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Recovery of Sulfur From Phosphogypsum: Conversion of Calcium Sulfate to Calcium Sulfide

By Margaret M. Ragin and Donald R. Brooks

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BUREAU OF MINES

UNITED STATES DEPARTMENT OF THE INTERIOR



U.S. Bureau of Mines
Secretary of the Interior
Department of the Interior
Washington, D.C.
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By Margaret M. Ragin and Donald R. Brooks

**UNITED STATES DEPARTMENT OF THE INTERIOR
Manuel Lujan, Jr., Secretary**

**BUREAU OF MINES
T S Ary, Director**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Btu/lb	British thermal unit per pound	in	inch
°C/min	degree Celsius per minute	mg	milligram
°C	degree Celsius	min	minute
deg	degree	mL/min	milliliter per minute
ft	foot	μm	micrometer
g/min	gram per minute	pct	percent
h	hour	r/min	revolution per minute

RECOVERY OF SULFUR FROM PHOSPHOGYPSUM: CONVERSION OF CALCIUM SULFATE TO CALCIUM SULFIDE

By Margaret M. Ragin¹ and Donald R. Brooks²

ABSTRACT

In a cooperative effort between the U.S. Bureau of Mines and the Florida Institute of Phosphate Research, with input from the phosphate industry, the conversion of phosphogypsum to sulfur has been investigated. The first step in the conversion scheme involves reduction of phosphogypsum to calcium sulfide. Effects of temperature, catalyst, reaction time, and type of reductant (carbon monoxide and coal) are discussed. It was determined that phosphogypsum could be reduced to calcium sulfide at 850° to 1,000° C using either coal or carbon monoxide as the reductant. The required temperature was lowered to 750° C using ferric oxide or magnetite as a catalyst for the reduction reaction. Results indicate that as the volatiles content of the coal is increased, reaction temperature may be decreased to obtain a given conversion, or if the reaction temperature is maintained constant, the conversion can be increased. Best results were 95- to 100-pct conversion using a high-volatile coal at 800° to 850° C. Addition of a catalyst increased calcium sulfide yield when low- or medium-volatile coals were used as reductants, but had little effect when high-volatile coals were used.

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INTRODUCTION

The phosphate industry in Florida is a vital segment of the Nation's economy. Phosphate fertilizer manufacturers produce wet-process phosphoric acid, which is a major ingredient for fertilizers. The phosphoric acid is made by the reaction of phosphate rock with sulfuric acid; phosphogypsum being the byproduct. This phosphogypsum waste material represents virtually all of the sulfur that has ever been used in the fertilizer manufacturing process and is therefore a potentially valuable mineral commodity.

Estimates indicate that over 500 million tons of phosphogypsum has accumulated in Florida stockpiles. In 1980, phosphogypsum was being generated at a rate of about 33 million tons per year. The projected accumulation by the year 2000 will be over 1 billion tons (1).³

Processes have been developed to produce sulfuric acid from gypsum, and commercial plants have been built in the Federal Republic of Germany, England, France, Austria, the Republic of South Africa, and Poland (2). The processes involve the reductive roasting of gypsum using coal, natural gas, carbon monoxide, or hydrogen to produce sulfur dioxide, which is converted to sulfuric acid. The U.S. Bureau of Mines has investigated the reductive roasting of gypsum (3), the conversion of calcium sulfide (CaS) to elemental sulfur (4), and sulfur dioxide emission control (5). The latter process involved the reaction of sulfur dioxide and hydrogen sulfide to produce elemental sulfur (Claus process).

The voluntary cooperation of the following Florida phosphate companies in offering valuable advice and

suggestions on the research efforts is gratefully acknowledged: Gardinier, Inc.; Agrico Chemical Co.; Farmland Industries; Royster Co.; W. R. Grace & Co.; Occidental Chemical Co.; Conserv, Inc.; International Minerals and Chemical Corp.; and CF Industries.

Numerous investigations of the environmental aspects and possible uses of phosphogypsum have been conducted by the Bureau, the U.S. Environmental Protection Agency, the U.S. Geological Survey, the Florida Institute of Phosphate Research (FIPR), the phosphate industry, and many universities (1-2, 6-8). In general, these investigations have characterized the phosphogypsum, established its environmental impact on air and water, and proposed several high-volume potential end uses. Some research has focused on conversion of phosphogypsum directly to sulfuric acid (9-10). Only a minimum amount of effort has been focused on the technology of converting the material to sulfur.

The consensus of the Florida phosphate fertilizer manufacturers is that the conversion of phosphogypsum to elemental sulfur would be very advantageous. The future need for additional phosphogypsum waste piles would be eliminated, and the sulfur could be recycled back into fertilizer production through existing sulfur-burning sulfuric acid plants. This could conceivably eliminate the need to purchase additional sulfur. In a cooperative effort with FIPR, the Bureau is investigating the conversion of phosphogypsum to elemental sulfur as part of its program to improve mineral resource accessibility and conservation. This Report of Investigation discusses the reduction of phosphogypsum to calcium sulfide.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance and advice of David P. Borris, executive

director of FIPR, and Mike Lloyd, research director of FIPR.

MATERIALS

The experiments were conducted with reagent-grade calcium sulfate (CaSO_4) (anhydrite) and air-dried phosphogypsum waste from central Florida. The chemical composition of the phosphogypsum waste is given

in table 1, and a screen analysis is shown in table 2. Commercial-grade carbon monoxide and coal were used as reductants. The analyses of the different coals used in these studies are shown in table 3. A chromium-doped iron oxide, reagent-grade ferric oxide (Fe_2O_3), and a 0.05- μm Fe_3O_4 (magnetite) served as catalysts.

³Italic numbers in parentheses refer to items in the list of references at the end of this report.

For the 3-in-rotary-tube furnace tests, phosphogypsum samples were obtained from two Florida phosphate producers. Chemical analyses of these samples, A and B, are given in table 4. The samples were air-dried and passed through a 20-mesh screen to ensure a uniform particle separation, permitting intimate mixing with the reductant particles. Coal sample 8 was obtained from a mine in Alabama and prepared for testing as the reductant in the rotary-tube furnace tests. The coal was crushed and pulverized to approximately 70 and 80 pct minus 100 mesh. Analyses of the phosphogypsum and coal were used to calculate the carbon-to-sulfur mole ratios.

Table 1.—Chemical analysis of air-dried phosphogypsum waste

	<i>pct</i>
CaO	1.1
CaSO ₄	70.4
H ₂ O	19.0
SiO ₂	6.3
Other	3.2
Total	100.0

Table 2.—Screen analysis of air-dried phosphogypsum waste

<i>Mesh size</i>	<i>pct</i>
Plus 28	1.4
Minus 28 plus 65	6.1
Minus 65 plus 100	17.2
Minus 100 plus 200	51.5
Minus 200	23.8
Composite	100.0

Table 3.—Analyses of coals used in this study

	Mois- ture, pct	Ash, pct	Volatile content, pct	Fixed carbon, pct	Heat content, Btu/lb
Sample 1:					
As received	6.04	13.03	7.81	73.12	11,819
Dried at 105° C	NAP	13.87	8.31	77.82	12,579
Sample 2:					
As received	2.76	4.32	18.54	74.38	14,605
Dried at 105° C	NAP	4.44	19.07	76.49	15,020
Sample 3:					
As received	1.78	4.69	19.31	74.22	14,730
Dried at 105° C	NAP	4.77	19.66	75.57	14,997
Sample 4:					
As received	1.31	7.90	20.35	70.44	14,220
Dried at 105° C	NAP	8.00	20.62	71.38	14,409
Sample 5:					
As received	13.73	8.42	20.32	57.53	12,076
Dried at 105° C	NAP	9.76	23.55	66.69	13,998
Sample 6:					
As received	1.98	7.07	23.53	67.42	14,191
Dried at 105° C	NAP	7.21	24.01	68.78	14,478
Sample 7:					
As received	2.71	3.05	33.21	61.03	14,212
Dried at 105° C	NAP	3.14	34.13	62.73	14,608
Sample 8:					
As received	2.32	2.09	38.59	57.00	14,545
Dried at 105° C	NAP	2.14	39.50	58.36	14,890

NAP Not applicable.

Table 4.—Chemical analyses of air-dried phosphogypsum waste used in rotary-tube furnace tests, percent

	Sample A	Sample B
CaO	0.8	1.9
CaSO ₄	61.1	51.4
H ₂ O	16.6	14.3
SiO ₂	18.9	27.9
Other	2.6	4.5
Total	100.0	100.0

EQUIPMENT AND PROCEDURES

All thermogravimetric analysis (TGA) tests were made using a standard apparatus consisting of a microbalance and tube furnace unit interfaced with a data analyzer that evaluates the weight changes. The experimental variables studied were reaction temperature from 680° to 1,000° C and carbon-to-sulfur mole ratio from 2 to 3.7. A heating rate of 50° C/min was used. Carbon monoxide of 100-pct concentration was used at a flow rate of 162 mL/min and provided an excess of carbon monoxide for the reduction.

Helium was used as purge gas. Sample preparation consisted of weighing the appropriate amounts of each constituent and combining them in plastic vials that were placed in a shaker mixer for 5 min. In the test procedure, approximately 50 mg of sample or mixture was weighed into the platinum crucible of the TGA apparatus. The reaction chamber was closed, and the system was purged with helium until the isothermal temperature was reached. When coal was the reductant, helium continued to flow

during the isothermal phase, but when the reductant was carbon monoxide, the helium flow was stopped and carbon monoxide was introduced.

Experiments were also conducted in a single-zone, hinged-type tube furnace fitted with a 1-in-diam by 30-in-long mullite tube. One- to seven-gram samples were prepared for testing by weighing the necessary components into plastic bottles and shaking them until they were thoroughly mixed. The raw materials were then transferred to ceramic boats and heated in the tube furnace. The furnace atmosphere was controlled by flowing measured amounts of the desired gases through the furnace during heating. When nitrogen was used, a fixed quantity was allowed to flow over the samples during initial heating, reduction, and cooling. When carbon monoxide was used as the reductant, the initial heating was done under flowing nitrogen and the gas flow was changed to carbon monoxide when the sample was at the desired temperature. Carbon monoxide was varied between 1 and 2 times the stoichiometric amount. At the end of the reduction time, the gas flow was changed back to nitrogen while the samples cooled. All samples were allowed to cool to 100° C or below in the furnace. Chemical analyses and

weights of the residues were used to calculate the yields of calcium sulfide.

Continuous testing was conducted in a rotary-tube furnace, which consists of a 3-in-diam by 6-ft-long mullite tube horizontally mounted in a rotation apparatus that supports the tube through the 36-in hot zone of the furnace. The arrangement, which is illustrated in figure 1, includes a screw feeder and a water-cooled discharge chamber for collecting the reaction product. The unit can be tilted to various angles of inclination and rotated at different speeds, which allows the retention time to be varied. Phosphogypsum and coal are weighed in amounts equivalent to the desired carbon-to-sulfur mole ratio and placed in a baffled rotary mixer for 10 min prior to being pressed into briquettes. The roll briquetter produces pellets approximately 3/4 in long by 3/8 in wide. These briquettes are placed in the hot zone of the furnace by a screw feeder while nitrogen flows countercurrently through the furnace tube. The product is discharged into a water-cooled, nitrogen-filled collection chamber, which is emptied at intervals into another nitrogen-filled chamber so that samples can be removed without allowing air into the system.

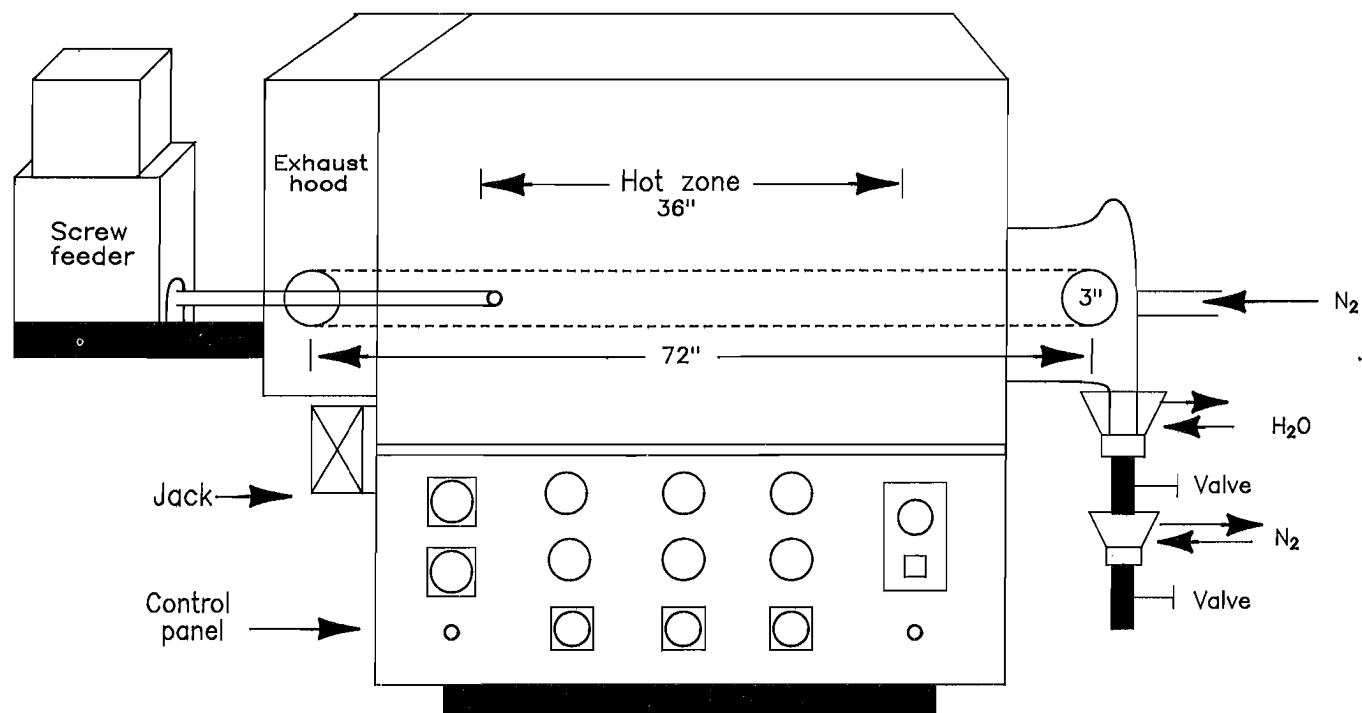


Figure 1.—Phosphogypsum reduction reactor.

RESULTS AND DISCUSSION

THERMOGRAVIMETRIC ANALYSIS

In initial tests using carbon monoxide as the reductant, a temperature of 850° C was required to achieve complete conversion of anhydrite to calcium sulfide. Investigations to determine if the addition of a catalyst could be used to lower the temperature and increase the rate of reduction were conducted. Anhydrite was used instead of phosphogypsum to eliminate the possible side effects caused by impurities in the phosphogypsum. Ferric oxide was determined to be an effective catalyst for the reduction of anhydrite to calcium sulfide in a carbon monoxide atmosphere at 680° C. The TGA curve in figure 2 shows that initially there was some weight loss, due to removal of moisture, prior to the point at which the isothermal temperature was reached. This loss was equivalent to the

weight loss obtained when the anhydrite was dried in an oven at 220° C for 1 h. The region beyond the onset of the isothermal conditions showed a marked decrease in weight. The largest amount of loss occurred in the initial minutes of the reaction. This reflected the reduction of calcium sulfate to calcium sulfide and indicated that the reaction is fast (11). X-ray analyses of the residue indicated that the major constituent was calcium sulfide. The presence of iron carbide was also identified in the residue and is consistent with data reported in the literature for the reduction of iron oxide in a carbon monoxide atmosphere with excess carbon monoxide present in the system (12). In other TGA experiments, magnetite was also shown to have the same catalytic effect as ferric oxide on the reduction of anhydrite to calcium sulfide with complete reduction occurring at 680° C.

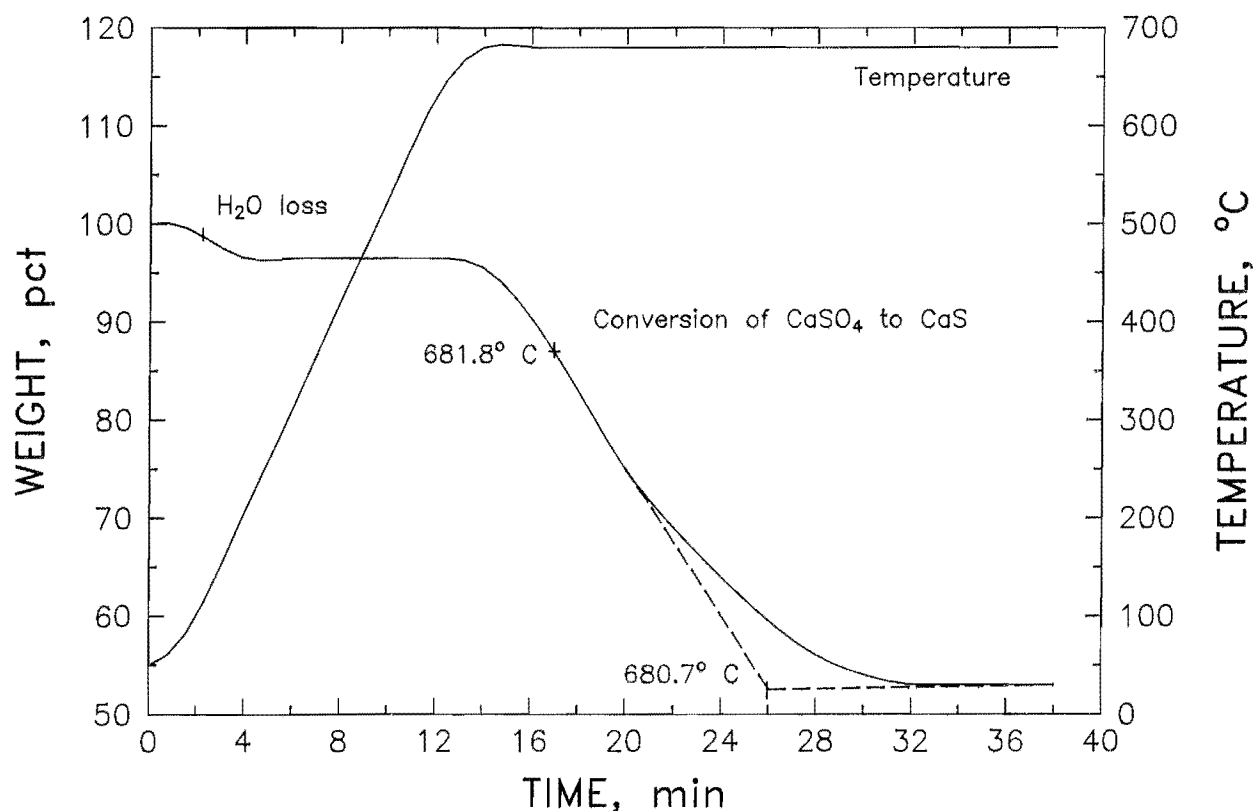


Figure 2.—Typical TGA curve showing conversion of calcium sulfate to calcium sulfide.

To determine the optimum amount of catalysts required, a series of experiments was conducted at 680° C using carbon monoxide as the reductant while varying the amount of magnetite. The results are shown in table 5.

Table 5.—Conversion of calcium sulfate to calcium sulfide using carbon monoxide as reductant at 680° C, percent

Fe_3O_4	Conversion
2.0	63.2
5.0	93.8
8.3	96.5
9.0	97.2
12.0	96.5
20.0	96.0

The reaction conditions used were essentially the same as results reported by Zadick (13), where 8.3 to 12 pct Fe_3O_4 was required to achieve a 97-pct reduction.

A series of experiments was conducted in the TGA apparatus to determine the effect of using carbon monoxide as the reductant at temperatures ranging from 750° to 900° C. The feed material was phosphogypsum, as received from Florida. The results of these experiments are summarized in table 6.

Table 6.—Reduction of phosphogypsum to calcium sulfide with carbon monoxide in TGA apparatus

Temperature, °C	Conversion, pct	Reduction time, min
750	8	40.0
800	60	24.5
850	100	15.5
900	100	12.0

The results indicate that a temperature of at least 850° C was required to obtain complete reduction of phosphogypsum to calcium sulfide. As expected, the data also showed that as the temperature was increased, the reaction rate increased.

Results from the tests conducted using anhydrite were the basis for a series using phosphogypsum as the feed material with ferric oxide and magnetite as the catalysts. The results of this series are given in table 7.

Table 7.—Conversion of phosphogypsum to calcium sulfide using carbon monoxide as reductant in presence of catalysts

Temperature, °C	Catalyst conc, pct	Conversion, pct	
		Fe_3O_4	Fe_2O_3
680	8.3	45	ND
745	8.3	98	ND
750	8.3	98	99
745	5.0	94	ND
750	5.0	97	97
775	5.0	98	ND

ND Not determined.

The results show that, for phosphogypsum, the temperature required for reduction is about 750° C. This is an increase of 70° C when compared with the reduction of anhydrite. This increase in temperature was probably caused by the impurities contained in the phosphogypsum.

ONE-INCH-DIAMETER-TUBE FURNACE TESTS

The investigation was continued by reducing calcium sulfate to calcium sulfide in a tube furnace. Initial experiments were conducted using anhydrite. A series of experiments using 100 pct CO as the reducing gas showed that a temperature of 850° C resulted in 99.9-pct conversion to calcium sulfide. At lower temperatures, the conversion was less; for example, at 800° C, only 85.4-pct reduction was observed. In previous experiments in the TGA apparatus, the reduction time was 25.5 min; whereas, for the tube furnace, the reduction time increased to greater than 30 min, as shown in table 8.

Table 8.—Effect of time on reduction of calcium sulfate with 100 pct CO at 850° C

Reduction time, h	Conversion, pct
0.5	89
1	100
2	100

The experiments previously described were conducted using 100 pct CO as the reductant. Since such a concentration would be difficult to obtain by heating coal or carbon, which is desirable from an economical standpoint, a series of experiments using a mixture of 5 pct CO and 95 pct N was conducted; the results are shown in table 9. As expected, the decrease in carbon monoxide concentration from 100 to 5 pct increased the time required to obtain complete conversion.

Table 9.—Effect of temperature on reduction of calcium sulfate with 5 pct CO

Temperature, °C	Reduction time, h	Conversion pct
800	2	61
850	1	84
850	2	99
900	2	100

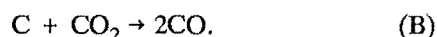
In another series of experiments, phosphogypsum, as received, was air-dried and treated in the tube furnace for 2 h using 10 pct CO and 90 pct N as the reducing gas, and the results indicated that a temperature of 900° C was required to obtain 99-pct conversion. This was an increase of 50° C when compared with the reduction of anhydrite. The temperature was lowered to 750° C by adding 8.3 pct

Fe₂O₃ or magnetite to the phosphogypsum prior to reduction. The required reduction time to obtain greater than 90-pct conversion was 2 h. These test results from the tube furnace parallel the results obtained in the TGA apparatus.

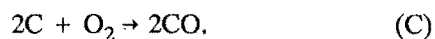
In experiments previously described, carbon monoxide had been used as the reductant for calcium sulfate. In actual practice, carbon is combined with oxygen to produce carbon dioxide in a powerful exothermic reaction:



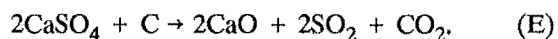
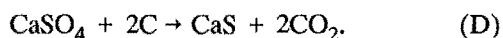
In an oxygen-deficient atmosphere, the carbon dioxide produced in reaction A can react with carbon to produce carbon monoxide:



Reaction B is favored by high temperatures. The combination of reactions A and B is shown in reaction C.



The reduction of calcium sulfate by carbon can yield calcium sulfide and sulfur dioxide. Preferential reduction can be achieved to yield essentially either calcium sulfide or sulfur dioxide by control of the amount of carbon added, relative to the amount of sulfate. The reactions for the conversion are shown in reactions D and E:



To produce calcium sulfide, the carbon-to-sulfur mole ratio in the charge should be slightly above the stoichiometric value of 2:1 (14).

Experiments using coal containing 23.55 pct volatiles as a reductant indicated that phosphogypsum could be converted to calcium sulfide in 2 h at 1,000° C. A series of tests using this coal was conducted to evaluate the effects of the carbon-to-sulfur mole ratio and the addition of magnetite catalysts on the reduction of phosphogypsum at 1,000° C. A nitrogen flow rate of 250 mL/min was used, and the reaction time was 2 h. Results of these experiments are given in table 10.

Table 10.—Effect of magnetite and carbon-to-sulfur mole ratio on reduction of phosphogypsum at 1,000° C with reaction time of 2 h

Carbon-to-sulfur mole ratio	Fe ₃ O ₄ addition, pct	Conversion to CaS, pct
2.0	0	83
2.0	9	89
2.8	0	87
2.8	9	94
3.2	0	84
3.2	9	96
3.7	0	90
3.7	9	96

These results indicate that conversion was increased by the addition of the catalyst and also by increasing the carbon-to-sulfur mole ratio. To evaluate the effect of coal volatile content on conversion, a series of experiments was conducted using coals with volatile contents ranging from 8.31 to 34.13 pct. A reaction time of 2 h was used with a nitrogen flow rate of 250 mL/min. The results, shown in table 11, indicate that conversion varies directly with volatile content between approximately 20 and 34 pct.

Table 11.—Effect of coal volatile content on reduction of phosphogypsum at 1,000° C

Coal	Volatile content, pct	Conversion to CaS, pct	
		2 C-S ratio	2.2 C-S ratio
1	8.31	75	85
2	19.07	75	87
3	19.66	74	85
4	20.62	78	88
5	23.55	83	ND
6	24.01	85	95
7	34.13	93	98

ND Not determined.

Since the high-volatile coal produced much higher conversion at 1,000° C, a series of tests was performed to determine if this coal would affect conversion at temperatures below 1,000° C. Results of these experiments, which were conducted with and without the addition of a catalyst, are shown in table 12. In both of these series, a mole ratio of fixed carbon to sulfur of 2.2 and a nitrogen flow rate of 5 mL/min were used.

These results indicate that reduction of phosphogypsum can be accomplished at temperatures lower than 1,000° C

with yield percentages in the high 90's. The results also show that the addition of the chromium-doped iron oxide catalyst had little effect on the conversion of phosphogypsum to calcium sulfide when the reductant was high-volatile coal.

Table 12.—Effect of high-volatile coal and catalyst on temperature for reduction of phosphogypsum with reaction time of 2 h

Temperature, °C	Catalyst G-3A ¹ addition, pct	Conversion to CaS, pct
900	0	98
	9	100
800	0	97
	9	97
700	0	54
	9	60

¹Chromium-doped iron oxide.

Varying the nitrogen flow rate from 5 to 250 mL/min and using a carbon-to-sulfur mole ratio of 2.2 and high-volatile coal, the conversion increased slightly as the flow rate decreased. The results of experiments conducted at nitrogen flow rates of 5 and 250 mL/min and at various temperatures are shown in table 13.

Table 13.—Effect of nitrogen flow rate on reduction of phosphogypsum with high-volatile coal at various temperatures with reaction time of 2 h

Temperature, °C	N ₂ flow rate, mL/min	Conversion to CaS, pct
1,000	5	99
	250	98
850	5	98
	250	96
800	5	97
	250	94

ROTARY-TUBE FURNACE TESTS

Experiments were conducted in the 3-in-diam-rotary-tube furnace to generate additional process information on a larger scale and establish ranges of operating conditions. In some of the initial tests, the phosphogypsum and coal particles had a tendency to adhere to the inside of the furnace tube on contact with heat. It was determined that briquetting the feed would alleviate this problem. The rotary-tube furnace was operated at various temperatures and retention times using coal sample 8, which contains 39 pct volatile material. Tests were conducted at feed rates between 25 and 30 g/min, and the angle of inclination was varied from 0.4° to 3.1° at tube rotation speeds of 4 and 8 r/min. In these tests, the carbon-to-sulfur mole ratio used was 2.2. Results of these experiments are shown in figure 3 and table 14. The relationship between temperature and calcium sulfide yield is illustrated in figure 3. For the lower rotational speed and the lowest two angles of inclination, at temperatures of 850° and 900° C, yield percentages in the high 90's were obtained. As the angle of inclination and/or speed of rotation of the tube was increased, the retention time decreased. The retention times associated with the yields produced at 900° C are given in table 14. Conversions of 99, 98, and 90 pct were accomplished at 900° C with retention times of 32, 21, and 11 min, respectively.

Table 14.—Rotary-tube furnace retention times at 900° C

Tube rotation, r/min	Angle of inclination, deg	Retention time, min	CaS yield, pct
4	0.4	ND	99
48	32	99
4	1.5	21	98
4	3.1	11	90
8	3.1	ND	79

ND Not determined.

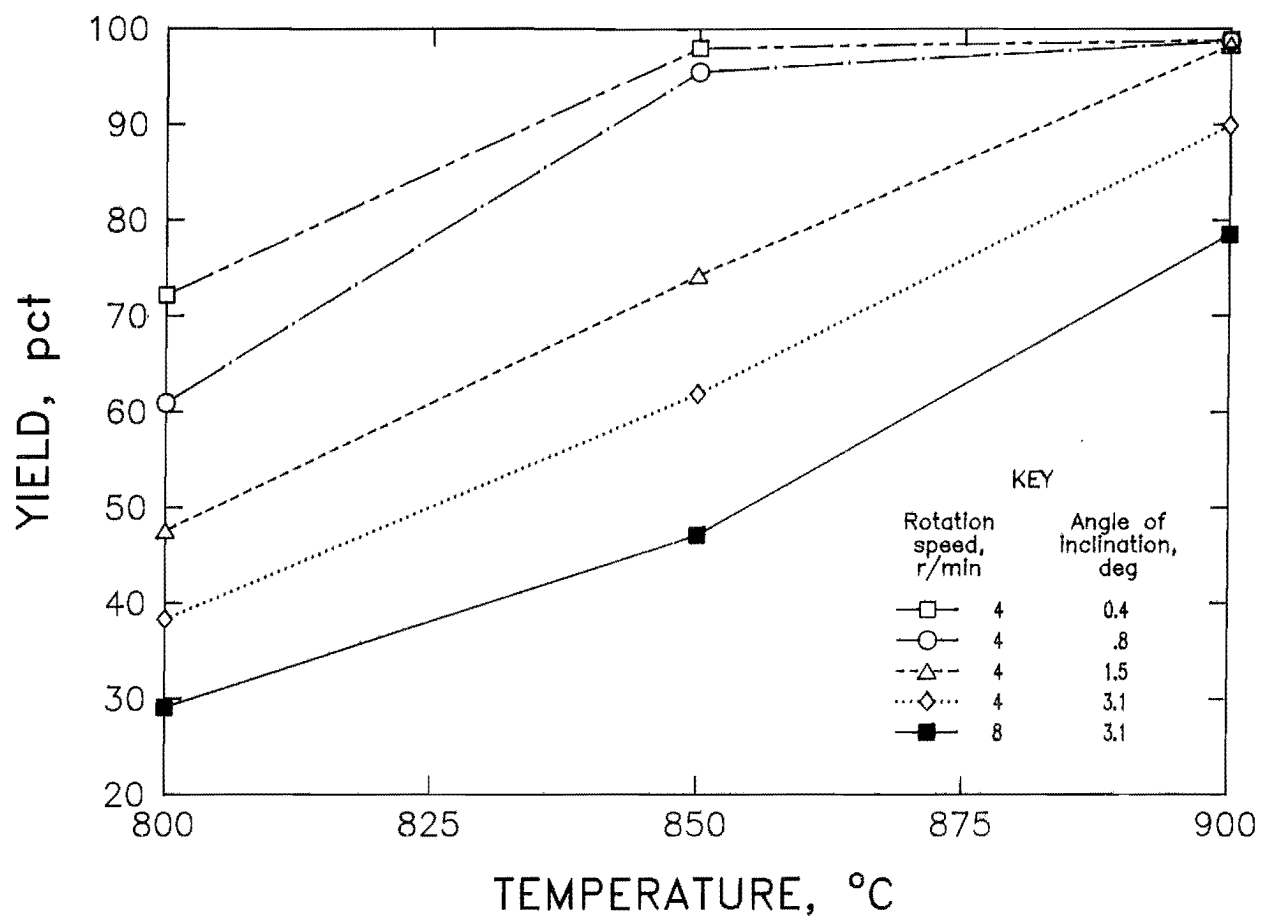


Figure 3.—Effect of temperature on calcium sulfide yield.

CONCLUSIONS

The conversion of calcium sulfate in phosphogypsum to calcium sulfide was accomplished using carbon monoxide as a reductant at a temperature of 900° C in a 1-in tube furnace. The required temperature was reduced to 800° to 850° C using high-volatile coal as the reductant. In a 3-in rotary-tube furnace, 98-pct conversion to calcium sulfide was obtained in approximately 20 min at a temperature of 900° C when high-volatile coal and a carbon-to-sulfur mole

ratio of 2.2 were used. Decreasing the retention time to approximately 10 min produced 90-pct conversion to calcium sulfide. Iron oxide catalyst enhanced the production of calcium sulfide from phosphogypsum when low- or medium-volatile coals were used. However, when high-volatile coals were used, the catalyst had little or no effect.

REFERENCES

1. May, A., and J. W. Sweeney. Assessment of Environmental Impacts Associated With Phosphogypsum in Florida. BuMines RI 8639, 1982, 19 pp.
2. Zellars-Williams, Inc. (Lakeland, FL). Evaluation of Potential Commercial Processes for the Production of Sulfuric Acid From Phosphogypsum. FL Inst. Phosphate Res. Rep. 01-002-001, Oct. 1981, 62 pp.
3. Martin, D. A., F. E. Brantley, and D. M. Yergensen. Decomposition of Gypsum in a Fluidized-Bed Reactor. BuMines RI 6286, 1963, 15 pp.
4. George, D. R., and J. M. Riley. Process for Recovery of Sulfur From Gypsum. U.S. Pat. 3,591,332, July 6, 1971.
5. Marchant, W. N., S. L. May, W. W. Simpson, J. K. Winter, and H. R. Beard. Analytical Chemistry of the Citrate Process for Flue Gas Desulfurization. BuMines IC 8819, 1980, 20 pp.
6. PEI Associates, Inc. Supplement to Region IV's Areawide EIS Central Florida Phosphate Industry. Ongoing U.S. EPA contract 68-03-3197 PN 3617-7; for information contact E. Mullin, project manager, Cincinnati, OH.
7. Miller, R. L., and H. Sutcliffe, Jr. Water Quality and Hydrogeologic Data for Three Phosphate Industry Waste-Disposal Sites in Central Florida, 1979-1980. U.S. Geol. Surv. WRI 82-045, Apr. 1982, 85 pp.
8. Austin, R. D. Sulfur From Gypsum. Paper in Proceedings of the International Symposium on Phosphogypsum. FL Inst. Phosphate Res., 1980, pp. 355-375.
9. Zellars-Williams, Inc. (Lakeland, FL). Evaluation of Fluid Bed Decomposition of Phosphogypsum. FL Inst. Phosphate Res. Rep. No. 01-002A-002, Aug. 1982, 124 pp.
10. Kendron, T. J., and G. M. Lloyd. Phosphogypsum, Source of Sulfur Dioxide: New Signs of Life? Phosphorus and Potassium, No. 137, 1985, pp. 33-36.
11. Swift, W. M., A. F. Panek, G. W. Smith, G. J. Vogel, and A. A. Jonke. Decomposition of Calcium Sulfate: A Review of the Literature. Argonne Nat. Lab., Argonne, IL, ANL-76-122, 1976, pp. 1-55.
12. Ross, H. U. Solid Fuels and Reductants for the Beneficiation and Reduction of Iron Ores. Paper in Iron Ore Reduction, ed. by R. R. Rogers (Proc. of Symp. of Electrotherm. and Metall. Div. of Electrochem. Soc., May 3-5, 1960). Pergamon, 1962, pp. 56-57.
13. Zadick, T. W., R. Zavaleta, and F. P. McCandless. Catalytic Reduction of Calcium Sulfate to Calcium Sulfide With Carbon Monoxide. Ind. and Eng. Chem., Process Des. and Dev., v. 11, No. 2, 1972, pp. 283-287.
14. Turkdogan, E. T., and J. V. Vinters. Reduction of Calcium Sulphate by Carbon. Inst. Min. and Metall., Sec. C, v. 85, 1976, pp. C117-C123.