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FIRST QUARTERLY TECHNICAL PROGRESS REPORT

on

CaO INTERACTIONS IN THE STAGED COMBUSTION OF COAL

to

US DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER

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

Period Covered: September 23, 1980-
December 31, 1980

January 30, 1981

by

Arthur Levy and Earl L. Merryman

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INTRODUCTION

The day when industry seriously turns to coal is fast approaching, and when it comes, industry will be concerned with controlling SO_2 and NO_x with the least expense and difficulty. The most direct way from industry's point of view would be to accomplish this dual control in-situ.

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 $CaSO_4$. Since CaS has a greater thermal stability than $CaSO_4$ it is therefore possible to fire at temperatures above 900 C (1650 F) and retain sulfur under proper stoichiometric conditions.

OBJECTIVES

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

The program is separated into three tasks:

Task 1. A fixed bed study of CaS production
Task 2. A fixed bed study of CaS oxidation
Task 3. A staged combustion study of coal and CaO treated coals.

A more detailed statement of the individual task objectives follows.

Task 1. CaS Formation

The objective of Task 1 is 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 environments. These studies focus primarily on reactions taking place in fixed beds in which different bed mixtures are exposed to various temperatures and gas-phase compositions.

Task 2. CaS Oxidation

The objective of Task 2 is to determine some of the boundary conditions for oxidizing CaS. Although not a large effort in the overall program it is 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 $CaSO_4$.

Task 3. Staged Combustion

Task 3 is the major activity in this program. In this phase, coal particles are burned under controlled conditions of staging. Task 3 is a parametric study of the principal dependent and independent variables, in part developed from Tasks 1 and 2 results. The objective of Task 3 reiterates the overall objective of this program to develop the basis for optimizing the S-capture chemistry of CaO under staged combustion conditions.

Task 3 is carried out in two parts: Part A aims to develop the basic parameters from reactions of coal in rich and lean methane flames, and Part B further carried out the optimization in a laboratory coal furnace.

Task 3A - Coal Combustion in Gas Flames. The objective of Task 3A is to develop the basic kinetic and chemical parameters which govern CaS and $CaSO_4$ formation in staged combustion.

Task 3B - Staged Combustion Coal Firings. The objective of Task 3B is to apply the Task 3A results to optimize NO_x-SO_x control in a staged coal-fired system.

SUMMARY

In the first quarterly report period literature from 1967 to the present was reviewed, a thermodynamic assessment of the CaO-FeS-FeS_2 system was made, and Task 1 experiments were initiated on the formation of calcium sulfide from calcium oxide - pyrite mixtures.

PROGRESS

Literature Survey

A manual and computerized scan of Chemical Abstracts covering the years 1967 to the present was made. A number of articles pertinent to this program were uncovered. The articles are referenced below, and a brief comment on their overall content is presented for those papers deemed most pertinent to the present Task 1 efforts. (Numerous articles are available on the CaO-SO_2 system. These are not listed here.)

(1) Skopov, G. V., et al. "Investigating the Chemical Action and the Sequence of Interactions of Iron Sulfide with Calcium Oxide and Calcium Carbonate", Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall., 1977 (4), pp 69-73 (Russian).

This Russian article appears most pertinent to the present Task 1 study and was therefore translated into English. The article provides useful information on the composition of the solid phases formed in the reaction of FeS_2 (pyrite) with CaO in the temperature range 650 to 1100 C. Temperature appears to be an important variable in determining the extent of CaS formation and SO_2 evolution in a FeS_2-CaO mixture; SO_2 predominates below 700 C, and CaS predominates above 700 C to about 1000 C.

(2) Toguzov, et al. "Study of the Feasibility of the Iron (II) Sulfide-Iron (II) Oxide-Calcium Oxide System", Kompleken. Ispol'Z. Mineo Sys'ya, 1980 (4), pp 51-55 (Russian).

This is another Russion article in which solid-solid reactions were studied. The authors looked at the systems FeS-FeO-CaO and FeS-CaO. The article has not yet been translated into English.

(3) Sohn, H. Y. and Rajamoni, K. "Successive Gas-Solid Reactions in A Porous Pellet: Application to the Reaction of Metal Sulfide in the Presence of Lime", Chem. Eng. Sci., 1977, 32 (9), pp 1093-1101.

This is a modeling study to describe the successive gas-solid reactions occurring in a porous pellet. Several references are included which may be of interest to the present study.

(4) Fahim, M. A. "Absorption Kinetics of Calcium Oxide with Gaseous Steam Containing Hydrogen Sulfide", J. Environ. Sci. Health, A14(3), pp 211-220 (1979).

This is a study of the reaction of H_2S with CaO in the temperature range 600 to 750 C. This paper will be of interest in the present Task 1 studies involving H_2S-CaO interaction.

(5) Westmoreland, P. R., Gibson, J. B., and Harrison, D. P. "Comparative Kinetics of High Temperature Reaction Between H_2S and Selected Metal Oxides", Environ. Sci. and Technology, 11 (5), p 488 (1977).

See comments of Reference 4.

(6) Freund, H. "The Kinetics of Limestone/Dolomite with H_2S under Rich Combustion Conditions". To be published.

This is a study of the reaction of H_2S with limestone/dolomite mixtures in the temperature range 1065 to 1310 C. Under fuel rich combustion conditions the author reports a significant loss in reactivity at high temperatures resulting in a low efficiency sulfur capture process. The study concludes that the H_2S absorption reaction is too slow to be a possible means of sulfur capture during entrained solids combustion.

(7) Vejvoda, et al. Sb. Prednasek-Vedeckotech Kong. Ustava. Vyzk. Vyvziti Poliv., 1977, pp 107-134 (Czech).

This is another study of the CaO-H_2S reaction kinetics in the 700-900 C range. The abstract indicates that the effect of CaO particle size on the reaction rate was examined. The paper is not presently available to us, but an attempt will be made to obtain an English translation of the work.

(8) Yang, R. T., et al. "Direct Evidence for the Existence of Gaseous Intermediates in the Calcium Sulfide-Calcium Sulfate Reaction:, J of AIChE, 1979, 25 (3) pp 547-548 (English).

This is a study of the CaS-$CaSO_4$ system and may be of interest later in the program.

Thermodynamics

Table 1 contains a listing of some of the reactions pertinent to the Task 1 experimental program. Free energies are listed for 800 K (980 F) and 1400 K (2060 F).

Reactions leading to the formation of CaS are shown in the first 20 equations in the table. The thermodynamics indicate that at 1400 K all of the reactions, except Reactions 1 and 19, favor CaS formation with Reaction 7 appearing most favorable thermodynamically.

Calcium sulfide formation is less favorable at lower temperatures. At 800 K four additional reactions (2, 4, 6, and 14) appear unfavorable. In most of these instances where the free energy goes positive, oxygen is a product, obviously then favoring the oxidation of CaS.

Generally, the reactions leading to the formation of gaseous S_2, SO_2, CO, CO_2, or H_2O show favorable thermodynamics for CaS formation. Reactions 2 and 14 at 800 K are the only exceptions and it is apparent that at higher temperatures these reactions also become favorable. Thus, it appears that 18 of the 20 equations listed in Table 1 could be thermodynamically favorable for CaS formation at combustion temperatures.

Thirteen of the remaining 14 equations do not involve CaS production. However, some are likely to be important in the CaO-FeS_2 system. Of particular interest is Reaction 23 which shows that FeS_2 can decompose significantly above about 1000 K. An equilibrated system at 800 K, however, shows little FeS_2 decomposition. However, in the presence of CaO significant sulfur can be released as shown in Equations 3 and 5.

Figure 1, from the report of Hsieh, et al(1) presents a useful display of approximate reaction temperatures for the CaO - $CaCO_3$- CaS-$CaSO_4$ system. This reaction scheme in conjunction with the free energy tabulation of Table 1 may prove useful in later analyses of the CaO-pyrite reaction systems.

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(1) Hsieh, B. C., Ashworth, R. A., and Switzer, G. W., Jr. "An Analysis of the Chemistry and Mechanisms for the High Temperature Desulfurization of Low Btu Gas When Using Lime or Limestone", Office of Coal Research Report, Contract No. 14-32-001-1236.

TABLE 1. POSSIBLE REACTIONS IN THE CaO/SULFUR SYSTEM

No.	Reaction	Δ F Kcal/mole 800 K	1400 K
1.	$FeS_2 + CaO \rightarrow FeS + CaS + 1/2\ O_2$	28.867	8.135
2.	$FeS_2 + CaO \rightarrow FeO + CaS + 1/2\ S_2$	2.543	- 17.625
3.	$3FeS_2 + 4CaO \rightarrow Fe_3O_4 + 4CaS + S_2$	- 50.926	- 62.636
4.	$3FeS_2 + 6CaO \rightarrow Fe_3O_4 + 6CaS + O_2$	25.548	- 21.584
5.	$2FeS_2 + 3CaO \rightarrow Fe_2O_3 + 3CaS + 1/2\ S_2$	- 14.762	- 38.546
6.	$2FeS_2 + 4CaO \rightarrow Fe_2O_3 + 4CaS + 1/2\ O_2$	6.742	- 18.020
7.	$2FeS_2 + 3CaO + O_2 \rightarrow Fe_2O_3 + 3CaS + SO_2$	- 87.336	-100.648
8.	$FeS_2 + CaO + C \rightarrow FeS + CaS + CO$	- 14.745	- 48.054
9.	$FeS_2 + 2CaO + C \rightarrow 2CaS + FeO + CO$	- 19.565	- 53.288
10.	$FeS_2 + 2CaO + C \rightarrow 2CaS + Fe + CO_2$	- 18.082	- 48.362
11.	$2FeS_2 + 4CaO + C \rightarrow Fe_2O_3 + 3CaS + CO$	- 49.447	- 74.209
12.	$FeS + CaO \rightarrow FeO + CaS$	- 4.820	- 5.234
13.	$2FeS + 2CaO + 1/2\ O_2 \rightarrow Fe_2O_3 + 2CaS$	- 50.992	- 34.290
14.	$FeS + CaO + C \rightarrow CaS + CO + Fe$	3.995	- 17.970
15.	$2FeS + 3CaO + 1/2\ S_2 \rightarrow Fe_2O_3 + 3CaS$	- 29.489	- 13.764
16.	$2FeS + 2CaO + Si \rightarrow 2CaS + SiO_2 + 2\ Fe$	- 87.628	- 81.696
17.	$CaO + H_2S \rightarrow CaS + H_2O$	- 14.980	- 15.008
18.	$CaO + COS \rightarrow CaS + CO_2$	- 22.684	- 22.365
19.	$CaO + 1/2\ S_2 \rightarrow CaS + 1/2\ O_2$	21.504	20.526
20.	$2CaO + 3/2\ S_2 \rightarrow 2CaS + SO_2$	- 29.566	- 21.050

TABLE 1. (Continued)

No.	Reaction	Δ F Kcal/mole 800 K	1400 K
21.	$CaO + SO_2 + 1/2\ O_2 \rightarrow CaSO_4$	- 65.178	- 29.203
22.	$CaSO_4 + 4CO \rightarrow CaS + 4CO_2$	- 44.520	- 42.277
23.	$FeS_2 \xrightarrow{\Delta} FeS + 1/2\ S_2$	7.363	- 12.391
24.	$FeS_2 \xrightarrow{\Delta} Fe + S_2$	33.466	5.302
25.	$FeS \xrightarrow{\Delta} Fe + 1/2\ S_2$	26.103	17.693
26.	$FeS_2 + O_2 \rightarrow FeS + SO_2$	- 65.211	- 74.493
27.	$FeS_2 + 5/2\ O_2 \rightarrow FeO + 2\ SO_2$	-164.109	-162.355
28.	$FeS + 3/2\ O_2 \rightarrow FeO + SO_2$	- 98.898	- 87.862
29.	$FeS + 1/2\ O_2 \rightarrow FeO + 1/2\ S_2$	- 26.324	- 25.760
30.	$FeS + O_2 \rightarrow FeO + SO$	- 41.085	- 41.236
31.	$2CaO + SiO_2 \rightarrow Ca_2SiO_4$	- 31.160	- 31.850
32.	$CaS + 2\ O_2 \rightarrow CaSO_4$	-159.256	-111.831
33.	$CaS + 3/2\ O_2 \rightarrow CaO + SO_2$	- 94.078	- 86.108
34.	$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S$	- 0.32	22.333

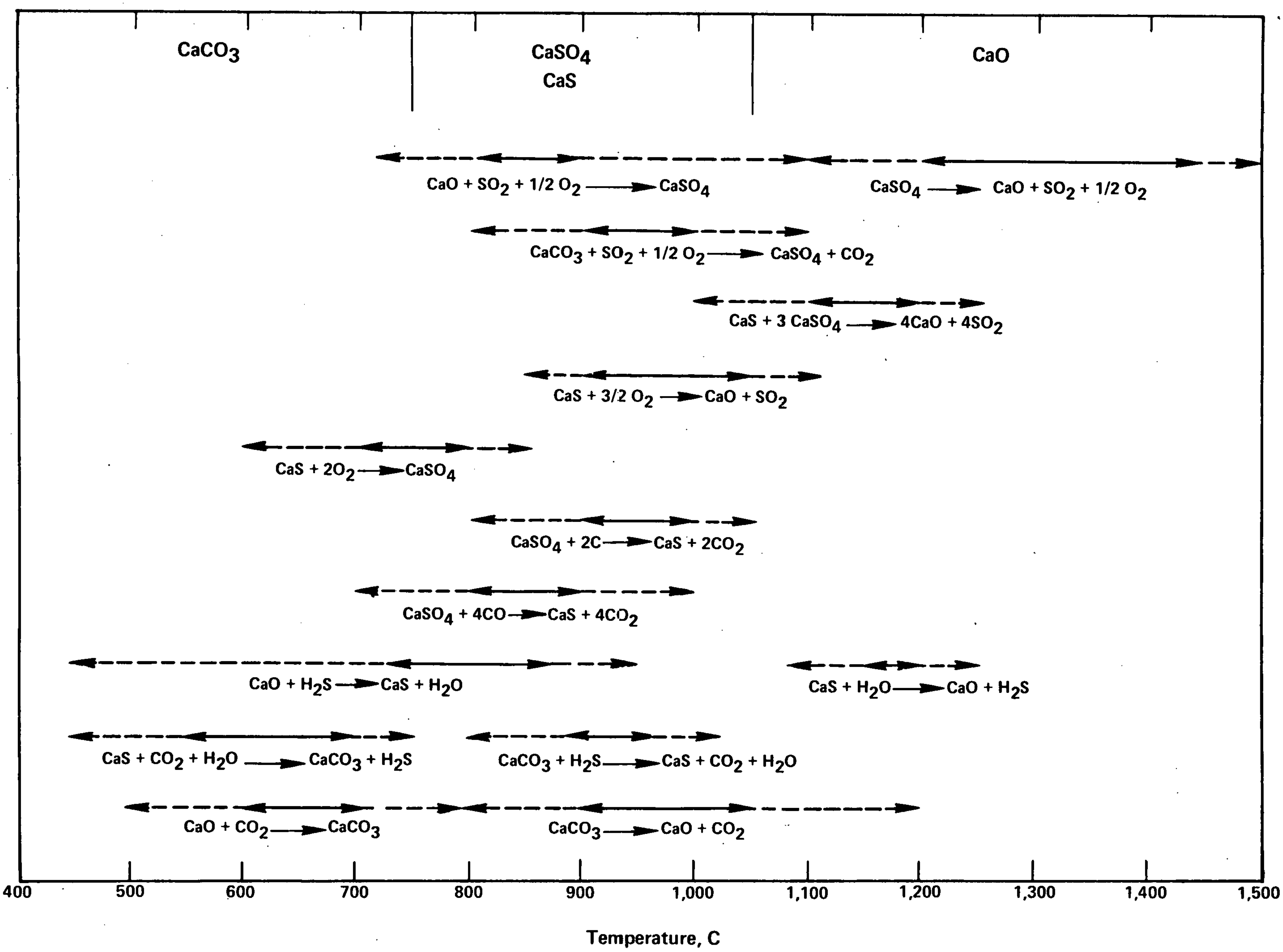

FIGURE 1. THE TEMPERATURE RANGES OF THE REACTIONS (1)

The equations in Table 1 will be used where appropriate as aids in interpreting data from the Task 1 studies involving reactions of CaO with sulfur bearing compounds. Other equations not listed in Table 1 will likely arise as the study continues and these will have to be considered (and possibly derived) as the task progresses.

Experimental Study of CaO-FeS_2 System

Three exploratory experiments were carried out reacting fine powders of calcium oxide with pyrite. The purpose of these experiments was mainly to observe the behavior of the mixed powders at elevated temperatures with regard to sulfur emissions, weight loss and speed of reaction. The reactions were carried out at 575 and 950 C for periods up to 40 minutes. The experimental procedure and results are described below.

Experimental Procedure. A parent mixture of CaO and FeS_2 was made up for these experiments. The mixture was made up at a CaO/FeS_2 mole ratio of 1.32 giving a Ca/S mole ratio of 0.66. The CaO was reagent grade material (Baker) with a reported purity of 98.8 percent. The pyrite used in the current experiments was a crude material containing about 76.2 percent pyrite. The impurities were analyzed as follows:

Percent								
Sulfur								
Pyrite	Sulfate	Organic	Fe	C	H	O	N	Ash
40.72	0.65	1.33	39.89	5.10	0.69	3.40	0.08	7.24

(A better grade pyrite has just been obtained from C. E. Minerals, King of Prussia, Pennsylvania. This material is being analyzed and will be used in future experiments.)

The mixture was blended and stirred in a glass container until a uniform color resulted. Samples weighing from 1-1/2 to 2-1/2 grams were removed from the parent mixture and placed in a small quartz boat. The boat and sample were accurately weighed to within 10 milligrams; then placed in a quartz tube reaction chamber which was preheated to the reaction temperature.

The quartz reactor was 1-1/4 inch OD and 24 inches long tapered at the exit end of the reactor to a 1/4 inch OD tube. Samples were placed in the entrance to the reactor via a tapered ground glass joint. The sample and reactor were thoroughly flushed with nitrogen prior to inserting the sample into the hot reaction zone. Nitrogen continued to pass over the sample at about 5 cc/sec during the entire run. The exit gases passed through one or two cold traps depending on the SO_2 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 in the exit gases. When the second trap was not used, the exit gases, with condensibles removed, were directed to a mass spectrometer for SO_2 analysis. Oxygen was also analyzed on the mass spectrometer.

At the completion of the 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 was then converted to an equivalent mole of SO_2 collected.

Results and Discussion

Two of the three runs this quarter were carried out at 575 C, the other at 950 C. At each temperature, sulfur deposits were evident at the exit of the reactor tube within seconds after inserting the sample into the hot reaction zone. A major portion of the sulfur was found to deposit on the walls of the 1/4 inch OD tube just prior to the first cold trap; this obstructed the view through the tube and made it difficult to estimate the duration of sulfur deposition in the experiments. It was apparent however, that considerably more sulfur deposited at 950 C.

Reaction at 950 C. The experiment at 950 C showed the evolution of both SO_2 and sulfur from the sample. The SO_2 which evolved from the heated mixture was collected in a cold trap containing H_2O_2 (downstream of the sulfur traps). The amount of SO_2 collected in the peroxide solution was about 4.9×10^{-3} moles, indicating that about 23 percent of the total sulfur in the pyrite was converted to SO_2.

In addition to the SO_2 evolved, an attempt was made to determine the amount of sulfur deposited on the walls outside the reactor by oxidizing the sulfur to SO_2 in a hot pure oxygen gas stream and collecting the SO_2 in H_2O_2. However, the peroxide solution appeared to trap very little of the oxidized sulfur. A weight loss of 0.33 grams (0.48 grams/gram of sulfur in original sample) was observed for the sample at 950 C over a period of 30 minutes. If one assumes this loss is due soley to the release of sulfur, then from the measured amount of SO_2 evolved, the amount of sulfur deposited on the walls would be about 0.173 grams or about 25.4 percent of the total sulfur in the original sample. It is apparent, however, that this procedure for determining the weight of sulfur deposited is questionable since some of the sulfur was oxidized to SO_2, showing that oxygen was present as an impurity in the system (adsorbed in the sample and tube walls, present in the N_2 gas, etc.)

Reaction at 575 C. The formation of SO_2 and sulfur was also evident at 575 C. Approximately 1.82×10^{-3} moles of SO_2 were evolved over a 40 minute reaction period. This amounts to about 12.6 percent of the total original sulfur in the sample, considerably less than at 950 C. The sample weight loss at 575 C was 0.095 grams or about 0.21 grams/gram of sulfur in original sample. Subtracting the weight of sulfur in the SO_2 collected (0.058 grams) from the total sample weight loss leaves a maximum of 0.037 grams for the weight of sulfur deposited on the walls outside the reactor or about 8.0 percent of the total original sulfur (again assuming the O_2 in the SO_2 comes from oxygen impurities in the system).

It would appear that oxygen is present in the system other than in the original sample (as CaO), since the total observed weight loss of the sample cannot account for the weight loss of sulfur as SO_2 and elemental sulfur. The same is true for the run at 950 C. This is discussed in more detail later.

The sample weight loss in the second experiment was 0.22 grams/ gram sulfur which compares favorably with the first run at 0.21 grams/ gram sulfur. It is apparent, however, that more attention will have to be given in future experiments to the possible oxygen impurity problem in order to obtain a reliable sulfur balance in the system.

From the experiments to date, it is evident that SO_2 and sulfur are evolved in the reaction of CaO with FeS_2 at temperatures at least as low as 575 C. The mixtures remain much the same color at 575 C (medium gray) and the particles do not adhere at this temperature. At 950 C, however, the mixture turns a charcoal to black color and the powdered materials tend to fuse. The composition of these solid materials have not yet been determined but some attention will be given to them during the next quarter work period.

The mixtures used in the experiments this quarter contained an excess of sulfur, and from the products evolved, suggest a reaction of the type:

$$1.32\ CaO + FeS_2 \longrightarrow 1.32\ CaS + FeO + XS_2 + Y\ SO_2$$

If the only oxygen available in the system were from the CaO, then Y = 0.16 moles and X = 0.26 moles. However, from the impurities in the pyrite, it is apparent that there are other sources of O_2. Assuming there is the reported 4.3 percent oxygen in the pyrite sample, the value of Y would increase to 0.37 moles and the value of X would be reduced to 0.155 moles. The Y value calculated in this way is compared with the measured moles of SO_2 produced in the experiments based on one mole of FeS_2 present.

		Moles of SO_2	
Run	Temperature, C	Measured	Calculated
1	950	0.460	0.372
2	575	0.252	0.372

The measured SO_2 value exceeds the calculated value at 950 C but is less than the calculated value at 575 C. Nevertheless, the data at both temperatures confirm that oxygen sources other than CaO are present in the system. The low measured SO_2 value at 575 C suggests that a larger fraction of the evolved sulfur compounds may have escaped as elemental sulfur rather than SO_2. Additional experiments are needed to confirm this.

One final comment, the measured weight loss of the samples at 950 and 575 C was 0.33 grams and 0.095 grams respectively. Assuming the evolved SO_2 measured by the peroxide method came solely from the solids, the calculated weight loss would have been 0.31 and 0.11 grams respectively. However, since a significant amount of elemental sulfur was also observed to form in the system, it is apparent that not all of the SO_2 came from the solids. The results suggest the presence of additional oxygen in the gas stream rather than the solid.

WORK PLANNED NEXT QUARTER

Experiments will continue next quarter studying the reactions CaO and FeS_2 in the temperature range 575 to 1000 C. Gaseous environment containing N_2 and small quantities of O_2, CO, CO_2 or H_2O will be used to determine their effect on the overall reactions. Careful considerations will be given to oxygen impurities in the gas stream. Effects of FeS_2 particle size and different Ca/S ratios will be examined. The reactions of H_2S and COS with CaO will also be examined. A TGA unit will be used during the next quarter to determine sample weight change as a function of time. This should provide a more detailed analysis of the data. The volatile species released in the reaction will be determined by mass spectrometric or chromatographic techniques. The remaining solids will be analyzed by X-ray and/or wet chemical techniques.