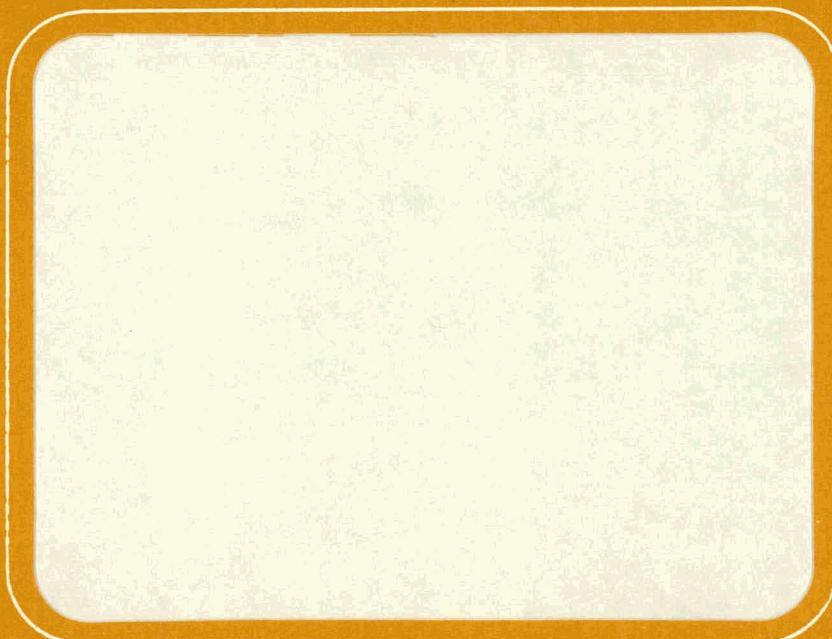


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SECOND QUARTERLY TECHNICAL PROGRESS REPORT

MASTER

on

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CaO INTERACTIONS IN THE STAGED
COMBUSTION OF COAL

to

U. S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER

Contract No. DE-AC-22-80PC-30301
Battelle No. G-7663

Period Covered: January 1, 1981-
March 31, 1981

April 30, 1981

by

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INTRODUCTION

It is widely recognized that alkaline oxides, especially CaO, can be most effective in capturing sulfur in-situ. It is equally well recognized that NO_x emissions due to fuel-bound nitrogen in coal can be effectively minimized with staged combustion. Both these aspects have been demonstrated separately at Battelle and other laboratories. It is the overall objective of this program to develop the basis for optimizing sulfur capture by CaO under staged combustion. Our approach to accomplishing this goal is via an experimental and interpretative study of the chemistry and interactions of CaO under simulated and actual staged combustion conditions.

In staged combustion, one fires first under reducing (fuel rich) conditions prior to oxidation in the second stage. Our studies wherein coals were treated with CaO, ie, impregnated with CaO for pulverized coal firing, or mixed and pelletized with CaO for stoker firing, suggest that conditions prevail under which CaO is first converted to CaS prior to being oxidized to CaSO₄. Since CaS has a greater thermal stability than CaSO₄,

it is therefore possible to fire at temperatures above 900 C (1650 F) and retain sulfur under proper stoichiometric conditions.

SUMMARY

In this second quarterly report period efforts were directed to Task 1. The CaO-FeS_2 reaction was studied as a function of temperature, reaction time, Ca/S mole ratio and particle size. All reactions were carried out under a nitrogen environment. The reactions were followed principally in terms of weight loss and SO_2 emissions. The decomposition of the pyrite produces S_2 which reacts with CaO to produce SO_2 and CaS . The extent of the reaction appears to increase monotonically between 555 and 970 C.

OBJECTIVES

This program is aimed at defining the chemistry and combustion kinetics necessary to optimize the sulfur capture with the ultimate application of reducing the SO_2 and NO_x in the firing of pulverized coal.

The program is 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 quarter's activities were confined to Task 1. The objective of Task 1 is to develop chemical and 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 environments.

PROGRESS

The efforts of this quarter were directed to a continuing study of the interaction of CaO and FeS₂ (Task 1) to determine the sulfur retention capabilities of the calcium in an oxygen-free environment. All of the experiments were carried out in an atmosphere of nitrogen.

The reactions were studied as a function of temperature, reaction time, Ca/S ratio and particle size. Various analytical techniques involving mass spectrometry, wet chemistry and X-ray diffraction were used to identify the products formed in the solid-solid reaction. Experimental procedures and results are discussed below.

Experimental Procedures

Essentially the same experimental procedures described in last quarter's report were used in the experiments this quarter. A quartz tube reaction (QTR) enclosed in a resistance furnace provided a controlled temperature chamber for studying the CaO-FeS₂ reaction. A sketch of the experimental apparatus is shown in Figure 1. Parent mixtures of fine powders of CaO and FeS₂ were used in the experiments. The mixtures contained Ca/S mole ratios of 0.5, 0.65 and 1.0. The parent mixtures were thoroughly mixed by hand and then rotated for several hours until the samples were uniform in color.

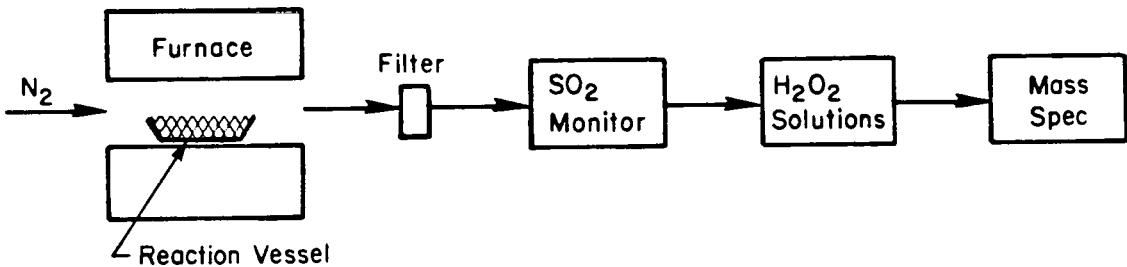


FIGURE 1. EXPERIMENTAL APPARATUS

Weighed samples were placed in a quartz boat or a stainless-steel container and inserted in the reactor at a predetermined temperature after thoroughly flushing the system with nitrogen. Nitrogen continued to pass over the sample during the entire run. Samples were exposed for 5 to 40 minutes at the set temperature. Gases evolving from the reaction were analyzed by mass spectrometry, wet chemical or electrochemical techniques. The solids from selected exposed samples were analyzed by X-ray diffraction.

Purity and Particle
Size of Reactants

The CaO used in this study was a Baker Reagent Grade material having a purity of 98.8 percent. A sieve analysis showed the CaO to be 100 percent less than -325 mesh (44 microns).

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 Colo. Sample contained 1.3 percent organic sulfur.

(b) Samples from C. E. Minerals of King of Prussia, Pennsylvania.

Most of the experiments this quarter were with Samples B and C, the purer grade pyrite material.

Results

The principal products of the CaO-FeS₂ reaction as examined to date appear to be S₂, SO₂, CaS, and pyrrhotite. S₂ results from the decomposition of pyrite to pyrrhotites, and SO₂ and CaS result from the

reaction of S_2 vapor with CaO. As a consequence, the experiments run this quarter were screened mainly for weight loss and SO_2 evolution.

Five series of experiments, comprising 21 reactions, have been run to date. The distinguishing features of the five series are as follows:

<u>Series</u>	<u>Pyrite*</u>	<u>Sample size, grams</u>	<u>Ca/S</u>	<u>Reaction Vessel</u>
I	A	1.60 to 2.50	0.65	quartz ^(a)
II	C	1.00	0.5	Stainless steel ^(b)
III	C	1.00	0.5	quartz
IV	C	1.00	1.0	quartz
V	B, C	1.00	0.5, 1.0	quartz

* See tabulation in sample purity section, p 4.

(a) All quartz reaction vessels were quartz boats ~ 2-1/2 inches long by 1/2 inch wide.

(b) Cylinder 3/8 inch O.D. x 2-1/2 inches long.

The results of these experiments are presented in Table 1. Figures 2, 3, and 4 show respectively

Figure 2 - Weight loss relative to sulfur in sample

Figure 3 - Fraction of sulfur in sample converted to SO_2

Figure 4 - Percent sulfur remaining in solid products,
as a function of the temperature of the reaction.

Series I. Sample weight loss data (solid circles) obtained from the reaction of CaO with the pyrite are plotted in Figure 2 as a 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.

The weight loss in each case involved primarily the release of elemental sulfur and the generation of sulfur oxide(s). (The pyrite used in Series I 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

TABLE 1. SULFUR RETENTION DATA

Run	Temp, C	Run Time, min.	Sample wt, mg Initial Sulfur	Weight Loss	Evolved, g/g S in Sample	SO ₂ S-Converted, percent
<u>Series I</u>						
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	--	--
<u>Series II</u>						
6	575	29	344	0.00	0.0046	0.7
7	575	30	344	0.00	0.0057	0.8
8	750	20	344	105	0.0249	3.6
<u>Series III</u>						
9	575	20	342	35	0.0142	2.1
10	750	22	344	130	0.0255	3.7
11	750	21	344	130	0.0286	4.1
12	970	20	344	100(a)	0.0476	6.9
12a	(970)	(15)	(344)	(180)	(0.0557)	(8.1)
<u>Series IV</u>						
13	750	15	265	115	0.0204	3.8
14	750	25	265	90	0.0196	3.7
15	970	15	265	100	0.0296	5.6
16	750	5	265	70	0.0200	3.8
<u>Series V</u>						
17(b)	750	11	268	40	0.0167	3.1
18(c)	750	10	361	180	0.0436	6.0
19(d)	750	9	265	110	0.0262	4.9
20(d)	750	10	270	80	0.0197	3.6
21(c)	750	10	351	140	0.0168	2.4

(a) Sample fused to quartz boat.

(b) Sample not out-gassed, Ca/S = 1.0, -325 mesh.

(c) Sample out-gassed, Ca/S = 0.5, -200 mesh Run 18, -325 mesh Run 21.

(d) Sample out-gassed, Ca/S = 1.0, -200 mesh Run 19, -325 mesh Run 20.

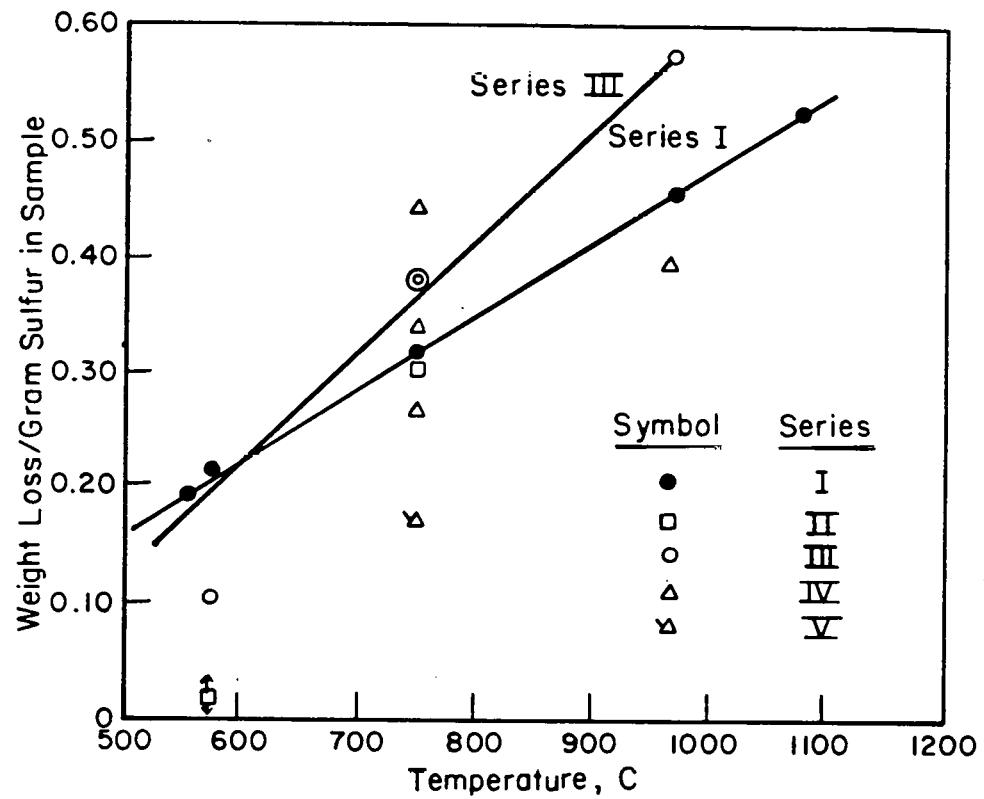


FIGURE 2. SAMPLE WEIGHT LOSS PER GRAM SULFUR
IN CaO-FeS_2 MIXTURES

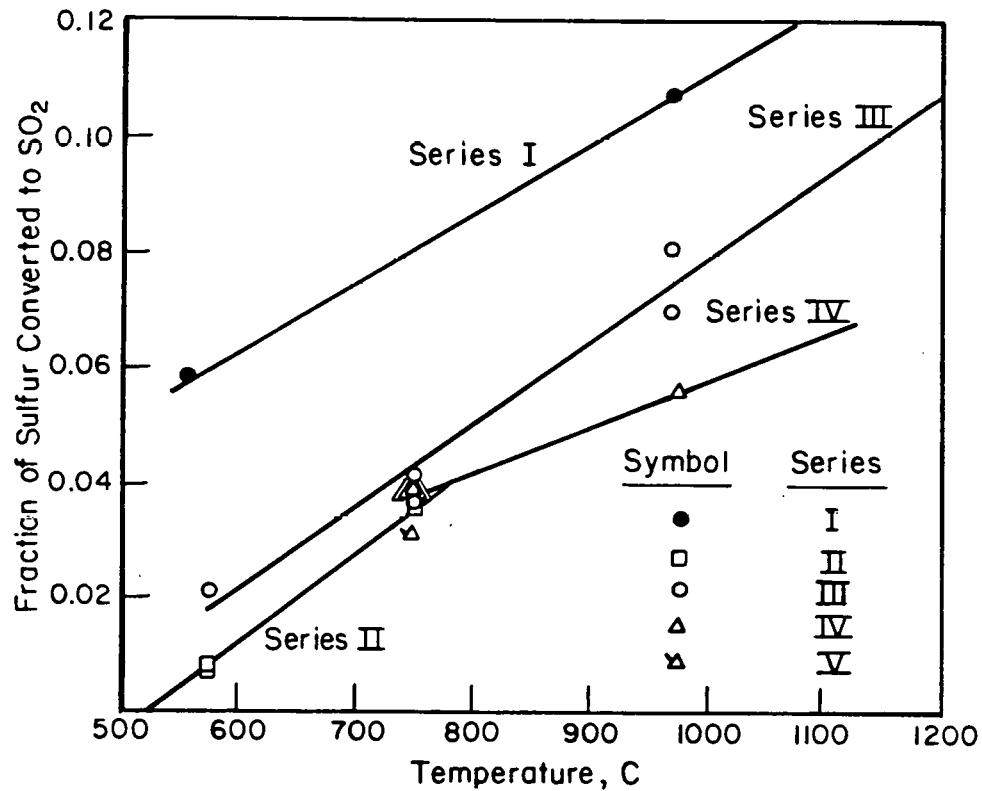


FIGURE 3. FRACTION OF SULFUR CONVERTED TO SO_2
IN CaO-FeS_2 MIXTURES

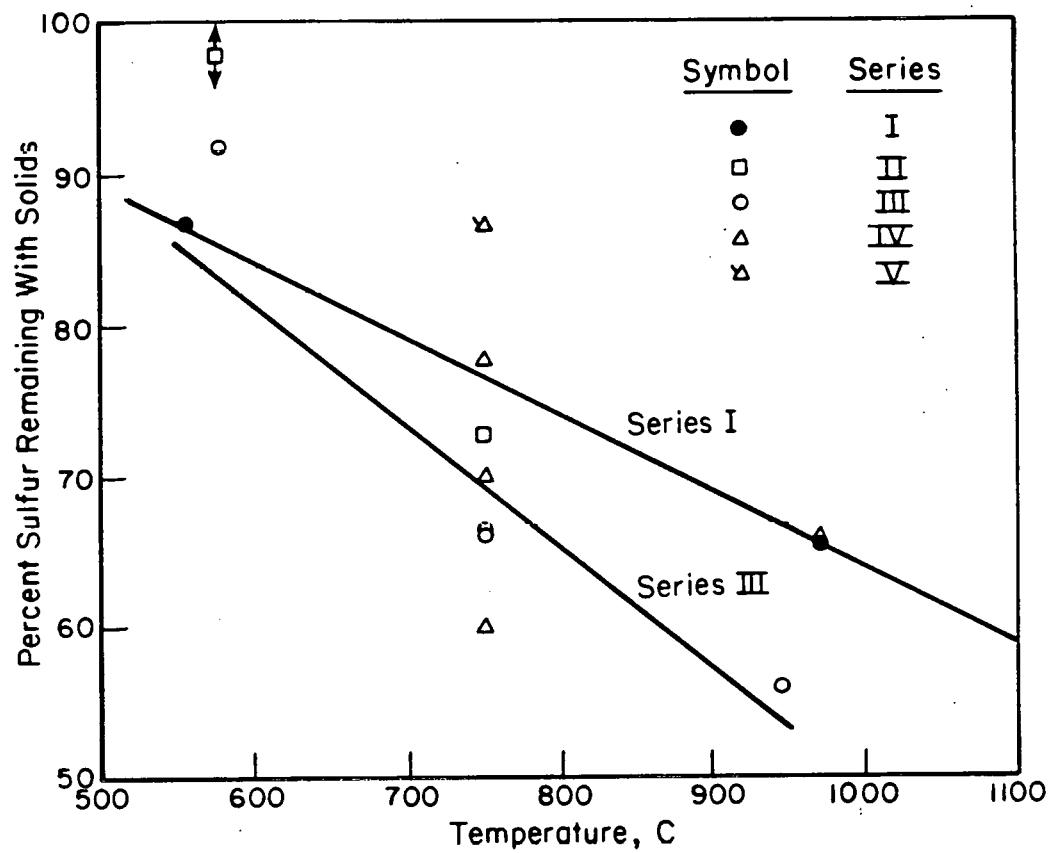


FIGURE 4. SULFUR RETENTION IN CaO-FeS_2 MIXTURES

mass spectrometer as primarily SO_2 . Other oxides such as S_2O or SO may also have been present, but these species are relatively unstable and likely converted to S_2 and/or SO_2 .⁽¹⁾

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 64 percent of the oxygen remained with the solid phase based on the amount of SO_2 evolved. Of course, oxygen available from impurities in the sample would 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. This leaves 87 percent of the sulfur staying with the solids at 555 C. Also, about 81 percent of the oxygen remained with the solids.

The fraction of sulfur oxidized to SO_2 and the percent sulfur remaining with the solids are shown as a function of temperature in Figures 3 and 4, respectively. The solid circles represent the Series I data.

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-

(1) Merryman, E. L. and Levy, A. "Disulfur and the Lower Oxides of Sulfur in H_2S Flames", *J. Phys. Chem.*, 76, (14), 1925 (1972).

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 and 1080 C, Runs 4 and 5 was not determined, but interpolating the data in Figure 4 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.

Series II. The low temperature runs at 575 C in this series suggest very little reaction. Weight loss was not measureable and SO_2 was minimal as seen in Figure 3. These results (Runs 6 and 7) are not corroborated by Runs 2 and 3 in Series I (Table 1); this may be due in part to the fact that crude pyrite was used in Series I, and in part to the use of a metal container with different geometry in Series II.

At 750 C, volatiles were emitted at levels more in line with those observed using a quartz container, although still slightly on the low side. Increasing the temperature appears to have reduced the container geometry effect. The data at 750 C using the stainless steel container are plotted as open squares in Figures 2 and 3 and are discussed below with data from the quartz boat experiments since only the sample containers were different in the Series II and III runs.

Series III. The weight loss data for this series are plotted as open circles in Figure 2. The sample weight loss at 970 C for Run 12 (Table 1) could not be used since the sample fused to the quartz container making the sample weight inaccurate. However, a recently completed repeat run at 970 C, Run 12a, produced a more valid weighing and has been included with this quarter's Series III data (values in parenthesis).

The weight loss at 575 C, Run 9 in Series III, was small and somewhat less than that observed in the first series, Run 3. At 750 C the weight loss was about 6 percentage points higher in the Series III data, Run 10, than that observed in the first series, Run 4. A repeat run in Series III at 750 C, Run 11, was in very good agreement with the

Run 10 data and tends to substantiate the higher weight loss in this series at 750 C. Weight loss from the stainless steel container at 750 C was slightly lower and more in line with the Run 4 data. The more recent run at 970 C, Run 12a, showed higher weight loss per gram sulfur in the sample than observed in the Series I data, as did Runs 10 and 11 at 750 C.

The plot in Figure 3 (open circles) shows that the amount of SO_2 evolved from the sample increased almost linearly with increasing temperature in the 575 to 970 C range. It is also seen in the Figure 3 data that much less SO_2 was evolved from the Series III mixtures containing the better grade pyrite compared to the Series I mixture with the low grade pyrite. The sulfur conversion to SO_2 dropped by 3 to 4 percentage points in going from the Series I to the Series III mixture. Undoubtedly, the sulfur impurities in the crude pyrite of Series I is affecting the amount of SO_2 formed.

Calculations similar to those used in the Series I data showed that the amount of sulfur remaining in the solid phase after each run of Series III was higher at 575 C and lower at 750 and 970 C than observed in the Series I data. The sulfur retention data of Series III are plotted as open circles in Figure 4. More oxygen remained with the solids containing the better grade pyrite. This is also reflected in the smaller quantities of SO_2 produced with the better grade pyrite (Figure 3).

Series IV. The sample weight loss data as a function of temperature are shown as open triangles in Figure 2. The three data points at 750 C show an unusually wide scatter in comparison with the Series III data varying from 0.26 to 0.44 gram weight loss per gram sulfur in the original sample. The average weight loss, however, is very close to that observed for the low grade (Rico) pyrite as seen in the figure. At 970 C the sample weight loss for the Series IV mixture was lower than for the other series mixtures.

The SO_2 data at 750 C in Figure 3 show that the fraction of sulfur in the original sample converted to SO_2 in the Series IV runs using a Ca/S ratio of 1.0 was nearly the same as that observed in the Series III data at a Ca/S ratio of 0.5. The SO_2 emission levels remained much lower than that

observed with the lower grade (Rico) pyrite for reasons explained earlier. Increasing the temperature of the Series IV mixtures from 750 to 970 C increased the conversion of sulfur to SO_2 . However, by comparison, there was noticeably less SO_2 produced at 970 C for the Series IV mixture than for the other series mixtures reacted at this temperature using lower Ca/S ratios. The sulfur retention was higher at 970 C for the Series IV than the Series III mixture but comparable to the Series I mixture (Figure 4.)

Overall, the studies with the -200 mesh better grade pyrite, Series II, III and IV indicate that, within the data variation, the Ca/S ratio in the range 0.5 to 1.0 had marginal effect on sulfur retention at 750 C (and likely at lower temperatures), but is more effective at higher temperature. At 970 C, for example, the SO_2 data indicated that less SO_2 was formed from the $\text{Ca/S} = 1.0$ mixture than from the $\text{Ca/S} = 0.5$ mixture. This trend is reflected in the calculated sulfur retention values from the Series III and IV mixtures which show increased sulfur retention at the higher Ca/S ratio, Figure 4.

Series V. All of the runs in this series were carried out at 750 C using the -200 and -325 mesh pyrite to examine particle size effect. The samples in Runs 18 through 21 were treated in a slightly different manner than the samples in all of the other runs, in that each sample from Run 18 on was out-gassed under vacuum for 15 minutes before reacting. This was done to provide quicker and better flushing of the system with nitrogen.

Weight losses were generally higher for out-gassed samples compared to samples that were not out-gassed as seen in comparing Run 18 with Runs 10 and 11, and Run 20 with Run 17 in Table 1. Also, the weight loss for Run 19 was higher than the average weight loss for Runs 13, 14 and 16 of Series IV. It is also apparent in comparing the SO_2 data of these same runs, that prior out-gassing of the samples produced a noticeable increase in SO_2 formation resulting in a corresponding decrease in sulfur retention in the solids. Except for Runs 17 and 20 using the -325 mesh material, the fraction of the total weight loss due to SO_2 remained about the same whether or not the sample was out-gassed. It appears overall that out-gassing may not be desirable in optimizing sulfur retention.

Comparing SO_2 data from Runs 18 and 21 at $\text{Ca/S} = 0.5$, it appears that the particle size of the pyrite had a significant effect on the conversion of sulfur to SO_2 in these mixtures. Less SO_2 was formed in the mixture containing the smaller -325 mesh particle size pyrite. Similarly for Runs 19 and 20 at $\text{Ca/S} = 1.0$, less SO_2 formed in the mixture containing the -325 mesh pyrite. The difference in the amount of SO_2 formed was less however between the two $\text{Ca/S} = 1.0$ mixtures with different particle size pyrite than in the two $\text{Ca/S} = 0.5$ mixtures.

Although the sulfur retention values are less accurate than the SO_2 data, the retention values are consistent with the SO_2 data in that the mixtures with -325 mesh pyrite which produced less SO_2 also retained more sulfur in the solids than did the corresponding -200 mesh pyrite samples.

Further comparison of the Run 17 data with comparable runs using -200 mesh pyrite ($\text{Ca/S} = 1.0$), i.e., Runs 13, 14, and 16, showed that the Run 17 mixture produced less SO_2 and retained considerably more sulfur in the solids than did the -200 mesh samples (see Figures 2, 3, and 4). However, more data are needed on the -325 mesh mixtures to establish the optimum mixture composition for retaining sulfur.

SO_2 Rate of Formation

The rate of SO_2 formation from the solids was estimated from the SO_2 concentration versus time curves obtained from the continuous monitoring SO_2 detector. Typical concentration versus time curves for SO_2 formation at 750 and 970 C are shown in Figure 5. Most of the SO_2 was formed from the solids within the first minute of reaction. Peak concentration 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 SO_2 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 SO_2 formation was taken from the slope of concentration versus time curves and are reported below as moles/sec per gram sulfur in sample at reaction temperature.

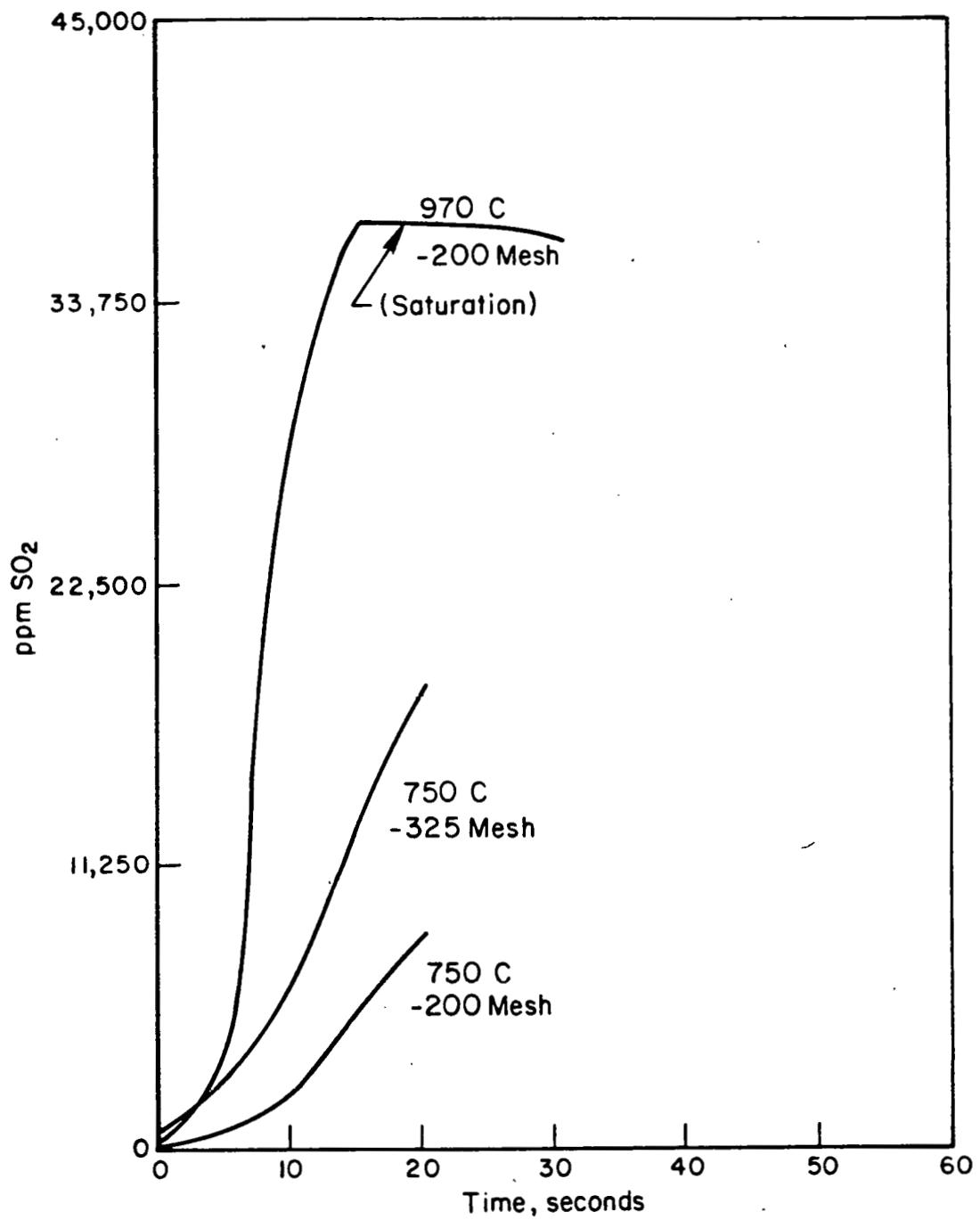


FIGURE 5. RATE OF SO_2 FORMATION FROM CaO-FeS_2 MIXTURES

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

The rate of SO₂ evolution increased by a factor of 5 in increasing the temperature from 750 to 970. Decreasing the pyrite particle size from -200 mesh to -325 mesh appeared to more than double the rate of SO₂ formation. Overall, the rates are very low and confirm the relatively small amount of SO₂ being formed in the system.

X-Ray Analyses

Two of the exposed solid samples were examined by X-ray analyses to determine the type of compounds present. The samples analyzed were taken from Run 11 at 750 C and Run 12 at 970 C. 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 1	750	CaO	100
Ca/S = 0.5		CaS	70
		Fe ₇ S ₈	20
		-Fe ₂ O ₃	9
		FeS ₂	6
Run 12	970	CaS	100
Ca/S = 0.5		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 Fe_9S_{10} . The unknown compound produced a very strong peak but could not be identified in the X-ray Powder Diffraction File.

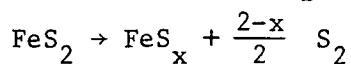
Although the X-ray data above are qualitative, it appears that the reaction at 970 C produced primarily CaS and a fewer number of compounds overall than did the reaction at 750 C.

DISCUSSION

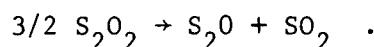
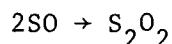
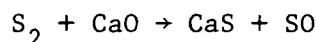
This quarter's experiments are showing that the CaO- FeS_2 system is a complex reaction system leading to a variety of sulfur and sulfur-oxide products. The very low reactivity at 575 C and the increasing reactivity at 750 and 970 C suggest a number of stepwise reactions taking place.

For the moment we suggest one consider the following reaction steps in this CaO- FeS_2 system:

1. Decomposition of FeS_2



2. S_2 (vapor) + CaO (solid) reactions



If we accept this sequence for the moment we note then that at most 50 percent of the S in the pyrite can react with CaO at $T < 1000$ C ($x = 1$). If we follow this sequence through to the production of SO_2 we then note only 50 percent of the S_2 vapor can be converted to a sulfur oxide, and only one-third of this 50 percent can yield SO_2 . This would say then, that at most only some 8 percent of the sulfur in pyrite would yield SO_2 in our current experiments. The only experiment which yielded more SO_2 than this was in Run 1 with the crude pyrite which yielded 10.7 percent and, as mentioned earlier, contained organic sulfur in addition to the pyrite.

This sort of analysis is rather circumstantial at this point but is corroborated by the data to date, and suggests that a more direct, more simple experiment is in order. Namely, rather than react the FeS_2 directly with CaO , why not separate the two reactants, and allow the S_2 vapor to sequentially attack the CaO ? This sequence will be explored in the coming quarter.

Pyrrhotite Formation. The X-ray data, although limited to date, suggest that sulfide formation at $T < 1000$ C is mainly the result of a gas (S_2)-solid (CaO) reaction. Apparently as S_2 leaves the pyrite, there is an approach to FeS at the temperatures and times reacted to date, and pyrrhotites Fe_xS_y are produced where $y/x > 1$.

The unknown product may be $\text{FeS} \cdot \text{CaO}$ as identified by Skopov, et al.⁽²⁾ in their TGA experiments. Solid-solid reactions do not appear to have occurred at the temperatures of our current experiments (based on the lack or very small amount of iron oxide products in the X-ray analyses).

WORK PLANNED NEXT QUARTER

Task 1 experiments will continue next quarter. As noted in the discussion section besides reacting mixtures of FeS_2 and CaO , the two compounds may be reacted in a sequential reaction, using the pyrite as a S_2 -generator, then contacting the S_2 with CaO . If this proves successful to our goals we will then introduce other gases with the S_2 vapor.

(2) Skopov, G. V., et al., "Investigating the Chemical Action and the Sequence of Interactions of Iron Sulfide With Calcium Oxide and Calcium Carbonate", *Izvestiya Vysshikh Uchebnikh Zavedeniy*, No. 4, *Tsvetnaya Metallurgiya*, 1977, pp 69-73.