Decomposition of Calcium Sulfate in a Two-Zone Reactor

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A new method of decomposing calcium sulfate has been demonstrated with a bench-scale fluidized bed reactor in which two reaction zones were established. A reducing zone was set up in the lower part of the reactor by partial combustion of natural gas and an oxiding zone in the upper part by the addition of secondary air. Through natural circulation in such a system, the solids were alternately reduced and oxidized. Both gypsum and anhydrite were decomposed in a continuous manner at temperatures ranging from 1910 to 2230°F. With temperatures of 2100°F and higher, the solids were 98 to 99% desulfurized, and with lower temperatures, the solids were desulfurized less. However, conversion to calcium sulfide was almost completely avoided over the whole temperature range. The process shows promise for treating waste and byproduct forms of calcium sulfate as well as natural minerals.
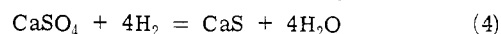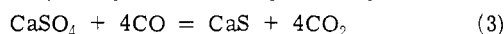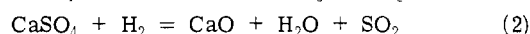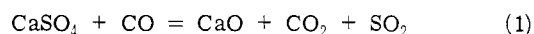
Introduction

Mounting piles of waste calcium sulfate from various manufacturing operations and industrial pollution control systems demand improved methods of utilization as do the very plentiful natural deposits of gypsum and anhydrite. To meet this demand, a new method of decomposing calcium sulfate has been conceived. The method is described below and the results of a preliminary demonstration of the method in a bench-scale reactor are presented.

Existing industrial processes for utilizing calcium sulfate suffer important limitations. Thus the well-known process for manufacturing cement-sulfuric acid requires a very large capital investment and major markets for both acid and cement. Moreover, this process does not lend itself to situations better served by methods which produce lime instead of cement. Such situations arise in the control of air and water pollution where calcium sulfate is a product of reacting lime with waste acid or dilute sulfur oxides. In these situations a process is needed which converts the recovered calcium sulfate back into lime so that it can be recycled.

Although a promising method of converting calcium sulfate into calcium oxide by reductive decomposition at high temperature was developed previously, it also has limitations (Wheelock and Boylan, 1963, 1966, 1968, 1971; Hanson et al., 1969). Reductive decomposition must be carried out under carefully controlled conditions of temperature and gas composition. Temperatures above the optimum range (2150 to 2250°F) cause sintering while temperatures below the optimum range cause incomplete desulfurization and formation of calcium sulfide. If the gas phase is highly reducing, calcium sulfide will be produced; but if it is weakly reducing, the rate of desulfurization will be slow. Even though reductive decomposition can be made to work well with gypsum or anhydrite from relatively pure massive deposits, it may be impractical for treating some types of calcium sulfate wastes with impurities which lower the sintering temperature of the solids below the optimum range of temperature for the process.

In order to overcome the limitations of straight reductive decomposition, a new process has been conceived whereby calcium sulfate is decomposed in a fluidized bed with two reaction zones where reducing conditions are maintained in one zone and oxidizing conditions in the other. Due to extensive natural circulation, the solid particles are exposed alternately to reduction and oxidation. The different zones are obtained by controlling the ratio of air to fuel in different parts of the bed. Some hydrocarbon fuel such as natural gas is burned within the bed to provide the necessary heat for the process. In the reducing zone the air to fuel ratio is kept well below the stoichiometric ratio required for complete combustion to provide copious amounts of carbon monoxide and hydrogen. In the oxidizing zone the ratio is kept sufficiently large to provide excess oxygen. As the solid particles pass through the reducing zone they undergo reactions such as

$$CaSO_4 + CO = CaO + CO_2 + SO_2 \qquad (1)$$
$$CaSO_4 + H_2 = CaO + H_2O + SO_2 \qquad (2)$$
$$CaSO_4 + 4CO = CaS + 4CO_2 \qquad (3)$$
$$CaSO_4 + 4H_2 = CaS + 4H_2O \qquad (4)$$

and as they pass through the oxidizing zone reactions such as

$$CaS + \tfrac{3}{2}O_2 = CaO + SO_2 \qquad (5)$$
$$CaS + 2O_2 = CaSO_4 \qquad (6)$$
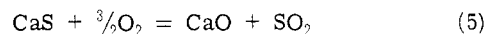
Just as in the process of straight reductive decomposition, reactions 1 and 2 are the predominant ones. However, whereas reactions 3 and 4 cannot be tolerated in the former process, they can be in the new one because of the built in mechanism for eliminating calcium sulfide. Since each particle is likely to pass through both reaction zones a number of times, any calcium sulfide produced in passing through the reducing zone is eliminated in subsequent passes through the oxidizing zone. In a similar way, any calcium sulfide produced in the oxidizing zone is eliminated in subsequent passes through the reducing zone. Without the need to prevent reactions 3 and 4, lower temperatures and higher concentrations of reducing gases can be employed than in the process of straight reductive decomposition.

Other processes have been suggested for decomposing calcium sulfate in a series of separate reduction and oxidation stages (Bollen, 1954; Campbell and Fisher, 1971). When these treatments are carried out in separate stages, it may be difficult if not impossible to utilize the heat produced by oxidation to help meet the energy requirements for reduction. Hence, these processes are not likely to be as thermally efficient nor as likely to provide as uniform and easily controlled temperature as one where reduction and oxidation are carried out in the same fluidized bed. In addition, the multistage processes require a more complicated system of reactors and may produce several gas streams, each having a different composition.

To demonstrate the new treatment method and the utility of a two-zone fluidized bed for decomposing calcium sulfate, a number of experiments were carried out with a bench-scale reactor.
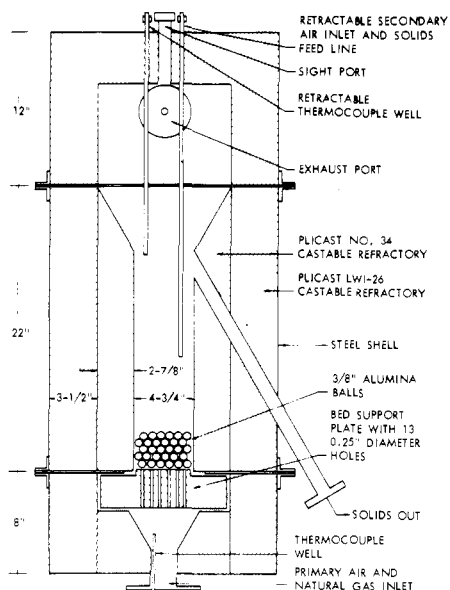
Figure 1. Details of fluidized bed reactor.

Figure 2. Apparatus used for laboratory work.

Experimental Section

Figure 1 is an illustration of the reactor used for the demonstration. The reactor was constructed of refractory materials for the most part and had a steel shell to prevent leakage of gases to the atmosphere. The outer shell was insulated to reduce heat losses. In operation, the reactor contained fluidized, reacting solids up to the overflow pipe which passed through the side of the reactor. Primary air and natural gas were admitted through the bed support plate at the bottom of the reactor and secondary air through a ceramic tube which passed through the top of the reactor and was immersed in the fluidized bed. The bed support plate was covered by several layers of alumina pellets to both protect the distributor and adjust the depth of the fluidized bed. Finely divided solids were pneumatically conveyed into the reactor by the secondary air and reacted solids were removed through the overflow pipe. Gases were removed through an exhaust port near the top of the reactor. The fluidized bed temperature was determined with a chromel–alumel thermocouple placed in a mullite ceramic protection tube inserted in the bed.

Two reaction zones were achieved by limiting the ratio of primary air to natural gas so that the lower part of the fluidized bed was reducing in character and by introducing sufficient secondary air so that the upper part of the bed was oxidizing. Since the bench-scale reactor was not sufficiently insulated to avoid relatively large heat losses, either the primary or secondary air or both had to be enriched with oxygen to achieve the necessary operating temperatures. Such enrichment would not be necessary on an industrial scale where the reactor could be insulated more effectively.

Apparatus used for controlling the flow of gases and solids to the reactor and for handling the reaction products is illustrated by Figure 2. Compressed air, oxygen, and natural gas were metered individually and mixed before reaching the gas distributor at the bottom of the reactor. Additional compressed air and sometimes oxygen were metered and mixed before being supplied as secondary air. Finely divided solids were introduced at a controlled rate into the secondary air by a screw feeder and were then transported by the air into the reactor. The gas which issued from the top of the reactor passed through cyclone separators and a bag filter to remove entrained solids and 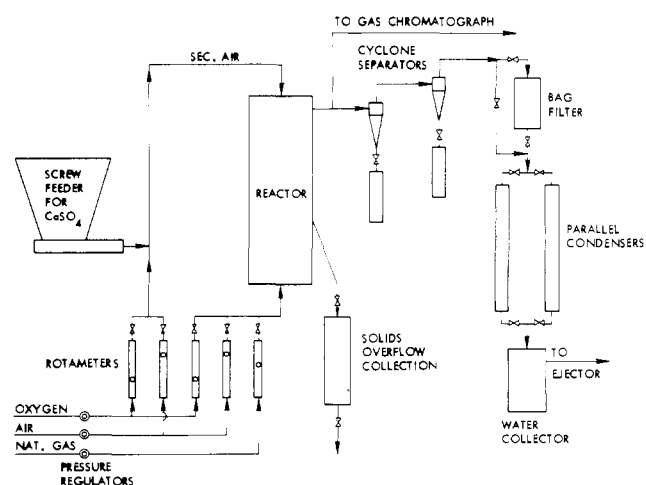then through a condenser to condense water vapor. After separation of the condensate from the gas, the gas was conducted to an ejector which vented to the atmosphere. The ejector was operated so that the gas pressure in the reactor was only slightly greater than atmospheric pressure. Samples of the product gas were collected from a point between the reactor and cyclone separator and were analyzed with a gas chromatograph for sulfur dioxide, carbon monoxide, carbon dioxide, nitrogen, and sometimes hydrogen. Since oxygen and argon were not separated by the chromatograph, their mixture was determined as a single component. Oxygen and argon were then partitioned by material balance. Samples of solids passing from the reactor through the overflow pipe and of solids entrained in the off-gas were collected and analyzed by wet-chemical methods for calcium and for sulfur in both the sulfate and sulfide forms.

Two natural ores of calcium sulfate which had been crushed and screened to −14 + 35 mesh size were used for the test operation of the reactor. One of these ores from Fort Dodge, Iowa, was predominantly gypsum whereas the other from Southard, Oklahoma, was predominantly anhydrite. The approximate chemical composition of the ores is given in Table I.

Natural gas used for the test operation had the following average composition as determined by gas chromatography:

Table I. Chemical Composition of Feed Materials

Constituent	Wt % in ore	
	Gypsum	Anhydrite
Anhydrite ($CaSO_4$)	. . .	73.4
Gysum ($CaSO_4 \cdot 2H_2O$)	94.7	24.4
Calcium and magnesium carbonates	1.6	0.6
Silica (SiO_2)	3.3	. . .
Sodium chloride (NaCl)	0.3	. . .
Other constituents	0.1	1.6
	100.0	100.0

Constituent	Mole %
Methane (CH_4)	88.2
Ethane (C_2H_6)	4.8
Nitrogen (N_2)	7.0
	100.0

Combustion tests showed that with an air to natural gas ratio of about 10, a neutral mixture of combustion products was produced; lower ratios produced reducing gas mixtures containing free hydrogen and carbon monoxide while higher ratios provided oxidizing mixtures containing free oxygen. Furthermore, the concentration of reducing gases increased as the ratio dropped below 10 or the concentration of oxygen increased as the ratio rose above 10.

For the demonstration runs the two-zone reactor was operated in a continuous manner. Before any given run, the reactor was preheated by burning natural gas with air in the reactor for several hours. Combustion was initiated by inserting a pilot light (created by burning natural gas with oxygen at the end of a long tube) through a port in the top of the reactor so as to heat the surface of the alumina pellets in the bottom of the reactor. When the surface of the pellets became incandescent, natural gas and primary air were admitted through the gas distributor and ignition occurred. After the reactor temperature reached 1900°F, the flow of secondary air and entrained feed (gypsum or anhydrite) was started. As the bed of fluidized solids accumulated, the flow rates of natural gas, primary and secondary air were adjusted to establish desired operating conditions. The ratio of primary air to natural gas had to be limited to about 6 or less in order to prevent precombustion below the distributor plate. It proved difficult to control the system temperature even though oxygen enrichment provided an additional means of control. Usually it required several hours to achieve essentially steady-state conditions where the solids feed and overflow rates, gas flow rates, product gas composition, and fluidized bed temperature were nearly constant. After conditions appeared constant, the run was continued for several hours during which time conditions were logged and samples collected frequently.

Results

A number of successful runs were made with the two-zone reactor. Various system parameters were changed from run to run so as to determine their effects on desulfurization of the solids and product gas composition. Average operating conditions prevailing during these runs and results obtained are presented in Table II. In most instances, the product solids which issued from the overflow tube were well desulfurized and only slightly contaminated with calcium sulfide. Moreover, useful concentrations of sulfur dioxide (5 to 10%) in the off-gas were realized. On the other hand, the fines entrained in the off-gas were desulfurized less and were contaminated with greater amounts of calcium sulfide than the overflow product. However, except for two runs (1-274 and 2-98) the rate of entrainment was only 4 to 12% as great as the product overflow rate. The two runs which exhibited the high entrainment rates were both made with gypsum which tended to decrepitate.

Key operating conditions are listed in Table II. These conditions include the total flow rate of air and oxygen introduced through both the bottom gas distributor and diptube as well as the ratio of equivalent amount of primary air to natural gas and the ratio of the total equivalent amount of primary and secondary air to natural gas. For all runs, the primary air to natural gas ratio was kept low to ensure highly reducing conditions in the lower part of the fluidized bed. Conversely, the overall air to natural gas ratio was kept high enough to ensure an oxidizing zone in part of the bed. When the overall air to natural gas ratio was below 8.9, the presence of carbon monoxide in the off-gas showed that the total quantity of air was insufficient to completely oxidize the fuel. On the other hand,

Table II. Results of Test Runs with Natural Ores of Calcium Sulfate

Run No.	Ore −14 + 35 mesh	Feed rate, g/min	Nat. gas flow, scfm	Air + O₂ flow, scfm	Prim. air/gas^a	Overall air/gas^a	Nominal bed temp, °F	Bed depth, in.	Holdup time, min	Off-gas Composition^b % CO	% O₂	% SO₂	Product solids % CaS	% Desulf	Entrained fines % prod.^c	% CaS	% Desulf
1-268	Gypsum	25	0.52	2.38	5.0	8.5	2120	9	186	1.2	...	3.3	0.1	98.4	9	5.3	78
1-274	Gypsum	50	0.67	3.24	5.0	8.5	1960	9	91	2.2	...	5.0	2.6	94.9	41	12.0	59
1-285	Anhydrite	40	0.67	3.31	5.0	8.7	2230	9	29	0.9	...	7.5	0.5	97.7	5	10.4	71
1-298	Anhydrite	33	0.60	2.86	5.0	8.9	2230	10	93	1.0	...	6.5	0	98.6	5	9.2	75
2-28	Anhydrite	33	0.60	3.14	5.0	10.0	2130	10	75	...	5.9	8.0	0.1	97.7	6	1.2	75
2-35	Anhydrite	45	0.54	2.81	5.0	10.4	2000	10	66	...	3.8	8.5	0	79.9	12	1.0	39
2-42	Anhydrite	42	0.51	2.86	5.1	10.6	1910	11	119	...	8.4	5.0	0.2	44.7	11	0.3	22
2-58	Anhydrite	39	0.54	2.81	5.0	10.7	2170	10	74	...	4.3	10.0	0.2	98.3	4	0.9	79
2-68	Anhydrite	31	0.56	3.08	5.4	10.7	2210	10	118	...	5.7	6.0	0.1	99.2	11	1.2	74
2-98	Gypsum	32	0.64	3.20	4.2	10.0	2170	10	63	...	3.2	5.2	0.4	98.7	28	2.6	81
2-103	Anhydrite	37	0.61	2.81	4.4	9.5	2100	10	118	...	4.5	7.5	0.1	98.8	7	1.5	67
2-107	Anhydrite	37	0.61	2.81	4.4	9.5	2200	10	79	...	5.2	7.5	0.9	98.4	9	1.9	78

^a Equivalent amount of air to natural gas ratio. ^b Volume composition on a dry basis. ^c Entrainment rate as a percent of product overflow rate.
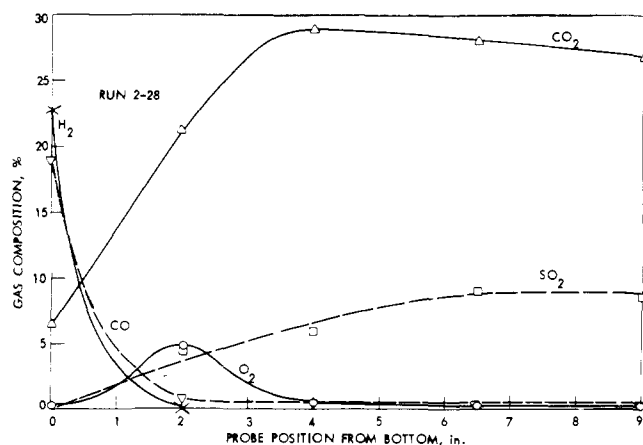
Figure 3. Gas composition profile with end of diptube 1.0 in. above the bottom.

Figure 4. Gas composition profile with end of diptube 4.0 in. above the bottom.

when this ratio was above 9.5, the presence of free oxygen in the off-gas indicated excess air. Interestingly enough the overall air to gas ratio seemed to have little effect on the desulfurization of the overflow product or on the concentration of calcium sulfide in this material. This result emphasizes an important difference between the new process and the process of straight reductive decomposition which is very sensitive to the overall air to gas ratio (Bollen, 1954).

Of course, the overall air to gas ratio did have a marked effect on the calcium sulfide content of the entrained fines with lower ratios causing higher concentrations of calcium sulfide and higher ratios lower concentrations (Table II). It appears that with excess air the fines were oxidized as they were elutriated from the reactor. The generally lower desulfurization and greater sulfide content of the fines as compared to the overflow product indicate that the fines were elutriated from the bed before having an opportunity to cycle a sufficient number of times through the two zones.

Temperature did not appear to have much effect on the results between 2100 and 2230°F. However, a comparison of the results obtained in runs 2-35 and 2-42 with other runs at higher temperatures shows that the desulfurization fell off as the temperature was reduced to 2000°F and then 1910°F. This indicates a decrease in reaction rate as the temperature dropped, but the calcium sulfide content of either the overflow product or the entrained fines was not noticeably greater at the lower temperatures. Again, this result is in sharp contrast to what would be obtained with straight reductive decomposition where the tendency to form calcium sulfide increases greatly as the temperature is reduced (Wheelock and Boylan, 1960). This finding is of special significance because it demonstrates that the oxidation mechanism was effective in reducing the calcium sulfide content of the product.

The average holdup or residence time of the solids in the reactor was estimated by dividing the weight of solids remaining in the bed after a run was completed by the average overflow rate during steady-state operation. Values obtained in this way were only approximate because the procedure neglected the entrained material and based everything on the quantity of solids left at the end of a run. Nevertheless, the residence time did not appear to be a critical parameter except possibly in a few runs (1-274, 2-35, and 2-42) made at lower temperatures. For most runs the conversion was so high that the results were insensitive to residence time.

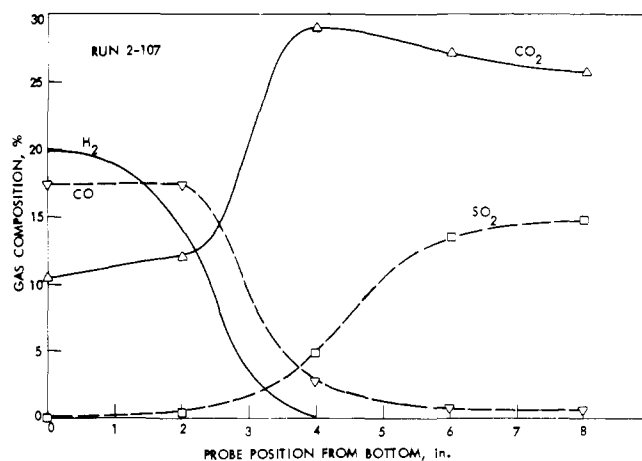In order to verify the existence of two reaction zones and to determine their relative size, the fluidized bed was

probed during several runs. For this purpose a gas sampling probe was inserted in the fluidized bed in place of the thermocouple well during portions of the runs. The probe was moved up and down to collect gas samples from various levels of the bed. These samples were analyzed with a gas chromatograph to provide a profile of gas composition along a vertical line parallel to and about 3 in. from the diptube through which secondary air was introduced into the reactor. The composition profile observed during run 2-28, where the end of the secondary air diptube was 1.0 in above the bottom of the fluidized bed, is illustrated by Figure 3. The presence of carbon monoxide and hydrogen shows that a reducing zone existed near the bottom of the bed and the presence of oxygen shows that an oxidizing zone was present above it. Furthermore, the profile indicates that the reducing zone was not very thick and neither was the oxidizing zone along the path of the probe. However, the oxidizing zone must have extended all the way to the surface of the bed near the secondary air diptube because 5.9% oxygen was found in the reactor off-gas.

A different gas composition profile was observed in run 2-107 where the end of the secondary air diptube was 4 in. above the bottom of the fluidized bed (Figure 4). In this case, the reducing zone was thicker and the oxidizing zone did not extend outward far enough to be intercepted by the probe. Again the presence of oxygen in the off-gas shows that an oxidizing zone must have been present, probably surrounding the diptube.

Even though the composition profiles were affected by the location of the secondary air diptube, the conversion of the solids did not appear to be materially affected. Thus, there seems to be little difference in the overall results between the last two runs where the end of the diptube was 4.0 in. above the bottom of the bed and the first ten runs where it was 1.0 above.

Industrial Application

Industrial application of the two-zone reactor will require further research and development, perhaps on a case by case basis since the properties of various forms of calcium sulfate vary greatly from one source to another. Whereas the natural minerals may be relatively pure and amenable to fluidized bed treatment, other forms may be very impure and too finely divided to be fluidized without pretreatment. The residue produced by lime or limestone wet scrubbers treating power plant stack gases may be largely calcium sulfite with gypsum being only a minor constituent. Hence, this residue is not a very likely candi-
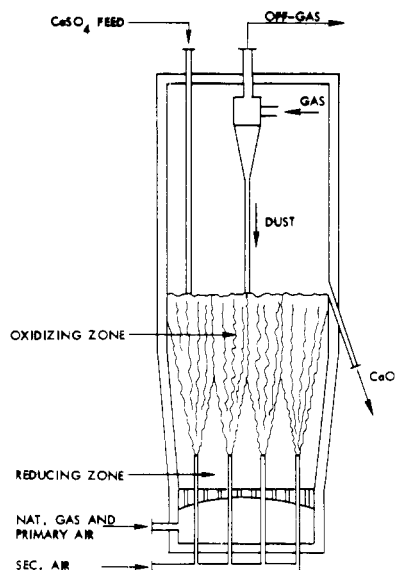
Figure 5. A two-zone industrial fluidized bed reactor.

date for treatment. On the other hand, calcium sulfate produced in a fluidized bed boiler which employs a fluidized bed of calcium oxide particles to capture sulfur oxides at high temperature is a good candidate.

In addition to chemical composition and particle size, other important properties of the solids to be treated are particle density, hardness, and decrepitation tendency. Small, light particles or soft particles which break easily may place an uneconomical limit on fluidization velocity. Moreover interparticle forces interfere with fluidization of very fine particles.

Although natural gas is an ideal fuel for the two-zone process, the dwindling supply of natural gas may dictate the use of other fuels. From a technical standpoint, a medium- or high-BTU gas produced from coal would be a good substitute; a low-Btu producer gas would tend to reduce the concentration of sulfur dioxide in the product gas because of the added nitrogen. Since industrial-scale, fluidized bed lime kilns have operated on fuel oil, the two-zone process may also be adaptable to this type of fuel. However, whereas oil is burned under strongly oxidizing conditions in a lime kiln, it would have to be burned with a substoichiometric amount of air in the present process to generate the necessary reducing gases. The process may also be adaptable to powdered coal but this may require considerable development.

Although simple in general concept (Figure 5), the design of an industrial two-zone reactor will require considerable engineering development. Since gas dispersion, solids circulation rates, and mass transfer are notoriously difficult to predict in fluidized beds, it will be necessary to build and test at least one intermediate size reactor before attempting to design a full-scale reactor.

Conclusions

A new method of decomposing calcium sulfate in a two-zone reactor has been demonstrated on a bench-scale. The process provides a high degree of desulfurization, product lime which is essentially free of calcium sulfide, and an off-gas rich in sulfur dioxide. In addition, the process is not nearly so sensitive to changes in operating conditions as the process of straight reductive decomposition, and it can be carried out at lower temperatures without excessive conversion to calcium sulfide. Furthermore, the process can be carried out in a fluidized bed reactor modified to provide a reducing zone in the lower part of the bed and an oxidizing zone in the upper part.

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