--
11	6	1100	"	0.42**	2.2
12*	7	1100	"	0.51**	2.6
13	6	1100	"	0.488	1.2
14(a)	6	1100	95.5	0.488	0.60

* Sample outgassed prior to run.

** Less accurate weighing here.

(a) A -325 mesh pyrite used in this run; all other runs used -200 mesh pyrite.

Discussion of Results

Overall, the results of the studies of the CaO-FeS₂ system show that the major volatile products from the reacting mixtures are SO₂ and elemental sulfur while the major condensed products at the higher temperatures are CaS and pyrrhotites. The sulfur retention in the solids increased with decreasing temperatures and increasing Ca/S mole ratio and time. The addition of charcoal to CaO-pyrite mixtures significantly decreased sulfur and SO₂ evolution from the solids. The chemistry of the reactions is discussed below.

CaO-Fe₂ Chemistry

X-ray and Chemical Analyses. Sample analyses from the reaction of CaO and FeS₂ at Ca/S mole ratio of 1.0 showed that CaS formation in the mixture increased with increasing temperature in the range 750 to 1100 C, reaching 48.8 percent conversion at 1100 C after 8 minutes reaction time. However, only 11 percent conversion was observed at 1100 C and 15 seconds reaction time suggesting that the formation of CaS in the mixtures was rather slow and may be kinetically limited in fast reactors such as pulverized coal combustors firing in fuel-rich modes. Higher temperatures may be beneficial, providing preferential oxidation of the sulfur to SO₂ does not occur prior to CaS formation in a staged mode. Temperature-time factors will likely be very important in maximizing CaS formation.

Sulfide formation at 750 C appeared to be too slow to be of much benefit in combustion processes. Most of the CaO remained unreacted at this temperature. Increasing the temperature from 970 to 1100 C, while increasing CaS formation, also brought about the formation of several unidentified compounds referred to as complex compounds. At these higher temperatures, the analytical data suggested that the CaO interacted with iron compounds to form complexes with the approximate formulas (CaO)_{1.8}FeS_{0.5} (970 C) and (CaO)_{1.2}FeS_{0.9} (1100 C). Formation of these calcium-containing materials could tie up the calcium and thus

prevent the formation of CaS which could account in part for the low conversion to CaS often observed in the CaO-FeS₂ mixtures.

Maximum complex compound formation appeared to occur at 970 C, tying up about 60 percent of the calcium. At 1100 C the complex had more iron and sulfur present but less calcium (about 50 percent); the formula for the complex at 1100 C was close to that reported by others working with CaO-FeS₂ mixtures⁽⁵⁾, i.e., CaO·FeS. Interestingly, the complex compounds were not formed when charcoal was added to a CaO-FeS₂ mixture. However, only a marginal increase in CaS formation was observed after 10 minutes reaction time, indicating the charcoal was altering reaction paths but was not necessarily in a way beneficial to the overall formation of CaS under the experimental conditions used. Effects of the charcoal at short reaction time were not examined. Thus, it is not clear from the data whether the CaS formed quickly in the presence of charcoal or over several minutes reaction time.

The iron in the CaO-FeS₂ reacting mixtures was retained as a sulfur-bearing species in complex compound formation and/or as pyrrhotites. Analytical data indicated from 65 to 85 percent of the iron may have been tied up in complex compound formation at the higher temperatures. Whether as complexes or pyrrhotites, the iron was able to retain a large amount of the sulfur in the mixture, thus reducing the amount of sulfur available for CaS formation. Although sulfur retention as sulfides of calcium or iron would be an acceptable means of keeping the sulfur in the solids under fuel-rich conditions, subsequent conversion to sulfates in the oxidizing region of the combustor would make the iron sulfates much less desirable because of their greater instability compared to calcium sulfate at comparable temperatures. Thus, one would prefer CaS formation in a fuel-rich zone with subsequent formation to CaSO₄ in the oxidizing region of the furnace, although problems arise in obtaining efficient conversion of CaS to CaSO₄ and in maintaining stable conditions for CaSO₄ as brought out later.

Reaction in the CaO-FeS₂ System

Based on the kinetics of pyrite dissociation⁽¹⁴⁾, pyrites will dissociate by

To account for our observations, the postulation is made that the initial step in the overall reaction of CaO with pyrite is the thermal decomposition of the FeS₂ to form pyrrhotites and elemental sulfur

Data from this study indicate that this reaction is feasible at temperatures at least as low as 575 C. Thermodynamic data also support the thermal instability of the pyrite at 575 C giving an equilibrium sulfur vapor pressure of 0.76 torr for the reaction

Although the vapor pressure of S₂ is low, in a dynamic flow system as used in this study, the FeS₂ would continue to lose sulfur to the gas stream as indicated by the experimental data. At 750 C, Reaction 13 has a sulfur vapor pressure above 1 atm indicating extensive dissociation of the pyrite at this temperature. This is also substantiated by experimental data at 750 C in this study.

As the temperature increases, the stability of the pyrrhotites decreases, leading ultimately to the formation of iron sulfide, i.e.,

A variety of pyrrhotites exist with complex formulas such as Fe₉S₁₀, Fe₁₁S₁₂, etc. If one assumes these compounds or associated complex

compounds, e.g., $(\text{CaO})(\text{FeS}_x)_y$, have different thermal stabilities, one would expect to observe different effects of temperature. This situation was observed and commented on in the CaO-FeS_2 short-term exposure studies.

As noted in the X-ray data, complex compounds, such as CaO-FeS_x , appear to be formed from the decomposition products of FeS_2 which tend to tie up the iron-bound sulfur. This process can account for a significant amount of the retained sulfur in the solids. The X-ray data indicate 50 percent or more sulfur retention by compounds other than CaS . However, due to the release of volatile products in the reaction, less sulfur can be retained as CaS .

Taking Reaction 12 as the initial step in the overall reaction process, it follows that the formation of CaS can arise from the reaction of elemental sulfur with CaO , i.e., for one mole of FeS_2 ,

where $y = \frac{2-x}{2}$, and $x = 0$ if elemental sulfur is used as the starting material in place of pyrite. Data from the CaO-S_2 reaction tend to confirm Reaction 15, as discussed below. However, for $x \neq 0$, the X-ray data, although they support the general nature of Reaction 15, suggest that the reaction may not proceed quantitatively as shown, but that the y -values for CaS and for SO may be different. This is discussed in more detail below.

Reaction of CaO With Sulfur

Studies of the reaction of CaO with elemental sulfur; and with sulfur vapors generated from FeS_2 , showed that elemental sulfur can react with the CaO to give CaS and SO as indicated in Reaction 15 if it is assumed that disproportion reactions such as,

are forming SO_2 , the major sulfur oxide observed in this study.

Examination of the data from the analyses of the solids remaining in the CaO -sulfur reactions yields values for y (CaS) in Reaction 15 as follows.

Experiment	y (moles CaS)	Moles $\text{SO}_2 \times 10^3$		
		Equation		Observed
		16	17	
FeS_2 (Run 2) $\text{S}_2 \xrightarrow{\text{CaO}} \text{CaS}$	5.0×10^{-3}	1.7	2.5	2.7
CaO-S_2 Mixture		0.82	0.27	0.39

Since, in accordance with Reaction 15, y is also the number of moles of SO produced, it follows that the postulation of SO_2 formation via Reactions 16 and 17 can be tested by comparing the calculated amount of SO_2 expected from Reactions 16 and 17 with that observed experimentally. The last three columns in the above tabulation show these comparisons. The experimental data are in excellent agreement with the amount of SO_2 formed via Reaction 17 thus tending to substantiate the reaction scheme set forth in Reactions 15 and 17. The end products formed in the reaction of CaO with sulfur vapors based on this sequence of reactions are thus CaS (solid) and SO_2 and S_2 , the latter arising from SO disproportionation and unreacted S_2 evolved from pyrite. The S_2 produced in Reaction 17 produces a cycle via Reaction 15. Accepting Reaction 17 as the source of SO_2 , one notes in the process that at most, 50 percent of the S in the pyrite can react with CaO . If one follows this sequence through to the production of SO_2 , it is seen that 50 percent of the S_2 vapor can be converted to a sulfur oxide, and only one-half of this 50 percent can yield SO_2 . This would say then, that at most only some 12.5 percent of the sulfur in pyrite would yield SO_2 in the current studies. Maximum yields of 12 to 14 percent SO_2 were observed in the CaO-FeS_2 studies, tending to confirm the reaction scheme for SO_2 formation.

Sulfur Oxide Formation in the CaO-FeS₂ Reaction

While SO₂ was observed in the reaction of elemental sulfur with CaO, the dioxide was also observed as the major gaseous product evolved from the reaction of pyrite with CaO. A postulated reaction scheme leading to SO₂ formation was presented and substantiated in the previous section for the CaO-S₂ reaction. Applying this scheme to the CaO-FeS₂ reaction produced inconsistencies in the data. Using the same procedures as in the previous section, values of y were calculated for CaS using the XRD data from selected CaO-FeS₂ samples. The calculated values are tabulated below for four samples.

Sample No.	Moles CaS Formed (y) $\times 10^3$	Moles SO ₂ $\times 10^4$ Reaction Sequence		
		15 and 16	15 and 17	Observed
1	1.33	4.42	6.65	3.07
2	2.42	8.07	12.1	4.62
3	4.00	13.3	20.0	9.98
4	2.26	7.53	11.3	0.36

In contrast to the data obtained in the reaction of elemental sulfur with CaO, the pyrite-CaO data are in better agreement with a Reaction 15-Reaction 16 sequence. However, the observed SO₂ values are still 25 to 43 percent lower than the calculated values for the sequence. Interestingly, the calculated SO₂ values for the Reaction 15-17 sequence are about twice the observed values for Samples 1 and 3 (somewhat more for Sample 2). Thus, it appears that, per mole CaS formed, only about half as much SO₂ is formed in the pyrite-CaO system as in the elemental sulfur-CaO system, suggesting additional as yet, undetermined steps may be taking place in retaining sulfur in the CO-FeS₂ system.

Very little SO₂ was observed in the presence of charcoal, Sample 4. As mentioned earlier, the chemistry of the reaction appears to be noticeably changed in the presence of charcoal as is also borne out in the SO₂ data.

Summary

The results of this study indicate that more than 70 percent of the sulfur in a CaO-FeS_2 mixture can be retained in the solid at temperatures up to 2010 F (1100 C) and at a Ca/S mole ratio of 3.0. However, even in the absence of oxygen, the CaO-FeS_2 chemistry indicates that some of the sulfur in the solid will be lost as SO_2 . This loss will be more prominent with increasing oxygen content of the gas stream. Thus in a two-stage LIMB-type coal firing process, one would likely observe less than 70 percent retention of the sulfur from the pyrite in the coal in the fuel-rich first stage because of (1) the presence of oxygen and (2) combustion temperatures greater than 2010 F.

Assuming the volatile sulfur in the coal is eventually released as H_2S and COS in the fuel-rich environment, chemical equations show that these materials can react on a one-to-one basis with CaO to form CaS without loss of sulfur. However, reaction times appear somewhat long for the complete capture process and some of the volatile sulfides will not likely have time to react with the CaO in the first stage environment and will probably be oxidized to SO_2 in the oxidizing second stage. Depending on the temperature of the second stage, some of the SO_2 produced from the H_2S and COS as well as from the pyrite sulfur, could react with the CaO in the second stage and be retained as CaSO_4 .

TASK 1B. SULFIDATION KINETICS

The objective of this phase of the program was to determine the kinetics of sulfidation of lime/limestone. This was to be conducted using essentially pure gaseous sulfides that might be encountered in the reducing zone of a typical two-stage combustion rig. Since limestones are the preferred sorbents for use in an utility boiler (cost, calcium content) the study was restricted to them.

Reactions of H₂S and COS With CaO

Background information on the reaction of sulfur bearing gases with solid sorbents is provided in References 15-30. In the present program, the reaction kinetics between COS and H₂S with a calcined limestone were investigated in the 1146-1373 K temperature range. The experiments were conducted using a microdifferential reactor, in contrast to the number of other research efforts which have used a thermal gravimetric technique. The microdifferential reactor is an effective tool for elucidating reaction rates and pathways under conditions when multiple reactions can occur^(1,17,18).

Experimental

The reactor used in this task is shown in Figure 18. The reactor is a quartz vessel 15 mm diameter and 37 cm long. The reactant gas stream flow is indicated by arrows. The gas is preheated to the furnace temperature prior to reaching the sample on the quartz frit. The quartz frit is a porous plug (150-200 μ) fused to the inner tube of the reactor. A Cr/Al thermocouple located 5 millimeters above the frit records sample temperature. Gas flows were controlled using critical flow orifices. The gases were vented to an exhaust hood after leaving the vessel. No analysis of the exhaust gases was performed in this study.

The volumetric gas flow through the reactor was maintained at approximately 65 cm³/sec (STP). The high gas velocity minimizes diffusion effects near the surface of the particles.

The physical characterization of the lime used in this study is indicated in Table 7. In a typical experiment, approximately 100 mg of sample was placed on the quartz frit of the inner tube of the reactor and then inserted into the outer reactor shell which is vertically supported in the furnace. A flow of inert gas (N₂) was passed through the bed of material for approximately 3 minutes prior to admitting the reactant gas. A three-way valve shut off the inert gas flow and started the

TABLE 7. CaO PARTICLE SIZE DISTRIBUTION

Sieve Opening Size, μ	Mesh Size, U.S.	Weight Passing, g	Wt.% Retained on Screen	Wt.% Greater Than Indicated Mesh Size	Wt.% Smaller Than Indicated Mesh Size
840	+20	0	0	0	0
420	+40	0	0	0	0
250	+60	13.07	17.4	17.4	82.6
177	+80	23.70	31.3	48.7	51.3
149	+100	9.629	12.7	61.4	38.6
74	+200	21.90	29.0	90.4	9.6
44	+325	3.953	5.2	95.6	4.4
<44	-325	3.359	4.4	100.0	0

Mean particle size = 220 μ

Surface area = 2.91 M²/gm

FIGURE 18. DIFFERENTIAL REACTOR

reactant gas flow. The reaction time clock was started when the reactant gas flow began.

The reactant gas flow was stopped at the end of an experiment and the inert gas flow started once again. The inert gas was allowed to flow through the reactor for approximately 3 minutes to purge any remaining reactant gas from the vessel prior to opening. The inner section was slowly removed from the vessel to allow the reactant bed temperature to equilibrate to the lower temperatures prior to exposure to the atmosphere. The exposed sample was then placed in a dried vial and sealed.

Experimental Results

The experimental runs carried out in this task are outlined in Table 8. In each of the first four series, CaO samples were placed in a flowing stream of COS and CO for different exposure periods. A moderate quantity of CO was used to shift the equilibrium of reaction to minimize the thermal decomposition of COS, viz.

TABLE 8. EXPERIMENTAL OUTLINE

Series No.	1	2	3	4	5	6	7	8
Reactant gas*	COS	COS	COS	COS	H ₂ S	H ₂ S	H ₂ S	H ₂ S
Concentration, ppm	4421	4421	4421	4421	4421	3850	4616	3850
Support gas*	CO	CO	None	CO	H ₂	H ₂	None	H ₂
Concentration, %	11.5	11.5	0	11.5	16.7	16.7	0	16.7
Reaction Temperature, K	1144	1242	1246	1352	1137	1242	1242	1373

* Remaining gas is nitrogen.

Based upon the thermodynamics of Reaction 18, a significant amount of COS could be expected to decompose at the temperatures under study. Calculated equilibrium gas concentrations for COS and H₂S at various temperatures are shown in Table 9.

Table 9 shows that at 1200 K and with a starting concentration of approximately 5000 ppm COS, the gas decomposes to produce 148 ppm COS, 4350 ppm CO, and 2175 ppm S₂ when no CO is used to shift the equilibrium. The introduction of 10 vol percent CO into the gas stream alters the equilibrium to produce a gas composition of 1031 ppm S₂ and 2436 ppm COS.

In the second part of the program, samples of CaO were reacted with H₂S and H₂ at different reaction times. Because Reaction 19 also proceeds to the right with increasing temperature, a quantity of H₂ was blended with the gas to shift equilibrium to the left.

In Experiments 5-8 no products of decomposition of H₂S were noted, including Test 7 which contained no excess hydrogen. This is in contrast to Experiments 1-4 where evidence of COS decomposition products was observed. The decomposition products produced discoloration of the reactor walls and deposited sulfur in the cooler regions of the reactor outlet. Increasing the amount of CO in the gas stream did not eliminate the problem in Experiments 1-4. As a consequence, modifications to the differential reactor exhaust system were required due to plugging of exhaust lines with elemental sulfur.

CaO/COS/CO Reaction. The runs in these series were made under the conditions specified in Table 8 for periods of 2 to 35 minutes. After approximately 10 minutes exposure to the reactant gas stream, all of the samples achieved approximately 60 percent conversion via Reaction 20.

TABLE 9. EQUILIBRIUM REACTANT GAS COMPONENTS

Reaction A				
$\text{COS} \rightleftharpoons \text{CO} + 1/2 \text{S}_2$				
Temp K				
	1000	1100	1200	1300
K_A	0.219	0.592	1.345	2.683
CO% (initial)	0.0	0.0	0.0	0.0
COS ^(a) , ppm	750	318	148	86
CO, pp.	3750	4180	4350	4420
S ₂ , ppm	1875	2090	2175	2210
CO% (initial)	10.0	10.0	10.0	10.0
COS ^(a) , ppm	4319	3604	2436	1488
S ₂ , ppm	89.7	447	1031	1505
Reaction B				
$\text{H}_2\text{S} \rightleftharpoons \text{H}_2 + 1/2 \text{S}_2$				
	1218	1338	1405	
K_B	0.0495	0.109	0.161	
H ₂ % (initial)	0.0	0.0	0.0	
H ₂ S ^(b) , ppm	2340	1650	1350	
H ₂ , ppm	2660	3350	3650	
S ₂ , ppm	1330	1675	1821	
H ₂ % (initial)	5.0	5.0	5.0	
H ₂ S ^(b) , ppm	4952	4786	4573	
S ₂ , ppm	24	107	213	
(a) Initial concentration of COS: 4498 ppm				
(b) Initial concentration of H ₂ S: 5000 ppm				
$K_A = \frac{P_{\text{CO}} P_{\text{S}_2}^{1/2}}{P_{\text{COS}}}$	$K_B = \frac{P_{\text{H}_2} P_{\text{S}_2}^{1/2}}{P_{\text{H}_2\text{S}}}$

Kinetic results of previous work in this system indicate that the reaction follows first order kinetics with respect to unreacted calcium oxide⁽²⁵⁾. Mathematically this can be represented as

$$\frac{-d\text{CaO}}{dt} = k(\text{CaO})$$

When plotted as the conversion versus time, the plot should appear linear. Conversion is defined as $-\ln(1-x)$ where x is the fraction of CaO converted to CaS.

$$x = \frac{\text{CaO}_i - \text{CaO}_t}{\text{CaO}_i}$$

For points of reference

<u>% Reacted</u>	<u>Conversion</u>
10	0.11
25	0.29
50	0.69
85	1.90

where

CaO_i = initial quantity of calcium oxide

CaO_t = calcium oxide remaining at time t

Results are displayed in Figures 19 through 22. A linear regression analysis of the data indicates correlation coefficients of 0.91 to 0.97. The values of the reaction rate constants extracted from these data are shown in Table 10.

The slopes of the lines drawn in Figures 19-22 were obtained by a least squares fit. The lines themselves however have been arbitrarily displaced to intersect the time zero point. This displacement probably results from the fact that the experiments have been run to too high an extent of reaction.

FIGURE 19. COS-CaO REACTION,
T = 1144 K

FIGURE 20. COS-CaO REACTION,
T = 1242 K

FIGURE 21. COS-CaO REACTION,
T = 1246 K

FIGURE 22. COS-CaO REACTION,
T = 1352 K

As an alternative, the reaction rate can be expressed as

$$R_0 = K S C_x^n$$

where

R_0 = initial reaction rate at $t = 0$; mg/50 mg CaO or mg/g-mole calcine

k = reaction rate constant cm/sec

S = surface area of the calcium oxide; $\text{cm}^2/\text{mg CaO}$

C_x = concentration of the reactant gas; atm or g-mole/ cm^3

n = reaction order

This expression is more commonly used in the literature, but is cumbersome to develop in this work. The reasons for this are:

- (1) The dependence of the reaction rate on the reactant gas was not established by varying C^n , although a value of $n = 1$ is probably correct.
- (2) The reported surface area was for an untreated stone, and is probably not representative of the surface characteristics after exposure to the high temperatures in the reactor.

The initial rate of conversion, R (at $t = 0$), R_0 , can be estimated from the slope

x = fraction of CaO consumed

$(1-x)$ = fraction of CaO remaining

$$-\ln(1-x) = Kt$$

and

$$\frac{dx}{dt} = k(1-x)$$

Hence the rate of conversion of $t = 0$ is determined by setting $x = 0$ which reveals $\frac{dx}{dt} = k$.

H₂S/H₂/CaO Reaction

The H₂S/CaO runs in these series were carried out under conditions shown in Table 8, Series 5 through 8. In Series 6, samples

were exposed to the reactant gas for periods from 2 to 30 minutes, while in the other three series samples were reacted for periods of 5 to 100 seconds. Increasing temperatures produced a moderate increase in the rate of Reaction 21, up to a maximum temperature of 1373 K,

The reaction rate constant at this temperature was $4.31 \times 10^{-3} \text{ sec}^{-1}$. A reduction in the hydrogen concentration in the reactant gas appears to have a minimal effect on the conversion of CaO to CaS; the slight increase in the rate constant in Series 8 is attributed to the increased H₂S concentration.

The data from Series 5 through 8 are displayed in Figures 23 through 26. A kinetic analysis similar to that described in the previous section was performed here. The linear regression analysis of the data indicates correlation coefficients of 0.94 or greater when first order kinetics are assumed. Tabulation of the rate constants are shown in Table 10.

Discussion of Results

CaO/COS Reaction

The kinetic data shown in Table 10 are in reasonably good agreement with results reported elsewhere in the literature^(2,3,11). The rate constants obtained in this study show a weak temperature dependence for Reaction 20, ranging from $9.62 \times 10^{-4} \text{ sec}^{-1}$ to $1.23 \times 10^{-3} \text{ sec}^{-1}$. The weak temperature dependence may be attributed to a decrease in reactivity of the sorbent at temperatures above 1173 K. This decline in reactivity is probably attributed to a decline in the surface area of the lime with increasing temperature⁽²⁷⁾. In this study, diffusion effects were minimized by using a fine powder, although diffusion effects through the product layer are not negligible after long retention time.

TABLE 10. RATE CONSTANTS FOR REACTIONS STUDIED

Series	Reaction	Temp, (K)	k, (sec ⁻¹)
<u>COS</u>			
1	$\text{CaO} + \text{COS} + \text{CO} \rightarrow \text{CaS} + \text{CO}_2 + \text{CO}$	1144	1.06×10^{-3}
2	$\text{CaO} + \text{COS} + \text{CO}_2 \rightarrow \text{CaS} + \text{CO}_2 + \text{CO}$	1242	1.16×10^{-3}
3	$\text{CaO} + \text{COS} \rightarrow \text{CaS} + \text{CO}$	1246	9.62×10^{-4}
4	$\text{CaO} + \text{COS} + \text{CO} \rightarrow \text{CaS} + \text{CO}_2 + \text{CO}$	1352	1.23×10^{-3}
<u>H₂S</u>			
5	$\text{CaO} + \text{H}_2\text{S} + \text{H}_2 \rightarrow \text{CaS} + \text{H}_2 + \text{H}_2\text{O}$	1137	9.19×10^{-4}
6	$\text{CaO} + \text{H}_2\text{S} + \text{H}_2 \rightarrow \text{CaS} + \text{H}_2 + \text{H}_2\text{O}$	1242	6.34×10^{-3}
7	$\text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O}$	1242	6.88×10^{-3}
8	$\text{CaO} + \text{H}_2\text{S} + \text{H}_2 \rightarrow \text{CaS} + \text{H}_2 + \text{H}_2\text{O}$	1373	4.31×10^{-3}

Note: CO concentration in Experiments 1, 2, and 4 is 11.5 percent, 0 percent in Experiment 3. H₂ concentration in Experiments 5, 6, and 8 is 16.7 percent, 0 percent in Experiment 7.

FIGURE 23. H₂S-CaO REACTION,
T = 1137 K

FIGURE 24. H₂S-CaO REACTION,
T = 1242 K

FIGURE 25. H₂S-CaO REACTION,
T = 1242 K

FIGURE 26. H₂S-CaO REACTION,
T = 1373 K

The data reported in this study agree with the data reported in Reference 17 by some 18 percent.

This Study:

Rate Equation: $\frac{d\text{CaO}}{\text{CaO}} = kdt,$

$k \text{ (sec}^{-1}\text{): } 1.06 \times 10^{-3} \text{ @ 1144 K and 4421 ppm COS.}$

Reference 16:

Rate Equation: $\frac{dx}{dt} = 78 C^{-2160/T} P_{\text{COS}}(1 - x);$

assume $x = 0$, $P_{\text{COS}} = 4421 \text{ ppm}$, $T = 1144 \text{ K}$,

$k = \text{Rate Constant (at } t = 0, x = 0) = 8.70 \times 10^{-4} \text{ sec}^{-1}.$

In another study, the reaction of COS with a solid sorbent was examined.⁽²⁵⁾ There were some significant differences in the experiments, however, The sorbent used in Ref. 25 was a fully calcined dolomite, while that used in this study was a calcined limestone. Also, the temperatures and gas concentrations used in Ref. 25 were slightly lower than used in this study, while the mean particle size was slightly larger.

Reference 25:

$k(\text{sec}^{-1}) = 1.08 \times 10^{-4} \text{ @ 1075 K, 2500 ppm,}$

$389 \mu\text{m mean particle size dolomite.}$

If we assume a temperature dependence similar to the $\text{H}_2\text{S}/\text{CaO}$ or $\text{H}_2\text{S}/\text{dolomite}$ reaction (3.6 - 3.9 kcal/mole) first order dependence on the COS concentration and linear dependence on the surface areas of the mean particle size of the sample, the rate constant from Ref. 25 would be approximately $6.7 \times 10^{-4} \text{ sec}^{-1} \text{ @ 1144 K, 4421 ppm and } 220 \mu\text{m mean particle size.}$ This extrapolation is only used to indicate a measure of agreement between two different studies using different techniques. The rate constant derived in this extrapolation is probably lower than what might be expected from a calcined dolomite relative to a calcined limestone.

CaO/H₂S Reaction

Four series of experiments were performed using H₂S as the reactant gas and CaO as the solid sorbent (Table 7). The temperatures chosen were similar to those used in the CaO/COS reaction. Reaction rate constants were reported in the range of $9.19 \times 10^{-4} \text{ sec}^{-1}$ to $6.88 \times 10^{-3} \text{ sec}$ for temperatures from 1137 to 1373 K. There appears to be no discernible influence of H₂ when present in large quantities*. The temperature dependence of the rate constant was difficult to determine because of what appears to be an anomalously high value reported at 1242 K. The reason for the high value is not clear and no kinetic re-examination was performed in this temperature regime.

The reasoning behind the assumption that the 1242 K rate constant is anomalously high is based upon rate constant data obtained from Ref. 30 and displayed in Figures 23, 24, and 26. Pell⁽³⁰⁾ used a powdered sample of dolomite to study the CaO/H₂S reaction at temperatures of 748 K to 1173 K with H₂S concentrations of 0.3 vol percent to 20.0 vol percent. Examination of the reported "final" rate constant (sec^{-1}) of the powdered samples at 0.38 vol percent H₂S corresponding to the 3850 ppm H₂S used in this study indicates the following relationship:

$$\text{Ref. 30: } k = 17.3 \exp \left(- \frac{11330}{T} \right) \text{ sec}^{-1} .$$

Data taken from Ref. 30 used to develop this rate constant expression has a correlation coefficient to 0.99. From this rate constant expression, an estimated rate constant can be determined and compared to the values obtained in this study:

Temp. (K)	Calculated Rate Constant (sec^{-1}), Ref. 30	Measured Rate Constant (sec^{-1}), This Work
1137	8.14×10^{-4}	9.19×10^{-4}
1242	1.89×10^{-3}	6.34×10^{-3}
1373	4.51×10^{-3}	4.31×10^{-3}

* We learn from R. Borgwardt, U.S. EPA, in work that is to be published that hydrogen caused a marked retardation in his kinetic rates.

One must exercise caution when comparing data from Ref. 16 to this work since the solid sorbent used in Ref. 30 was dolomite, while a calcined limestone was used in this study. However, rate constants have been reported for Reaction 21 with calcined dolomite and calcined limestone that are approximately equal at 973 K⁽¹⁵⁾. Based upon this information, the comparison of data in this work to Ref. 30 is reasonable.

Because of the large scatter in the rate constants obtained, no activation energies are reported. However, the rate constant reported in test series 5 and 8 are relatively close to values obtained from Ref. 30. The activation energy reported in Ref. 30 is 22,546 cal/mole. Evidence presented here supports this calculated activation energy. Table 11 lists activation energies obtained from literature sources.

TABLE 11. H₂S/CaO ACTIVATION ENERGIES^(a)

Reference	Temperature (K)	E cal/mol	Comments
4	1060-1144	10,000	Calcined dolomite
11	873-1073	3,600	1% H ₂ S reacted with calcined dolomite; mean particle size = 389 μ
12	573-1073	5,160	1.9-7.0 vol % H ₂ S reacted with reagent CaO powder; <100 mesh
16	748-1173	22,546	0.3-20.0 vol % H ₂ S reacted with calcined dolomite; -80 to +325 mesh

- (a) Reactions involving calcined dolomites (MgO · CaO) will only produce CaS because of unfavorable thermodynamics for producing MgS.

Additional Reactions

As mentioned earlier, the decomposition products were noted in inlet and outlet streams of the reactor using COS as the reactant gas. The presence of CO did not appear to shift the equilibrium of reaction (22)

Although thermodynamics predicts significant decomposition at the temperature used here (see Table 9) the rate at which the equilibrium is approached is uncertain. However, qualitatively it appears that COS/CO/S₂ may approach equilibrium. In the event the sulfidation of CaO may be markedly influenced by the following additional steps.

Step 23 would compete primarily with (20), since COS and S₂ would still comprise the dominant gaseous sulfides.

If steps 20 and 23 are the primary steps for sulfur devolatilites, the rate expression

$$R = kSC_x^n$$

would be modified to

$$R = kSC_x^n C_y^m$$

where two components are now included in the rate equation.

Summary

Calcined limestone samples were exposed to COS and H₂S gas streams for various time periods. Gaseous concentrations were in the range of 3000 to 5000 ppm, limestone quantities were approximately 100 mg.

The reaction of COS with CaO exhibited a weak temperature dependence in the range of 1144 to 1373 K. The reaction followed first order kinetics with respect to the unreacted sorbent for both the COS-CaO and H₂S-CaO reactions. The addition of CO to the COS gas mixture (or H₂ to the H₂S) exhibited little influence on the reaction kinetics.

The reaction rate constant k determined for both systems from $dX/dt = K(1-x)$ are comparable to those reported by other researchers. The observed values are

<u>System</u>	<u>k, sec^{-1}</u>
CaO + COS	$9.62 \times 10^{-4} - 1.23 \times 10^{-3}$
CaO + H ₂ S	$9.19 \times 10^{-4} - 6.34 \times 10^{-3}$

The temperature dependence of the CaO-H₂S reaction was not clearly defined since the highest rate constant observed was not at the highest temperature. A possible explanation for this anomaly is the loss of active surface area on the sorbent at the highest temperatures.

TASK 2. CaS OXIDATION

Objective

The objective of Task 2 was to determine some of the boundary conditions for oxidizing CaS. Although not a large effort in the overall program, it was a necessary one to assure that the high CO conditions of Stage 1 reactions do not interfere or alter the Stage 2 oxidation process in converting CaS to CaSO₄.

Experimental

The microdifferential reactor procedure used in the Task 1 H₂S-CaO and COS-CaO studies was used in the study of CaS oxidation. Oxygen and nitrogen mixtures containing up to 2 percent oxygen were passed over CaS at 1000 C for periods up to 360 seconds. Exposed samples were analyzed for sulfide and sulfate.

CaS/O₂ Reaction

The global oxidation of CaS is described by Reaction 27:

Reaction 27 however only partially describes the reactions occurring in the CaS bed in the presence of oxygen. Additional reactions which may also be occurring include

The number of potential competing reactions cited here complicate any assessment of the data. Analysis indicates that at contact times in excess of 60 seconds in a flowing oxygen stream, nearly all of the sulfur remaining in the sample was in the form of a sulfate. However, a large part of the original sample sulfur was evolved via Reactions 28 or 29.

Analysis of samples taken at contact times of 60 seconds or less suggests that nearly all of the sulfur in the sample was unreacted sulfide, but that some 20 to 30 percent of the original sulfur was volatilized to SO₂ or S₂, again presumably via Reactions 28 and 29.

Attempts to correlate sample weights with reaction time were confronted by the apparent weight gain of some samples and weight loss of others. This peculiar "oscillatory" behavior has been reported elsewhere in the literature under conditions similar to those used here.⁽³¹⁾ Reactions which contribute to the increase in weight include Reactions 27 and 30, while 28, 29, and 32 account for the loss in weight. The oscillatory behavior is attributed in Ref. 31 to a cyclic formation and decomposition of the CaSO_4 .

The formation of CaSO_4 proceeds via Reaction 27 which also acts as a means of isolating the core of the CaS particle. At the CaSO_4 -CaS interface the CaSO_4 begins to decompose via Reaction 32. No further oxidation of CaS will occur behind the CaSO_4 -CaS interface because the O_2 partial pressure has been greatly reduced by the CaSO_4 formation. The apparent weight loss is then attributed to the decomposition at the CaSO_4 interface via reaction 32. The mass loss results from the loss of SO_2 from the particle.

This brief examination of the oxidation of CaS brings out several important items relative to LIMB processes. It is rapidly obvious that conversion of CaS to CaSO_4 is much oversimplified by the global reaction of Reaction 27. Oxidation involves at least the six reactions cited above, and could involve many more. The significance of these various reactions on the CaS oxidation studies is discussed further at the end of this report in terms of CaO -CaS- CaSO_4 equilibria.

TASK 3 - METHANE-COAL STUDIES

Objective

The objective of this task was to define the chemical and kinetic parameters governing CaS and CaSO_4 formation in the fuel-rich stage of a staged combustor.

Experimental Procedures

Coals impregnated with CaO were burned under fuel-rich conditions in two separate environments. Coal was injected in the pre- and post-combustion zone of a near-stoichiometric methane flame to determine the effects of temperature, residence time, equivalence ratio, and Ca/S mole ratio on the retention of sulfur in the ash.

In another series of experiments, coal firings were made in the absence of the methane flame. The purpose of these runs was two-fold, (1) to clarify the effects of the CO₂ and H₂O generated from the methane flame on sulfur retention in the ash, and (2) to examine briefly the extent to which the sulfur-bearing compounds in the coal volatiles react with lime (CaO) in the absence of the methane combustion products.

Small quantities of treated coal were burned in a premixed methane flame environment to determine the sulfur retention chemistry at various temperatures, times, and equivalence ratios. The methane flame was used to provide a high temperature combustion environment for the coal reactions. The combustor and associated apparatus are described below.

Combustor

The combustor used in this task is shown in Figure 27. The combustor was fired in a downward direction to minimize ash fallout on the hot tube walls. A water-cooled Meker-type burner was used to stabilize the methane flame. Pulverized coal (80 percent -200 mesh) was fed to the burner through a 1/8 in. O.D. brass tube using nitrogen or air on a carrier gas. Fairly uniform distribution of coal particles was attained by flaring the end of the 1/8 in. tube or locating a cone shape rod at the end of the tube. The coal particles were fluidized prior to entering the 1/8 in. tube by passing the carrier gas over the surface of the coal placed in a rotating 1 in. O.D. by 12 in. long cylindrical tube feeder. This procedure provided a fairly steady feed rate of coal and produced an elongated coal flame as shown in the figure.

FIGURE 27. COAL BURNER SETUP

To control the postflame temperature, a high temperature resistance furnace was installed around the 53 mm I.D. quartz tube enclosing the downstream region of the flame from approximately the burner head to the flue gas exit (~30 inches). Temperatures could be maintained to at least 2300 F over this region with the furnace; this allowed more accurate evaluation of residence time affects. The residence time values were determined from the postflame temperature readings corrected for radiation. An average temperature was used which was determined by averaging the maximum postflame temperature and the temperature at the point of sampling, T_s , assuming a linear decrease in temperature, i.e.,

$$T_{avg} = \frac{T_{max} + T_s}{2}$$

Residence times ranged from about 0.13 to 0.65 seconds at temperature based on the total gas input flow values. Since 70 percent or more of the input gases was N_2 , and the combustion reactions would not alter the total moles of gas significantly, the gas input flow values sufficed for calculating residence times.

Temperatures. Temperatures were obtained from Pt/Pt 10 percent Rh and chromel-alumel thermocouples inserted into the post-flame region at approximately 6 inch intervals below the burner head. Four platinum thermocouples of different wire diameter (0.12 to 0.50 mm) were used at the first 6-inch position to provide the radiation correction. By extrapolating the temperature readings obtained at the 6-inch location to zero wire diameter, a radiation correction term was determined for each thermocouple. The temperature correction equation

$$\Delta T = \frac{1.25 \epsilon \sigma T_w^4 D_w^{.75}}{\lambda} \left(\frac{\eta}{\sigma \gamma} \right)^{.25} \quad (I)$$

was then used in the form

$$\Delta T = CT_w^4,$$

where C represents all terms other than T in Equation I; C was then calculated by determining ΔT from extrapolation and using the wire temperature T.

It was assumed in calculating T at different temperatures that C did not vary significantly with temperature. Since some of the terms in Equation I are temperature dependent, the radiation correction terms were in greater error at temperatures significantly removed from the T value used to determine C.

Analytical

The flue gases from the M-C burner were analyzed for SO₂, CO, CO₂, and O₂; particulate samples were collected for C, H, N, and S analyses. The instruments used to measure the gaseous components were:

SO ₂	Electrochemical (Faristor)
CO	NDIR
CO ₂	NDIR
O ₂	Paramagnetic.

A quadrupole mass spectrometer was used in some runs to measure CO₂, O₂, and N₂.

Fuel-rich firings produced significant amounts of H₂S and lesser quantities of COS and CS₂. Sulfides (as well as CO) interfere with SO₂ analysis by the electrochemical method. Other analytical procedures were therefore used to at least partially circumvent the interference problem and allow determination of total sulfides. In so doing, the SO₂ in the original gas sample was first removed and determined by absorption in hydrogen peroxide solution. The remaining sulfides were then analyzed as a group by oxidizing them to SO₂ in excess oxygen over iron oxide at 425 C or over platinum gauze at 800 C. The oxidized sulfides were then determined by absorption in hydrogen peroxide, or by the electrochemical method provided CO levels were not high (<1 percent).

Firing Conditions-General. Most of the coals used in this study were Illinois No. 6 pulverized to 80 percent-200 mesh and treated with lime to give a Ca/S ratio of 3.8. The coals were fed to the methane-coal (M-C) burner at rates of 1 to 2-1/2 grams/minute. The g-moles of coal per minute based on a composition of $(CHS_{.025})$ entering the burner ranged from 0.50 to 1.0 of the total moles/minute of methane fed to the burner.

Most of the runs were made under fuel-rich conditions. The equivalence ratio, defined as

$$\phi = \frac{(F/A)_{\text{actual}}}{(F/A)_{\text{stoich}}} \quad (I)$$

was calculated in a number of different ways throughout this study. In each case, however, the ratio was determined either from the total amount of fuel (coal + methane) and oxygen fed to the burner, ϕ_{tot} , or from the total coal input plus oxygen remaining in the gases after complete combustion of the methane to CO_2 and H_2O . In the latter case, the ratios have been reported as ϕ_{coal} and/or $\phi_{\text{volatiles}}$ based either on the total amount of coal fed to the burner or on the volatiles from the coal, respectively. However, for a given coal, it is apparent that the two ϕ values are directly related since the volatile content of the coal will remain a constant fraction of the total coal, therefore,

$$\phi_{\text{volatile}} = a\phi_{\text{coal}} \quad (II)$$

The value of "a" for the coals used in the current study is about 0.62. Thus, as far as data correlation is concerned, either of the ϕ values will show the same trends, for example, ϕ versus sulfur retention (S_R) or ϕ versus carbon burnout (B_c).

It is apparent from the above procedure for calculating the equivalence ratio for coal that $\phi_{\text{coal}} = \infty$ when only enough oxygen is present to oxidize the CH_4 . Also, the above procedure does not distinguish between preflame and postflame injection of the coal. It is apparent in preflame coal injection that the coal volatiles would be

competing with the methane for oxygen. The ϕ_{coal} value here could easily be different from that in postflame coal injection. Data were not available to determine the difference. However, in most of the runs of this study, the coal was injected after the methane flame where the ϕ_{coal} values could be determined more accurately. Preflame injection was used only in the earlier initial runs.

Results

Methane-Coal Firings

Pertinent data from the methane-coal firings are presented in Tables 12 and 13. Table 12 includes data primarily on firing conditions and ash analyses while Table 13 contains data on the analyses of gaseous components in the flue gas streams. In Runs 1 through 7, the coals were injected prior to the gas flame. In Runs 8 through 16, the coals were injected downstream of the flame. In all runs except Run 1, the coals were treated with lime to give a Ca/S mole ratio of 3.8.

Equivalence Ratio. From the data, it appears that the major experimental parameters effecting the sulfur retention process were temperature, residence time, and Ca/S mole ratio. The equivalence ratio (ϕ_{tot} or ϕ_{coal}) as calculated in this study does not present a strong correlation with data, as for example with sulfur retention or carbon burnout. This is seen in Figures 28A and 28B which include most of the data obtained in this study. Runs 14, 15, and 16 of Table 13 also bring out the absence of a trend in the ϕ vs. sulfur retention data. A meaningful equivalence ratio in a binary fuel system such as used in this study is difficult if not impossible to define.

Temperature, Residence Time Effects. Although these two variables are somewhat interdependent, their effects on sulfur retention have been readily observed in the data. In some instances, the individual effects can be isolated.

It is evident from the fuel-rich firings, that increasing the temperature and/or residence time in the combustor increased the carbon burnout and decreased sulfur retention in the ash. This is seen in comparing ash sulfur retention data in Runs 2 and 3, Runs 4 and 5, and Runs 12 and 13 in Table 13. For a highly fuel-rich environment (Run 2), up to 85 percent retention of sulfur can be obtained at short residence times of about 130 msec and temperatures around 2075 F. Carbon burnout, however, was poor. Increasing the residence times to 300 msec at 2075 F (Run 3) decreased the sulfur retention to about 50 percent. Adding a small amount of oxygen to the incoming gas stream improved sulfur capture, but did little to improve carbon burnout as noted in Run 4 of the table.

A further increase in the residence time to greater than 500 msec in the fuel-rich firings reduced the sulfur retention in the ash to even lower values. Only at a very low combustion temperature (1800 F) was sulfur capture greater than 50 percent in the ash (Run 13). Also, this run contained no oxygen in the postflame gases. It is evident from the data that a combined increase in combustion temperature and residence time resulted in a major loss of sulfur in the ash. At temperatures higher than 2150 F and residence times greater than 525 msec, no more than 35 percent sulfur retention was observed in any of the ash samples in the fuel-rich firings. Increasing the oxygen to a fuel-lean environment, as in Run 10, gave a marginal 5 percent increase in capture at 2160 F. Carbon burnout appeared exceptionally low in this run. Overall, however, carbon burnout, was greatly improved at the higher temperatures and longer residence times. Good sulfur capture appears to be obtained only at the expense of low carbon burnout as shown in the next section.

Comparing the sulfur retention data in Table 12, determined from the sulfur remaining in the ash, with that from the sulfur species measured in the flue gas, shows a large discrepancy between the two sets of data. In all but three runs, Runs 4, 10, and 14, the flue gas data were significantly higher than the ash data. Since methods for determining total sulfur in ash samples are more reliable than current

FIGURE 28. EFFECTS OF EQUIVALENCE RATIO

TABLE 12. SULFUR RETENTION IN TREATED COAL FIRINGS
(BTC Coal, Ca/S = 3.8)

Run No.	ϕ		Temp. F	Residence Time (msec)	Percent Sulfur			Percent Sulfur Retained		Carbon Burnout
	Total	Coal			Total	Sulfate	Sulfide (c)	Ash	Flue-Gas	
1(a)	2.1	∞	2070	130	3.29	--	--	37	--	45
2(b)	1.8	∞	2070	130	3.04	--	--	85	--	12
3	1.7	∞	2075	300	2.39	--	0.98 [1.27]	51	87	37
4	1.3	4.9	2075	300	3.17	--	1.01 [1.51]	79	74	34
5	1.3	4.1	2530	550	2.19	2.21	--	32	79	76
6	1.1	2.0	2360	565	1.89	1.89	--	25	92	84
7	1.1	1.5	2395	545	2.4	2.49	--	34	61	78
Post-Flame Injection, High Temperature Furnace										
8	1.3	3.4	2250	645	1.42 (1.46)	1.44 (0.96)	(0.48)	22	81	85
9	1.1	1.3	2215	645	1.29 (1.08)	1.31 (0.69)	(0.32)	18	53	90
10	0.94	0.73	2160	655	2.36	2.44	--	40	43	69
11	1.2	2.2	2250	175	1.2	1.44 (0.38)	(0.22)	20	92	76
12	1.2	2.4	2250	530	1.2	1.57 (0.29)	(0.16)	18	38	83
13	NA	2.1	1800	600	2.6	3.02 (0.44)	(0.16)	55	89	47
14	1.2	∞	2170	560	1.78	1.33	--	33	24	56
15	1.2	2.7	2200	545	1.68	1.69	--	26	49	75
16	1.2	1.9	2200	540	1.93	1.96	--	29	64	77

(a) Raw coal, 5.21 percent S

(b) BTC coal, 3.14 percent S

(c) [] includes all oxidizable sulfur

() sulfide, outside laboratory analysis.

TABLE 13. TREATED COAL FIRINGS--GAS ANALYSIS
(BTC Coal, Ca/S = 3.8)

Run No.	ϕ		Percent						PPM				Percent Sulfur Retention
	Total	Coal	CO ₂ ^(a)	CO		Excess O ₂		SO ₂ ^(d)	Sulfides	Total	Calc'd		
				Measured	Calc'd ^(b)	Measured	Calc'd ^(c)						
3	1.7	∞	4.5	3.7	--	0	0	25	335	360	2685	87	
4	1.3	4.9	13.2	2.1	--	0	0	125	425	550	2105	74	
5	1.3	4.1	11.3	1.6	1.3	0	0	295	25	320	1500	79	
6	1.1	2.0	11.3	<0.2	1.7	4.0	1.5	95	10	105	1330	92	
7	1.1	1.5	12.5	0.4	0.7	2.3	2.2	615	15	630	1625	61	
8	1.3	3.4	11.5 ^(e1)	2.66	--	0	0	20	305	325	1735	81	
9	1.1	1.3	12.9 ^(e2)	1.28	--	0	0	245	215	460	980	53	
10	0.9	0.7	11.3 ^(e3)	0.18	--	3.5	2.5	230	45	275	485	43	
11	1.2	2.2	11.5	2.0	2.7	0	0	15	90	105	1365	92	
12	1.2	2.4	11.3	3.9	3.5	0	0	130	710	840	1365	38	
13	NA	2.1	11.2	0.8	0.7	2.1	0.5	115	--	115	1005	89	
14	1.2	∞	10.0 ^(f1)	3.50	--	0	0	35	540	575	760	24	
15	1.2	2.7	11.0 ^(f2)	3.06	--	0	0	25	545	570	1120	49	
16	1.2	1.9	12.0 ^(f3)	2.34	--	0	0	145	300	445	1250	64	

(a) Measured CO₂ with coal.

(b) Calc'd values taking into account the unburned carbon in the ash.

(c) Based on the coal combustibles C, H, N, and S.

(d) Determined by the peroxide method.

(e1) Calc'd CO₂+CO 15.9%.

(e2) " " 13.6%.

(e3) " " 10.9%.

(f1) Meas'd CO₂ before coal add'n 12.0%; calc'd CO₂ 10.4%.

(f2) " " 11.3%; " 10.3%

(f3) " " 11.4%; " 10.2%

methods for determining total volatile sulfur species in the flue gas in fuel-rich firings (e.g., H_2S , COS , CS_2 , S_2 , and SO_2), the ash sulfur retention data are considered more reliable. Incomplete oxidation of the gas phase sulfides in the iron oxide or platinum converters coupled with possible loss of elemental sulfur in the sample lines could explain most of the higher values observed in the oxygen-depleted flue gas data. Results and discussions in this study have therefore centered almost entirely on the ash data.

Sulfur Retention Vs. Carbon Burnout. The sulfur retention-carbon burnout data from all the firings of this study are plotted in Figure 29. The equation for the line is given by $S_R = 93.7 - 0.827 B_C$ where S_R = sulfur retention and B_C = carbon burnout.

These data are very similar to Freund and Lyon's data.⁽¹⁰⁾ Their data indicate a sharp drop in sulfur retention beyond 90 percent carbon burnout. However, at this point, there is only about 20 percent sulfur remaining in the ash.

FIGURE 29. SULFUR RETENTION DECREASES WITH CARBON BURNOUT

Sulfide-Sulfate Analyses of Particulate Samples. Ash samples from several runs were analyzed for sulfide and sulfate content (to more clearly identify the chemistry taking place in the capture process). Three different analytical methods were used, (1) wet chemistry, (2) X-ray diffraction, and (3) X-ray fluorescence.

Wet Chemistry. The wet chemical methods, although they do not distinguish the type of compounds present, are generally considered reliable for determining sulfides and sulfates in ashes. Several samples were analyzed for sulfide, sulfate, and total sulfur content. These data were presented earlier in Table 12.

Problems were encountered throughout this study in analyzing the ashes for sulfides. The wet chemical analyses suggested serious interference problems and were therefore considered unreliable. On the other hand, sulfate analyses on several samples indicated the sulfur in the ash was totally sulfate (i.e., no sulfides present). Furthermore, the sulfur in the sulfate agreed fairly well with the total sulfur in the ash as determined by a different analytical method. To further check the reliability of the data, identical ash samples were analyzed for sulfides and sulfates by an outside laboratory. Data from the various analyses are included in Table 12. The numbers in parentheses are from the Commercial Testing and Engineering Lab; all other numbers are from Battelle.

In comparing data, it is apparent that most of the values are in serious disagreement. Many of the values differ by more than a factor of three. The Commercial Testing (CT) values for sulfate analysis are consistently lower than those from Battelle, even though similar analytical methods were used by both labs. Sulfides were present in the ashes according to the CT data, while the Battelle sulfide data are uncertain. However, it is evident even from the CT data, that in most ashes only about 1/3 of the sulfur in the ash is present as sulfide with the remainder as sulfate. Thus, sulfates appear to be dominating in the capture process. Nevertheless, it is evident that more reliable analyses of the ashes are needed before a reliable interpretation of results can be made.

X-Ray Data. Two ash samples were analyzed by X-ray diffraction (XRD) and by an X-ray energy dispersion method (EDM). The latter method identifies the major elements in the ash above mass 23 (sodium). XRD was used primarily to identify calcium compounds in the ash; elemental composition was also derived from these data. The results are presented in Table 14.

TABLE 14. X-RAY ANALYSES OF ASH SAMPLES

Sample No.	ϕ_{tot}		Percent (Normalized)							Ca/S Mole Ratio
			Al	Si	S	Ca	K	Fe	Cl	
1	1.8	XRD	3.1	7.1	7.6	79.0	0.5	2.8	--	8.3
		EDM	3.04	5.69	9.33	79.75	1.02	2.16	--	6.75
		ASTM	--	--	--	--	--	--	--	4.43
2	1.14	XRD	3.0	7.2	4.6	81.4	0.7	2.9	0.3	14.2
		EDM	3.15	6.14	5.55	81.71	1.35	2.10	--	11.78
		ASTM	--	--	--	--	--	--	--	13.75

Both ash samples in Table 14 were obtained from CaO treated coals ($\text{Ca/S} = 3.8$) burned under fuel-rich conditions. Sample No. 1 was burned at an equivalent ratio, $\phi_{tot} = 1.8$ and showed a sulfur retention of about 85 percent. Sample No. 2 was burned at $\phi_{tot} = 1.14$ and showed a sulfur retention of 25 percent. Sulfur retention in these samples was determined by standard ASTM methods.

The X-ray data show that calcium is by far the major metal constituent in the ash, as would be expected. Sulfur is present in the ash in amounts increasing with increasing equivalence ratio, ϕ_{tot} . However, the amount of sulfur in Sample 1 determined by X-ray analysis is less than that determined by the ASTM Method. Ca/S ratios determined by each method in Sample 2 are all in good agreement. The X-ray data

are reported on a semi-quantitative basis making the ASTM data the more reliable in cases where discrepancies exist, as in Sample 1.

Attempts to identify CaS in the ash samples by XRD were unsuccessful. The X-ray patterns showed CaO present and a small amount of CaSO₄. The CaS pattern, if present, was too weak and could not be distinguished from the CaSO₄ pattern. However, since the ASTM Method indicated that Sample 2 had about 7.8 percent CaSO₄, it would appear that the XRD method may not be sensitive enough to detect small quantities of CaS. In view of this, other more sensitive methods were considered for sulfide determination in the ash samples. These included X-ray fluorescence and a combined Raman-IR technique. The latter method, however, was not developed sufficiently to provide useful data at this time.

X-Ray Fluorescence. Two samples that were previously analyzed by the wet chemical method were also analyzed by X-ray fluorescence (XRF). This method relies on a shift in the peak wavelength with different concentrations of sulfate and sulfide in the sample.

Mixtures with different sulfate and sulfur concentrations were made up initially as standards. Peak shifts were determined for each mixture. The unknown samples were then run and peaks compared with the standards to give a measure of the sulfate and sulfide content of the unknowns. (It is estimated that the peaks can be read to within ±5 percent.)

Data from the two samples are shown in Figure 30. These samples were taken from Runs 15 and 16 of Table 12. In comparison with the standards, it is apparent that the ash samples contain a significant amount of sulfide, the peak values showing a sulfide content well over 50 percent. Run 15 is estimated to have about 68 percent sulfide and Run 16, 61 percent sulfide.

These data are in sharp contrast with the wet chemistry data which showed only sulfates present. The XRF data appear more reasonable in view of the fuel-rich environment used. Furthermore, the data show the expected trends in that the run with more oxygen, Run 16, yielded less sulfide. However, there is not yet sufficient data from the XRF method to firmly establish the validity of the results presented here.

FIGURE 30. X-RAY FLUORESCENT MEASUREMENTS OF ASH SAMPLES

To help confirm the XRF method, ash samples spiked with known amounts of sulfide and sulfate were analyzed by XRF and the accuracy of the results determined. Two 50 mg standard solid samples were prepared for XRF analysis. One sample containing 50 percent sulfide and the other 78 percent sulfide. Analyses indicated 53 percent and 100 percent sulfide, respectively. The XRF data are reading high in the sample containing mostly sulfide. It appears that more work is needed to confirm the reliability of the XRF method particularly at the higher sulfide levels. Possibly the use of larger samples (100 mg) would improve the accuracy of the method. The XRF method appears to have the capability of detecting relatively small quantities of sulfide in ash samples.

Flue Gas Analyses. Analyses of the various flue gas components for the runs in Table 12 are presented in Table 13. All values were averaged over the duration of the run and are reported on a moisture-free basis. The treated coal used in all the firings had a Ca/S mole ratio of 3.8.

CO₂, CO, O₂ Analyses. The carbon oxides and oxygen were measured continuously in all runs except Runs 1 and 2. As seen in the table, the measured CO₂ values ranged from 10.0 to 13.2 percent in the runs except for Run 3 which was noticeably out of line at 4.5 percent and probably in error. Relatively high CO levels were observed in most of the runs as would be expected in the fuel-rich firings of this study. An indication of the accuracy of the CO₂-CO data can be seen in Runs 8, 9, and 10 where the total measured CO₂ and CO values (in parentheses, Column IV) are compared with calculated values. The calculated percentages were determined from the total feed rate of methane and coal taking into account the unoxidized carbon remaining in the ash after combustion. The maximum observed deviation between measured and calculated values was 11.3 percent indicating fairly good agreement between the values.

Calculated CO values were also made on a number of runs using the measured CO₂ in the flue gas and unburned carbon values from the ash to derive the CO concentrations. The values are reported under the CO heading in the table. Although larger deviations are observed here than in the CO₂ + CO data, generally the agreement between measured and calculated CO values were within experimental error.

Calculated oxygen levels were also made in several of the runs for comparison with measured values. Although all of the runs except one were made under fuel-rich conditions, oxygen was observed in several of the runs. Incomplete combustion of the coal can result in some oxygen remaining in the flue gases. Taking this into account, calculated O₂ values from C, H, N, S analyses of ashes show oxygen could be present in the flue gas of four of the runs in Table 13. As seen in the O₂ columns in the table, oxygen was observed only in each of the four runs where calculated values showed it could exist thus tending to substantiate the overall reliability of the data. The agreement between measured and calculated values, however, range from fair to poor. The measured O₂ values were consistently higher than the calculated values which might be indicative of a small air leak.

Gaseous Sulfur Compounds. Under fuel-rich firing conditions one would anticipate some gaseous sulfide formation, primarily H₂S and COS. As stated earlier, the presence of sulfides was determined indirectly by first oxidizing them over iron oxide at 425 C or platinum gauze at 800 C and then adsorbing the resulting SO₂ in hydrogen peroxide or measuring it electrochemically (Faristor). The platinum gauze proved to be approximately 80 percent efficient in converting sulfide to SO₂ as determined from standard mixtures of H₂S in N₂. The coal firing data were corrected accordingly. The hot platinum gauze converted very little SO₂ to SO₃ as evidenced by passing mixtures of SO₂-O₂-N₂ over the gauze. The SO₂ originally in the flue gas stream was determined by adsorption in hydrogen peroxide or electrochemically after first removing the sulfides in a CuSO₄ solution.

The SO_2 and gaseous sulfide data are shown in the last five columns in Table 12. The sulfide data in Run 11 are low due to insufficient oxygen in the gas stream to oxidize the sulfides to sulfur oxides. Excess oxygen was present in all other runs. All samples showed both SO_2 and sulfides present in the flue gases with a relatively large amount of sulfides present in several runs as might be expected in fuel-rich firings. In Run 13, only the total sulfur oxide concentration was measured by passing the flue gas sample through the platinum gauze converter.

The measured total gaseous sulfides-oxides in the gas stream (next-to-last column) gave sulfur capture values from 24 to 92 percent. As stated earlier, the gas data generally produce much higher capture values than those determined from the ash data as seen in Table 12. The data from the gaseous sulfur compounds still appear low compared to the ash data. The reason for this discrepancy is not clear at this time. One could reason that elemental sulfur is being formed and depositing in the sample filters or in the sample line. However, particulate analyses do not indicate this is happening and the sample lines do not appear to have sulfur deposits.

In any event, the gaseous sulfur species concentrations must be considered questionable. Species produced in the fuel-rich firings may be causing interference problems in the analytical methods, or a sulfur-bearing species is being produced, which to date has not been measured accurately. Sulfur in the particulate and therefore sulfur retention values determined from particulate analyses are considered more reliable since attempts were made to collect most of the particulates, minimizing bias sampling effects.

Coal Combustion in Absence of Methane Flame

Several experiments were made in the absence of the methane flame to determine the extent to which CO_2 and H_2O from the flame might be affecting sulfur capture. In these runs, pulverized coal was fed with air into a high temperature reaction zone. A resistance furnace

was used to maintain the reaction zone at the desired temperature. The reactor was a 1-1/8 inch ID quartz tube approximately 18 inches long. A fairly constant temperature was maintained over about 14 inches of the tube.

Independent variables were temperature, equivalence ratio, and Ca/S mole ratio. Residence times were approximately constant at 550 ± 25 msec for the four runs at 2100 F. The run at 2280 F, because of the slightly higher temperature, decreased the residence time to 515 msec.

All of the runs were made in a fuel-rich environment. The equivalence ratio, ranged from 1.9 to 3.6 based on an average coal feed rate of 1.5 grams/min. Data for the unburned BTC coals were reported earlier in Table 12. Ash data from the five runs made in the absence of the methane flame are presented in Table 15.

Sulfur retention ranged from about 72 to 83 percent in the runs. Carbon burnout was calculated for three of the five runs and found to be fairly low as would be expected from the high ϕ values used in the runs. Carbon burnout ranged from 50 to 65-1/2 percent and increased with temperature at constant ϕ and Ca/S ratios.

The sulfur retention data are plotted as a function of ϕ in Figure 31. As seen in the figure, sulfur retention increased with increasing equivalence ratio at constant temperature and Ca/S ratio in

TABLE 15. SULFUR RETENTION IN FURNACE EXPERIMENTS

Run	Coal Feed g/min	Ca/S	Temp F	Residence Time msec	Ash, Wt. Percent					Percent		
					C	H	N	S	Ash	O ₂	Sulfur Retention	Carbon Burnout
1	1.9	3.8	2100	525	--	--	--	3.96	62.00	--	73.0	--
2	2.4	3.8	2100	550	37.55	1.41	0.59	3.73	55.50	1.14	76.7	49.8
3	3.6	3.8	2100	575	--	--	--	3.79	55.53	--	78.0	--
4	2.4	3.8	2280	515	28.66	0.96	0.49	4.77	65.82	0-00	82.9	67.5
5	3.0	1.5	2100	550	51.64	0.69	0.94	3.71	43.99	0-00	71.9	54.4

FIGURE 31. EFFECT OF EQUIVALENCE RATIO
ON SULFUR RETENTION

the range covered. The increase was more noticeable below $\phi = 2.5$. Increasing the temperature at constant $\phi = 2.4$ increased the sulfur capture by about 6 percent point. Decreasing the Ca/S mole ratio from 3.8 to 1.5 decreased the sulfur retention by about 6 percentage points. The effects of temperature and Ca/S ratio are not great in the range covered, but still measurable.

It is apparent that good sulfur capture was observed in each of the fuel-rich runs in this study. The capture percentages are considerably higher than observed in the methane-coal studies at comparable carbon burnout values.

CaS Stability in Fuel-Rich Environments

The preceding experiments show quite clearly that CO_2 and H_2O in the combustion products affect the stability of CaS in fuel-rich combustion zones. In this section, results of a more detailed examination of CO_2 , H_2O , and CO in CaS stability are presented.

Experimental Procedure

The microdifferential reactor technique was used in these experiments. In a typical run, 60 to 70 mg of CaS was spread evenly over quartz frit sample holder, sealed to the removable inner tube. The sample was inserted into the reactor after thoroughly flushing the entire system with nitrogen. The nitrogen continued to flow through the system while the sample was equilibrated to reaction temperature. The N_2 purge gas was then stopped and the reacting gas containing various mixtures of CO_2 , CO, O_2 , H_2O , and N_2 was admitted. The gases were passed through the sample for a predetermined time interval, ranging from a few seconds to 15 minutes. After leaving the reactor, the gases were directed to a sampling train where they were analyzed for CO, CO_2 , SO_2 , and O_2 during each run. The CO and CO_2 were analyzed by NDIR, the SO_2 by an electrochemical (Farister) method and O_2 by the paramagnetic

method. The exposed solid samples were cooled in nitrogen before removal to the atmosphere and sealed in a glass container for later analyses.

Effects of Combustion Products on CaS Stability

Data from the above studies and from the earlier M-C studies showed that the supplementary methane flame products (CO_2 and H_2O) were affecting the combustion of the coal in the MC burner, suggesting that the sulfur capture chemistry may also be affected. It seemed important, therefore, to explore in more detail the effects of CO_2 and H_2O as well as CO and O_2 , on the sulfur capture process. The reactor used in these studies is the same as that used in the earlier H_2S -CaO and COS -CaO studies of this report (Figure 18).

Gases. Cylinders of CO_2 , CO , air, and N_2 were used to provide the gas mixtures in the experiments. The gases have reported purities as follows:

<u>Gas</u>	<u>% Purity</u>
CO_2	99.8
CO	99.5
Air	--
N_2	99.9

A nitrogen stream, saturated at room temperature with distilled water, was used to provide the H_2O vapor for studying the effects of H_2O on the CO_2 -CaS reaction.

CaS. The CaS used in the runs was a fine powder (100% -325 mesh) and had a reported purity of 99 percent. Samples after exposure were placed in glass vials and sealed to prevent further exposure to the atmosphere and thus minimize sample oxidation prior to analysis.

Experimental Conditions. Four series of runs were carried out. The experimental conditions used in each run are shown in Table 16. All the runs with the exception of two were carried out at near 2100 F and 10 minutes reaction time. Continuous monitoring of the reactants and products showed that short exposure time runs, such as in Runs 2, 3, and 4 were not needed since methods could be used from the continuous tracings of reactants and products to obtain concentration vs. time data at short and longer time intervals.

Gas mixture velocities from about 105 to 121 cc/sec were used in each of the runs except Run 23, which had a gas velocity of about one-half that of the other runs. The higher velocities were used to minimize diffusion effects near the surface of the particle. As seen later, the lower flow rate did not appear to significantly effect the rate data, tending to confirm that diffusion effects were minimal.

Gas compositions varied in most of the runs as seen in the mole fraction data in the table. The reactant CO_2 and the diluent N_2 were present in each run. Series I, Runs 1 through 10, involve only the reaction of CO_2 with CaS . Water vapor was added to the CO_2 - N_2 mixtures in Run 11. In Series II, Runs 12 through 15, the effects of CO on the CO_2 - CaS reaction were examined. Water vapor was added to the CO_2 - CO - N_2 mixture in Run 16. In Series III, Runs 17 through 19, oxygen was added to the CO_2 - N_2 mixture to examine the combined effect of O_2 and CO_2 on CaS oxidation. Finally, in Series IV, Runs 20 through 23, the combined effect of CO and O_2 on the CO_2 - CaS reaction was examined.

Experimental Results. At the high CO_2 concentrations used, compared to the CaS concentration, the CO_2 level remained essentially constant during any given run. Changes in the concentration of products formed in the CO_2 - CaS reaction, primarily CO and SO_2 , were followed continuously to develop the kinetic data. The results are presented below for each series of runs.

TABLE 16. EXPERIMENTAL CONDITIONS
 $T = 2100\text{ F}$, $t = 10\text{ min}$)

Run	Total Flow Rate, cc/sec	Initial Mole Fraction					Initial wt. CaS mg
		CO ₂	CO	H ₂ O	N ₂	H ₂	
<u>Series I</u>							
1(a)	116	.093	--	--	--	0.91	62.9
2(b)	"	"	--	--	--	"	63.9
3(c)	"	"	--	--	--	"	65.2
4(d)	"	"	--	--	--	"	60.2
5	"	"	--	--	--	"	62.3
6(e)	"	"	--	--	--	"	60.8
7	111	0.10	--	--	--	0.90	59.6
8	109	0.080	--	--	--	0.92	67.7
9	106	0.060	--	--	--	0.94	61.1
10	105	.040	--	--	--	0.96	68.2
11	119	0.93	--	0.028	--	0.88	61.5
<u>Series II</u>							
12	117	.091	.010	--	--	0.90	62.8
13	117	.082	.017	--	--	0.90	69.9
14	117	.075	.025	--	--	0.90	68.6
15	117	.057	.043	--	--	0.90	61.7
16	120	.072	.025	0.028	--	0.90	67.8
<u>Series III</u>							
17	117	.095	--	--	0.0035	0.90	65.0
18	117	.098	--	--	0.0071	0.99	62.5
19	120	.092	--	--	0.0091	0.90	67.7
<u>Series IV</u>							
20	121	.072	.024	--	0.0091	0.89	61.2
21	118	.073	.025	--	0.0091	0.89	62.8
22	121	.055	.042	--	0.0091	0.89	62.8
23	64	.066	.073	--	0.0140	0.85	62.4

(a) $T = 1920\text{ F}$, $t = 15\text{ min.}$ (c) $t = 0.05\text{ min.}$ (e) $T = 2285\text{ F}$
(b) $t = 0.5\text{ min.}$ (d) $t = 0.25\text{ min.}$

Series I. CO₂-CaS Reaction. The overall reaction is postulated to be,

The experimental data are presented in the plots in Figures 32, 33, 34, and 35. Figures 32 and 33 show the amount of SO₂ formed in the CO₂-CaS reaction as a function of time while Figures 34 and 35 show similar data for CO. Figures 32 and 34 show the effect of changing the initial CO₂ concentration on SO₂ and CO formation respectively, all at constant temperature, 2102 F. Figures 33 and 35 show the effect of temperature on the SO₂ and CO formation.

As seen in the figures, the SO₂ and CO concentrations show a linear dependence with time during the first 25 to 45 percent of the reaction (zero order reaction). At longer reaction times, the data begin to tail off approaching, in several runs, the limiting concentrations of SO₂ and CO obtainable from the CO₂-CaS reaction. Other runs, e.g., Runs 1, 5, and 6 of Figure 33, suggest incomplete reaction of the CaS. The tailing off in all of the runs is likely due to the formation of solid products in the CaS mixture. Only the early reaction times (before tailing) were used to develop rate data.

Reaction Rates and Order of Reaction - Constant Temperatures. Figures 32 and 34 show the effects of changing the initial CO₂ concentration on the formation of SO₂ and CO at T = 2100 F. It is apparent from the data that reducing the initial CO₂ concentration decreased the rate of formation of SO₂ and CO. The apparent rates of SO₂ and CO formation determined from the linear portions of the curves in the figures are tabulated below. (The apparent rates are given in units of mole/sec throughout this report. Rates in units of mole/cc sec are obtained by dividing the apparent rates by the total flow of gas in one second, i.e., the flow rates. The rates discussed in this report are apparent rates unless noted otherwise.)

FILE:B:PI.DAT PLOT 1 - MOLES SO₂ x 10⁺⁵ vs. TIME

FIGURE 32. SO₂ RELEASE RATES IN THE CO₂-CaS REACTION

FILE:B:PI.DAT PLOT 1 - MOLES SO₂ x 10⁺⁵ vs. TIME

FIGURE 33. SO₂ RELEASE RATES IN THE CO₂-CaS REACTION

FILE:R01.DAT PLOT 2 - MOLES CO x 10⁴ vs. TIME

FIGURE 34. CO RELEASE RATES IN THE CO₂-CaS REACTION

FILE:R01.DAT PLOT 2 - MOLES CO x 10⁴ vs. TIME

FIGURE 35. CO RELEASE RATES IN THE CO₂-CaS REACTION

Run	Rate x 10 ⁶ (moles/sec)		$\frac{R_{CO}}{R_{SO_2}}$	$\frac{\text{Mole } SO_2 \times 10^4}{\text{Mole CaS-sec} \times 10^2}$
	SO ₂	CO		
5	2.24	5.53	2.5	0.26
7	2.94	7.03	2.4	0.36
8	1.83	4.73	2.6	0.20
9	1.41	4.23	3.0	0.17
10	1.18	3.71	3.1	0.12

These apparent rates can be represented by the equation

$$R = k(CO_2)^n = k' \quad , \quad (I)$$

where k' is a constant during a given run at constant temperature since the CO_2 concentration remained essentially constant during the run. The ratio of rates R_{CO}/R_{SO_2} shown above indicate at CO is being produced on the average about 2.7 times faster than SO_2 .

The data in the last column of the above tabulation show that very little SO_2 was produced in one second from the CO_2 -CaS reaction. Less than 1/2 percent of the sulfur in the CaS was converted to SO_2 in the one second time interval. The percent conversion depends on the CO_2 concentration as well as on the available CaS surface area.

The concentration vs time curves for SO_2 , Figure 2, were used to determine the approximate order of reaction of CO_2 with CaS. The fractional time method was used as represented by the equation,

$$n = 1 + \frac{\log t_y' - \log t_y}{\log a - \log a} \quad (II)$$

where n is the order of reaction, a the initial concentration of CO_2 , and y the fractional time. A fractional time of 0.3 was chosen, i.e., the time necessary for 0.3 of the reaction to take place. The extent of reaction in each case was within the linear portion of each curve.

Several methods could be used to determine n . In the present work, $\log t_{0.3}$ vs. $\log a$ was plotted for each of the runs in Figure 32. Most of the data points from the plot could be represented by a straight

line giving a slope of 0.80 resulting in $n = 1.8$ in Equation I above. Another straight line through the data which took into account a widely deviating point gave a value of $n = 2.1$. The order of reaction appears to be close to 2.0.

Temperature Effect. Figures 33 and 35 show the effect of temperature on the SO_2 and CO formation, respectively. Rates for the different runs are tabulated below.

Run	Temp F	Rate $\times 10^6$ (mole/sec)		$R_{\text{CO}}/R_{\text{SO}_2}$
		SO_2	CO	
1	1919	0.91	2.60	2.9
5	2105	2.24	5.53	2.5
6	2284	2.46	9.29	3.8

The ratio of rates $R_{\text{CO}}/R_{\text{SO}_2}$ in Runs 1 and 5 appear consistent with the chemistry for the CaS-CO_2 reaction. The ratio for Run 6 appears high. It is possible that at the higher temperature some of the CaS is converted to CaO which would then retain some SO_2 , yielding a low rate of SO_2 evolution and consequently the high value for $R_{\text{CO}}/R_{\text{SO}_2}$.

Using the straight line portions of the curves in the figures and rate Equation I, k' values were calculated and a plot of $\log k'$ vs. $1/T$ was made as shown in Figure 36. The CO data yield an activation energy, $E = 11.3$ Kcal/mole. A parallel line through SO_2 data further suggests that the SO_2 rate at the high temperature is low, consistent with the comments made above.

H_2O Effect. The addition of H_2O to the $\text{CO}_2\text{-N}_2$ mixture (Run 11) did not appear to effect the rates of sulfur release or CO formation. Comparing Runs 5 and 11 in Figures 32 and 34, which were run at nearly the same CO_2 concentrations, show the rates to be identical. The measured values are

Rate x 10 ⁶ (mole/sec)			
SO ₂ + H ₂ S		CO	
with H ₂ O	without H ₂ O	with H ₂ O	without H ₂ O
2.25	2.24	5.52	5.53

The addition of H₂O to CO₂ changes the general chemistry as follows:

Hence the sulfur release in Run 11 is SO₂ and H₂S.

Data using higher CO₂ concentrations (near 0.20 mole fraction) showed the SO₂ + H₂S formation rate increased significantly (nearly doubled) with the addition of H₂O. However, the increase was likely due

FIGURE 36. TEMPERATURE DEPENDENCY FOR CO AND SO₂ YIELDS

to the formation of H_2S which was not distinguished from SO_2 in the analysis. While the above data showed no similar increase, it may be that the different initial CO_2 concentration used in the two runs may have some effect. As shown in the Series II runs, however, the H_2O did have a noticeable effect there.

Series II. CO Effects on CO_2 -CaS Reaction. Based on Reaction 28, the addition of CO would be expected to retard the reaction of CO_2 with CaS. The effects of CO on the rate of SO_2 formation from the CO_2 -CaS reaction are shown in Figure 37. All of the runs were carried out at constant temperature, 2100 F. The CO/ CO_2 ratio was varied from about 0.1 to 0.8 in the runs (Runs 12 through 15). It is apparent from the data and comparison of rates in Figure 2 that the presence of the added CO had a marked retarding effect on SO_2 formation. The rate of SO_2 formation decreased from 2.24×10^{-6} mole/sec with no added CO, Run 5, to 0.050×10^{-6} mole/sec with 4.3 percent CO present, CO/ CO_2 mole ratio = 0.8, Run 15. Taking into account the decrease in rate from the lower CO_2 concentration in Run 15 (5.7 percent CO_2 , $RSO_2 = 1.35 \times 10^{-5}$ mole/sec), the rate decreased by more than a factor of 25 in Run 15 compared to Run 5.

The addition of water to the CO_2 -CO- N_2 mixture, Run 16, increased the apparent rate of SO_2 formation as seen in comparing Runs 14 and 16 in Figure 37. These two runs had comparable CO_2 and CO concentrations. As mentioned earlier, the rate increase was probably due to the formation of H_2S from the reaction of H_2O with CaS. The SO_2 detector measures the combined concentration of SO_2 and H_2S and the reported data therefore represent total SO_2 and H_2S . The ($SO_2 + H_2S$) rate increased by a factor of 2.8 from Run 14 to Run 16.

Series III. O_2 Effects on CO_2 -CaS Reaction. The addition of oxygen to the CO_2 - N_2 mixture could lead to an overall reaction such as,

FILE: B:P5.DAT PLOT 5 - MOLES SO₂ x 10**5 vs. TIME FIGURE 37. SO₂ RELEASE IN THE PRESENCE OF CO

The overall effect here would be to reduce the amount of CO formed and/or increase the amount of SO₂ formed. The effects of O₂ on the CO₂-CaS reaction in terms of the SO₂ formation are shown in Figure 38. All three runs were carried out at constant temperature, 2100 F. Small amounts of oxygen, ranging from 0.35 to 0.91 mole percent of gas mixture, were added to the incoming gas. As seen in the figure, the initial rate of formation of SO₂ increased with increasing O₂ concentration. The data are as follows.

Run	<u>Mole percent Oxygen</u>	<u>RSO₂ x 10⁶ (mole/sec)</u>	<u>RCO x 10⁶ (mole/sec)</u>	<u>RCO/RSO₂</u>
17	0.35	3.16	4.8	1.5
18	0.71	6.90	4.5	0.65
19	0.91	9.52	4.0	0.42

By comparison, each of the runs with oxygen, Runs 17, 18, and 19, had higher rates of SO₂ formation than did a comparable run without oxygen, Run 5.

The total amount of SO₂ formed in the reaction increased with increasing O₂ concentration. The amount of CO formed decreased with increasing O₂ concentration. The rate of CO formation and the rate ratio R_{CO}/R_{SO₂} also decreased with increasing O₂ level indicating the preference of the O₂ reaction with CaS over the CO₂-CaS reaction. However, it appears that the overall reaction cannot be represented simply by Reaction 31 since this reaction would give a R_{CO}/R_{SO₂} ratio of 1.0. The reaction of CO₂ and O₂ with CaS may occur independently. From the above rate data, the reaction of CO₂ and O₂ with CaS appears to be first order in O₂.

Series IV. Combined Effect of CO and O₂ on the CO₂-CaS

Reaction. In this series of runs, both CO and O₂ were added to the CO₂-N₂ gas mixture. All runs were carried out at 2100 F. The results of these runs are shown in Figure 39. In Runs 20, 21, and 22, the oxygen concentration remained constant at approximately 0.91 percent

FILE:B:P6.DAT PLOT 6 - MOLES SO₂ x 10 ** 5 vs. TIME

FIGURE 38. EFFECTS OF OXYGEN ON THE CO₂-CaS REACTION

FILE:B:P4.DAT PLOT 4 - MOLES SO₂ x 10 ** 5 vs TIME

FIGURE 39. CO AND O₂ EFFECTS ON SO₂ PRODUCTION

(Table 15). Runs 20 and 21, which also had the same CO concentration (2.5 percent) show good reproducibility in the early reaction straight-line portion of the curves. However, as time progressed, the curves deviate somewhat suggesting some differences in the solid product chemistry.

In Run 22, the CO concentration was increased to about 4.2 percent. This increase reduced the SO₂ formation rate significantly as seen in the figure. The apparent rate data for each run are tabulated below.

<u>Run</u>	<u>RSO₂ × 10⁶ (Mole/sec)</u>
20	3.61
21	3.45
22	0.95
23	2.48

As in the Series II runs, the presence of large amounts of added CO in these runs prevented the determination of the rates of formation of CO from the CO₂-CaS reaction.

The rate dropped by nearly a factor of 4 in Run 22 compared to Run 20. However, the CO₂ concentration in Run 22 was lower than in Run 20 which would account for some of the drop. Nevertheless, most of the decrease in the SO₂ rate appears to be due to the added CO since earlier data (Figure 32) indicate the decrease in CO₂ in Run 22 would produce only about a 20 percent decrease in rate.

Run 23 was carried out at a lower flow rate than the other runs in this study. This run was made at 6.6 percent CO₂, 7.3 percent CO, and 1.4 percent O₂ (Table 15). Although comparison with a similar run at higher velocity cannot be made in the present data, the observed lower rate of SO₂ formation in Run 23 appears reasonable in view of the higher CO concentration in this run. One might even expect the rate to be lower due to the high CO level, but the higher O₂ concentration in this run would tend to offset some of this drop. Overall, there does

not appear to be a significant effect on the SO_2 formation rate due to the lower velocity, indicating diffusion effects are likely minimal.

Reaction of Coal Volatiles With Lime

The reaction of lime with the volatiles from two different coals was briefly explored. The purpose of these experiments was to determine the extent of reaction of the volatile sulfur species released from the coal with CaO , as distinguished from the non-volatile sulfur species in the coal. The two coals used were Illinois No. 6 and Ohio 6A. Because of the inability to control the rate of volatilization from each coal, only a qualitative comparison of results, is presented here.

Of the two coals studied, the Illinois No. 6 coals showed significant evolution of volatile sulfur species below 1020 F while the Ohio 6A coal showed practically none. Above 1110 F volatile sulfur species were also evident from the Ohio 6A coal. In exposing the volatiles to the lime samples, each coal was rapidly heated to about 1300 F to assure evolution of sulfur species from each coal. The CaO samples were maintained at 2100 F during exposure to the volatiles. Data from the runs are tabulated below. Included with the data is a run using FeS_2 in place of the coal. Sulfur vapor from the decomposition of FeS_2 (1300 F) was also exposed to CaO at 2100 F. Weight of the CaO was approximately 60 mg in each run.

<u>Sample No.</u>	<u>Sample</u>	<u>Percent of Total Sulfur in Sample Captured by CaO</u>	<u>Percent of Sulfur Evolved from Sample Captured by CaO</u>
1	Illinois No. 6	1.4	
2	Ohio 6A	1.6	
3	FeS_2	1.7	7.4

Each coal sample at the start contained 35 ± 2 mg of sulfur. The pyrite contained 132 mg. From the analysis of the exposed CaO samples for sulfur content, it is seen from the above tabulation that less

than 2 percent of the total sulfur in the original sample was captured by the CaO in each run. However, based on the fraction of sulfur evolved from the FeS₂ sample, the percentages are higher, but still not impressive. In any event the volatile sulfur compounds from the coal do not appear to react readily with the CaO under the experimental conditions used in the above runs.

As mentioned earlier, the rate at which the volatiles evolve from the sample could be important in determining the extent of sulfur pickup. Rapid volatilization rates producing momentarily high concentrations of volatiles coupled with high gas velocities through the CaO sample could result in less sulfur pickup than runs at lower volatilization rates, depending on the CaO-sulfur species reaction rate. Assuming comparable rates of volatilization, it appears that most of the sulfur would not be retained when momentarily contacting CaO. However, total contact time with the CaO may have been short (<100 msec) in the above runs (depending on volatilization rates) and longer exposure times could be beneficial. A more controlled and detailed study of the reaction of coal volatiles with lime is needed to provide a better understanding of the capture process with the coal volatiles.

Discussion of Results

Past studies of fuel-lean firings with CaO-treated coals have indicated effective sulfur capture below 2100 F but a significant deterioration of capture efficiency above 2200 F. This is related primarily to CaSO₄ decomposition kinetics. In fuel-rich firings as carried out in this study, one might anticipate the formation of the more stable CaS over CaSO₄ with a subsequent improvement in sulfur capture at temperatures above 2200 F. This has not been the case in the coal firings in this study.

Although data taken at the shorter residence times (e.g., 130 msec) have indicated that iron and/or calcium sulfides are produced in the ash, it appears from the more reliable analytical data that most of the sulfur remaining with the ash is in the form of sulfate rather than

sulfide regardless of temperature, residence time, or equivalence ratio. The lack of CaS formation in the ash samples is consistent with the earlier CaO-FeS₂ studies which indicated the unlikely formation of much CaS at residence times less than 2 seconds, even in the absence of oxygen. These kinetic limitations may be a major problem in achieving good sulfur capture in fuel-rich combustion of coals.

The CaO-FeS₂ studies also indicated much of the sulfur could remain with the solids as pyrrhotites and/or FeS in the absence of oxygen. However, it appears that the presence of oxidants (O₂ and CO₂) in the coal firings resulted in much of the iron-bound sulfur being converted to sulfates and gaseous sulfur species.

Sulfur Capture Chemistry

Sulfates. The predominance of sulfate over sulfide in the fuel-rich environments was somewhat unexpected, but further consideration of competing processes appears to justify the results. If we go back to our earlier work on the chemistry of the FeS₂-CaO system we note that the pyrite produces S₂ which in turn reacts with CaO to produce CaS and ultimately SO₂. It is quite possible in the environment of the current experiments that the sulfur vapor released in the decomposition of pyrite is so readily oxidized by oxygen in the system that the S₂ + CaO reaction takes place only as a minor component. Under such circumstances the SO₂ would then react preferentially with the CaO to produce CaSO₄.

If sulfates are predominating under fuel-rich conditions, one would expect to observe a decrease in capture efficiency above 2200 F as was observed in the fuel-rich firings. Furthermore, it would appear that the fuel-rich conditions would impose even more severe limitations on the CaSO₄ stability than fuel-lean combustion, due not only to the lack of oxygen in the gas stream, but also to the favorable reducing reaction that can take place between CaSO₄ and CO and/or carbon, i.e.,

and

On the other hand, the presence of large amounts of CO_2 in the current coal firings has reduced the effectiveness of the above reactions to remove CaSO_4 . However, data from the CO_2 study show that the CO_2 (and possibly H_2O) from the gas flame was effectively oxidizing the carbon in the coal, e.g., $\text{C} + \text{CO}_2 = 2\text{CO}$ as well as the volatile carbon compounds; based on the data, about 55 percent of the carbon was oxidized and no unburned volatiles left the combustion system. The CO_2 was therefore consumed, producing CO in the process and forming CaSO_4 formation. Nevertheless, it is evident that the high, sustained temperatures in the fuel-rich firings of this study were detrimental to the overall capture chemistry.

Effects of CO_2 on CaS . The study of the reaction of CO_2 with CaS indicated not much sulfide was being consumed by CO_2 at the temperature and residence time encountered in the combustor.

Although the thermodynamics for the reactions,

$$\Delta F_{1500} = +28734 \text{ cal/mol}$$

$$\Delta F_{1500} = +43724 \text{ cal/mole}$$

are not favorable, a measurable loss of CaS at temperatures around 1700 to 2240 F can take place. Thus, if the kinetics are favorable and high CO_2 and H_2O levels are present in the gases, the above reactions could help explain the low CaS concentrations observed in the ash of the treated coals.

Examination of the CO_2 - CaS data suggests the overall reaction is

The rate data show the R_{CO}/R_{SO_2} ratio to average about 2.7 which is close to the 3.0 ratio for Reaction 36. However, the order of reaction with respect to CO_2 for Reaction 36 was evaluated at approximately 2, i.e.,

$$R = k(CO_2)^2. \quad (I)$$

suggesting an initial two-step process such as

followed by

with Reaction 37 being the rate determining step. Assuming Reaction 38 to be much faster than Reaction 37 leads to the same overall results as Reaction 36.

The temperature dependency data for the CO_2 -CaS reaction yielded an activation energy of around 11.3 Kcal/mole. This low activation energy indicates Reaction 37 is not very temperature dependent. Furthermore, from the SO_2 and CO formation rates, it appears that the CO_2 -CaS reaction is slow. In the typical 1-2 second residence time encountered in pulverized coal-firing units, the data suggest that less than 1 percent of the CaS would react with the CO_2 at 2100 F and at a CO_2 concentration of about 10 percent. The percent CaS depletion would increase only slightly at higher temperatures, based on the low activation energy of the reaction.

High CO levels likely to be encountered in fuel-rich combustion would tend to stabilize the CaS in the presence of CO_2 . However, even in a fuel-rich firing, oxygen is present in varying amounts. This could lessen the CO effects and decrease the CaS stability considerably. The deciding factor would be the availability of the oxygen for reaction with CaS.

Data from this study indicate that the oxygen reacts with the CaS at a much faster rate than does CO_2 . It is also apparent that the O_2 -CaS reaction is producing a significant amount of SO_2 . Based on the SO_2 rate data the reaction is calculated to be first order in O_2 . The

data indicate that over a ten-minute time period, oxygen and CO_2 will react with CaS to release all the sulfur in the CaS as SO_2 . At shorter reaction times, other sulfur compounds, i.e., CaSO_4 , may also be formed as transients. If CaSO_4 is produced, it would also be slowly decomposed to give SO_2 .

Water vapor also enhances the depletion of CaS via Reaction 39

This reaction is thermodynamically favorable at 2060 F. Data indicate the overall rate of formation of SO_2 and H_2S from CaS could be more than doubled in the presence of H_2O . However, this would give only an extra 1-2 percent depletion of the CaS in a 1 to 2 second time interval at 2100 F.

It thus appears that the reaction of CO_2 with CaS will not cause marked depletion of the CaS in a fuel-rich environment. Water and in particular, oxygen may cause noticeable depletion of the CaS. However, the extent of depletion of the CaS will depend primarily on the availability of the oxygen for reaction with the CaS and on the extent to which the CaS surfaces are exposed to the oxygen. Overall, it appears that a fuel-rich environment is favorable for retaining the sulfur in a reduced state, i.e., as CaS, once the CaS has formed. The rate at which the CaS can be produced is another problem.

Sulfur Retention. A consistent trend in all the coal firings was the relationship between sulfur retention and carbon burnout. Within the range of variables covered in the fuel-rich firings, the percent sulfur retention (S_R) is correlated by the relationship,

$$S_R(\%) = 93.7 - 0.827 B_C$$

where B_C is percent carbon burnout. A correlation coefficient of 0.918, obtained from all the data taken in this task, substantiate the relationship between S_R and B_C . The above relationship is valid primarily in the fuel-rich coal firings where carbon burnout is incomplete, i.e., B_C 100. Removing the methane combustion products, CO_2 and H_2O , appears to coincide with increased retention of sulfur in the ash. This could

be due to increased stability of the sulfides in the ash in a more reducing atmosphere.

Firing in a fuel-lean combustion mode produces primarily CaSO_4 . Thus, CaSO_4 stability becomes the deciding factor in sulfur capture, showing increased stability below 2200 F but decomposing rapidly above this temperature. Thus, in fuel-lean firings, fairly large amounts of CaSO_4 can be formed at the lower combustion temperatures (2100 F) giving rise to high sulfur capture while still maintaining good carbon burnout.

A more complicated situation exists in the fuel-rich firings although CaSO_4 still appears to be the major sulfur compound present in the ash. The M-C data suggest that a very rapid heat up of the coal particles followed by rapid cooling of the gases to temperatures below 2100 F may provide the optimum conditions for maximizing sulfide formation and obtaining overall maximum sulfur capture. This procedure appears to have been used by Flament⁽³²⁾ in his work.

The uncertainty in the analyses of sulfides and sulfates in these ashes presents a problem in clarifying the sulfur capture chemistry. Furthermore, inconsistencies exist in determining sulfur capture efficiency from ash and flue gas data. The presence of gaseous and solid sulfides appear to cause analytical problems which have yet to be resolved satisfactorily.

SR versus Bc Chemistry. Although the interrelation between sulfur retention, S_R , and carbon burnout, B_c , may be very complex or even coincidental, one can partially rationalize the relationship in terms of competing reactions between variables affecting the S_R and B_c processes during combustion. For example, if one postulates the retention of sulfur in fuel-rich combustion as

the effect of increasing oxygen levels on the process would be to oxidize the sulfides, with an overall effect of reducing S_R at the expense of producing SO_2 , i.e.,

and/or

Conversely, the added oxygen would tend to increase carbon burnout, e.g.,

giving higher B_C values. These two opposing effects of the oxygen would result in a relationship such as that expressed the S_R - B_C correlation. Residence time would, within limits, affect S_R and B_C in a manner similar to oxygen, i.e., increasing the residence time would give more time for carbon burnout and more time for sulfide conversion. The complexity of the situation increases significantly in realizing the main products of coal combustion, CO_2 and H_2O , can interact with sulfur-bearing compounds such as CaS and possibly H_2S formed in fuel-rich combustion.

The fact that changing the temperature of combustion does not effect the linear relationship between S_R and B_C suggests that the reaction process for S_R and B_C have similar temperature dependencies at least over the range of temperatures examined. The linear relationship also suggests that the S_R and B_C reaction processes remain similar throughout the fuel-rich combustion range studied although other reactions could occur if they have similar temperature dependencies.

Interferences - Discrepancies

SO_2 Formation and Sulfur Retention. Data from several runs of this study have shown increased SO_2 levels with increasing oxygen concentrations in the feed gases. However, the results have not always been consistent. Interferences from gaseous sulfides formed in the

fuel-rich environments may be a cause of some of the observed inconsistencies in SO_2 data which may also be a cause of the inconsistency observed between the sulfur capture values obtained from the ash and gas phase data. (Although analysis of sulfides and sulfates in the ashes are still uncertain, total sulfur analysis of the ash is considered reliable and more so than gas phase sulfur compound analyses at this time.)

The production of small amounts of SO_2 (5 to 10 percent) in the absence of oxygen was clearly shown in the FeS_2 -CaO studies. The SO_2 was shown to occur through SO formation and disproportionation. Interestingly, coal runs with zero oxygen also showed about 5 percent of the sulfur as SO_2 . However, in contrast, about 80 percent of the sulfur in FeS_2 remained with the solids at 2000 F, while about 33 percent of the sulfur in the coal remained with the solids. The difference in retention may be due to

- 1) the higher temperature in the coal runs, 2170 F
- 2) the loss of organic and/or volatile sulfur compounds
- 3) the presence of carbon and hydrogen in the reacting system
- 4) the presence of an oxidant (CO_2) in the sulfur capture environment.

The higher temperature should not have caused significant decomposition of the sulfur compounds formed, for example CaS or CaSO_4 , but would have increased reaction rates. This could be beneficial, leading to more reaction of the volatile sulfur compounds with lime. Also, the presence of carbon in the system was shown to enhance sulfur capture in the FeS_2 -CaO study. Thus, of the four possibilities listed above, the last one (CO_2) appears to be the most likely cause of the differences observed in sulfur retention in the FeS_2 -CaO and treated coal studies.

SUMMARY AND DISCUSSION

In the following pages we review the accomplishments of this program, giving special emphasis to their meaning relative to the LIMB process. The LIMB process is synonymous with staged combustion and because of this, this study has been focused on the combustion chemistry of calcium sulfide. Two key questions that stand out in this regard are, what is the role of CaS in the LIMB process? and is CaS formation critical to the operation and optimization of LIMB?

It became only too evident from the studies of the late 60's and early 70's that limestone additions to coal firings were only of minimal efficiency at best in retaining sulfur. Due to the instability of CaSO₄ at temperatures above 2100 F it was rare to see sulfur capture efficiencies greater than 30 percent. With the advent of LIMB-thinking it was logical to consider the staged burner in its individual modes, i.e., a fuel-rich mode where sulfur might be tied up initially as CaS, followed by an oxygen-rich mode where the CaS is converted to CaSO₄ and the remaining fuel is burned out. At first glance the chemistry might be considered straightforward

It is on this basis then that we have examined various aspects of the CaS chemistry in this program.

CaS Formation

The Task 1 studies have brought forth two important results, e.g.,

- the production of CaS is quite dependent on the source of sulfur in the coal
- the rate of formation of CaS may be too slow in LIMB.

The CaS studies suggest that the paths of sulfide formation may be quite dependent on the pyritic and organic sulfur levels (and possibly on the nature and rate of devolatilization of sulfur species). The chemistry suggested by our studies is as follows,

CaO-Pyrite

CaO-Organic S

As the chemistry illustrates, the conversion of pyrite to CaS, even in a zero-oxygen environment is less than 100 percent, due to the release of SO₂. It follows then that a coal containing more pyritic sulfur might prove less effective than a coal containing more organic sulfur in a LIMB firing. This observation was not explored further in this program but examination of sulfur retention results from our EPA program⁽⁸⁾ on the development of a coal-limestone pellet tend to support this chemical hypothesis. Figure 40 shows two sulfur capture curves for coal-limestone pellets made with Illinois No. 6 and Ohio 6A coals. The pyritic-organic sulfur percentages (weight percents) in these coals were

	<u>Pyrite</u>	<u>Organic S</u>
Illinois No. 6	28.2	56.6
Ohio 6A	52.3	47.0

FIGURE 40. SULFUR CAPTURE WITH LIMESTONE-COAL PELLETS⁽⁸⁾

It is of interest that the capture efficiency of Illinois No. 6 was significantly higher than that of Ohio 6A. It should be pointed out that this observation is made without consideration of the ash content of the coals, which were similar but not identical.

CaS Kinetics

Kinetically CaS will be produced by two general routes in a LIMB firing, by gas-solid and solid-solid kinetics. The solid-solid rates will obviously be slower than the gas-solid rates. As we have

shown, pyrite will first pyrolyze to pyrrhotites and/or FeS and S₂, where the S₂ vapor will react with CaO to form CaS. CaO will also react with pyrrhotites and FeS to produce CaS, but at significantly higher temperatures and slower rates. In all probability FeS will be oxidized to SO₂ at a much faster rate than it will be reacted with CaO. Hence, part of the pyrite-CaO chemistry will occur via SO₂ + CaO conversion to CaSO₄.

The gas-solid kinetics will involve primarily the reactions of S₂, H₂S, and COS with CaO, and will be governed in part by the rates of devolatilization of these sulfur species. A possibly disturbing factor in terms of LIMB combustion based on our H₂S-CaO and COS-CaO kinetics is that the rate constants for these reactions are low, possibly by two orders of magnitude too slow for efficient utilization of CaS in the first stage of the LIMB burner. Our kinetic results are consistent with the results of Pell, running around 10⁻³ sec⁻¹.^{*} For example, allowing up to one-half second to produce CaS in the fuel-rich environment of a LIMB burner would yield only 0.2 percent conversion at a temperature of 2500 F. This result would say that if chemical kinetics are the only limiting factor, there would be no advantage to incorporating limestone with coal in a LIMB firing. This statement is somewhat substantiated by the results of Flament⁽³²⁾ and Case et al⁽³³⁾. Both these studies report that sulfur capture in LIMB firings is more efficient when limestone is added with the tertiary (external) air.

CaS Oxidation

In the temperature ranges of interest to this study CaS oxidation will occur primarily via sulfite and sulfate formation:

* Recent unpublished results of R. Borgwardt. U.S. EPA, suggest higher rates.

Kinetically the reaction is controlled by the diffusion of O_2 to the CaS particle, but the oxidation is rapid.

Coal Combustion Studies

The coal combustion studies in this program were confined to firing CaO-impregnated coals under fuel-rich conditions. These firings were in the environment of near-stoichiometric methane flames, combustion products, and in a hot non-flame environment. Since the CaO was included with the coal in all instances the results are mainly applicable to LIMB situations where limestone is added with the fuel. In essence the results are as follows

- A high correlation exists between retention (S_R) and carbon burnout (B_C)
- A limited amount of the sulfur in the coal is converted to CaS
- A significant amount of the sulfur is present as CaSO_4
- The CO , CO_2 , and H_2O in the combustion products can interact with CaS and may hinder the CaS formation process.

The significance of these results relative to LIMB are discussed below.

S_R - B_C Correlation

The high correlation between sulfur retention and carbon burnout, Figure 29, tends to support the work of Freund and Lyon⁽¹⁰⁾. Figures 41 and 42 from their work are reproduced here. As Freund and Lyon point out, sulfur retention and carbon burnout are the result of several independent, external variables, such as equivalence ratio, Ca/S ratio, flame shape (residence time), and temperature; the correlation of S_R and B_C is a function of only some of these variables.

FIGURE 41. CORRELATION OF SULFUR RETENTION VERSUS CARBON CONVERSION (10)

FIGURE 42. EFFECT OF EQUIVALENCE RATIO ON SULFUR RETENTION (10)

The significance of these correlations to LIMB is tied to the "degree of richness" needed in the fuel-rich section of the burner to favor CaS production. Bass, Freund and Lyon⁽³⁴⁾ also recognize this factor in some of their studies. We discuss this further in the following section, relative to the equilibria among CaO-CaS-CaSO₄.

CaS-CaSO₄ Formation

The low sulfur conversion to CaS in these studies prompted us to look more critically at the influence of other species on the CaS stability. The CO₂ and the CO studies showed very significant interaction with CaS. Following the work of Turkdogan⁽³⁵⁾ it appears that a large part of the explanation can be found in their studies. Applying Turkdogan's logic to a LIMB situation in the reducing zone of the burner, pyrite will dissociate and the sulfur vapors plus the H₂S and COS from the organic sulfur will react with CaO to form CaS, SO₂, and CO,

Depending on the equivalence ratio of the reducing zone CO₂ will compete further for the sulfur species to produce SO₂ and CO

If we then consider the chemistry at the calcination surface of the limestone after sufficient time to form CaS, that sulfide can also be removed by CO₂. Some of these reactions include

Turkdogan considers the equilibria among these reactions and comes up with the sulfide-sulfate diagram of Figure 43. In this diagram the dashed line through the peaks represents the invariant for the coexistence of CaO, CaS, and CaSO₄. The abscissa, CO₂/CO ratio, is a representation of the oxygen activity for desulfurization of burnt lime. It is quite apparent from these curves that significant sulfide formation with low SO₂ evolution calls for very rich mixtures. This conclusion is also borne out by our studies in the FeS₂-CaO-C systems where CaS formation was considerably more efficient.

Turkdogan and Vinters⁽³⁶⁾ have examined the reduction of CaSO₄ by carbon. In the temperature range 900-1100 C they show that the relative amounts of CaS and SO₂ produced are dependent on the amount of coal in the system. This result is shown in Figure 44 from their study.

In the absence of carbon most of the SO₂ evolution would result from the reaction

In fuel-rich systems, in the presence of excess carbon and high CO levels, one could also expect CaSO₄ conversion to CaS via

Discussing the present results in terms of Turkdogan's calcination studies raises important questions about where one may want to add limestone to LIMB. The addition of lime with the coal may prove less desirable than adding lime to the secondary or tertiary air in LIMB. It would appear that the CaS-CaSO₄ chemistry is rather complex. To optimize a LIMB system via CaS formation in the fuel-rich early stages of combustion may be restricted to being able to produce the sulfide in short residence times at higher temperature. This appears to be borne out by the present work, the work of Freund^(9,10) and the LIMB results reported by Flament⁽³²⁾ and EERC⁽³³⁾.

FIGURE 43. SO_2 CONTENT AS A FUNCTION OF OXYGEN ACTIVITY(35)

FIGURE 44. CONVERSION OF SULFUR TO SO_2 AND CaS (35)

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