

HIGH TEMPERATURE SULFUR REMOVAL SYSTEM DEVELOPMENT
FOR THE WESTINGHOUSE FLUIDIZED BED COAL GASIFICATION PROCESS

D. L. Keairns, R. A. Newby, E. P. O'Neill, D. H. Archer
Westinghouse Research Laboratories
Pittsburgh, Pennsylvania 15235

ABSTRACT

High temperature sulfur removal can be achieved with calcium based sorbents (e.g. dolomite) in fluidized bed coal gasification systems now being developed for power generation. The use of dolomite offers the opportunity to meet environmental emission standards, to minimize energy losses, and to reduce electrical energy costs.

In addition to achieving the removal of sulfur from the low Btu gas, the complete sulfur removal system must be integrated with the total power plant and environment to assure compatibility. Critical requirements to achieve a commercial system include establishing criteria for "acceptable" sorbents, establishing integrated sulfur removal/gasification process design parameters, predicting trace element release, predicting sorbent attrition, developing an economic regeneration and/or once-through process option, developing a spent sorbent processing system, and establishing safe and reliable disposition options for spent sorbent. Design and operating parameters are being developed and potential process limitations identified.

This work is being performed as part of the Westinghouse Coal Gasification Program. The project is being carried out by a six-member industry/government partnership comprising ERDA, Public Service of Indiana, Bechtel, AMAX Coal Co., Peabody Coal Co. and Westinghouse. This work has been funded with federal funds from the Energy Research and Development Administration under contract E(49-18)-1514. The content of this publication does not necessarily reflect the views or policies of the funding agency.

INTRODUCTION

The production of a low Btu fuel gas from coal for combined cycle electric power generation provides the potential for improved thermal efficiency and reduced power costs compared with conventional power plants with flue gas desulfurization and can provide acceptable environmental impact. The ability to produce the low Btu gas at elevated pressure (e.g. 1500 kPa) with removal of sulfur and particulates from the high temperature gas (e.g. 800-900°C) will enable the maximum thermal efficiency to be achieved. Calcium-based sorbents, such as limestone and dolomite, have been proposed for the high temperature sulfur removal.

Westinghouse has been working on the development of a multi-stage fluidized bed gasification process for combined cycle power generation since 1970.^(1,2) The goal of the program is the integration and operation of a gasifier/power-generating plant on a scale which will demonstrate the commercial operation of the process. An integrated program is underway to proceed from bench-scale laboratory research through pilot scale development and system design and evaluation to the operation of a demonstration plant. The pilot development is now being carried out in a 15 ton/day process development unit.

Westinghouse is investigating gas cleaning systems for high temperature operation (800-900°C), intermediate temperature operation (e.g. 650°C), and low temperature operation. Work has been carried out on both sulfur removal and particulate control systems. This document is limited to an overview of the high temperature sulfur removal system development work on calcium-based sorbents. This system was selected for the base concept based on the potential for high system efficiency and the high kinetic efficiency of removing hydrogen sulfide under the proposed operating conditions with an economically available sorbent. Alternate systems, such as the use of iron oxide or low temperature processes, have not been excluded as candidates for the demonstration plant and are also being studied. An intermediate temperature process is attractive in that it reduces the materials problems while maintaining a relatively high plant efficiency.

The approach to the development of the calcium-based sulfur removal system includes laboratory experimental programs utilizing pressurized thermogravimetric analysis, pressurized fluidized bed reactors, and physical and chemical characterization to develop basic data and to develop screening techniques; data analysis to develop design criteria; systems analyses to assess the technical, economic, and environmental impact of alternate sulfur removal system concepts and to assess the impact of these alternatives on the total power plant.

SULFUR REMOVAL SYSTEM

The basic gasification process utilizing the high temperature calcium-based sorbent system is illustrated in Figure 1. The gasification process has been described.^(1,2) The sulfur removal process options are indicated in Figure 1: in-bed desulfurization and external desulfurization. In situ desulfurization of the fuel gas within the recirculating bed devolatilizer combines the sulfur removal and coal devolatilization in a single vessel. This approach requires compatible coal and sorbent behavior and the ability to separate sorbent and char. The external desulfurizer requires a separate vessel and associated components but provides greater flexibility. Both systems are being assessed through process simulations, PDU operation, and engineering analyses.

Two basic sulfur removal systems have been identified and investigated: once-through sorbent operation and regenerative operation. The reference once-through system and regenerative system concepts are illustrated in Figure 1. An alternate once-through system concept is also indicated which has been considered. A number of spent sorbent processing and regeneration processes have been investigated. Similarly, a number of disposal and utilization options are available. These process alternatives will be discussed in the following sections. Other options such as pretreatment of the sorbent to improve its attrition behavior or sulfur capacity and the addition of "getters" to remove alkali metals to prevent gas turbine corrosion are also being considered.

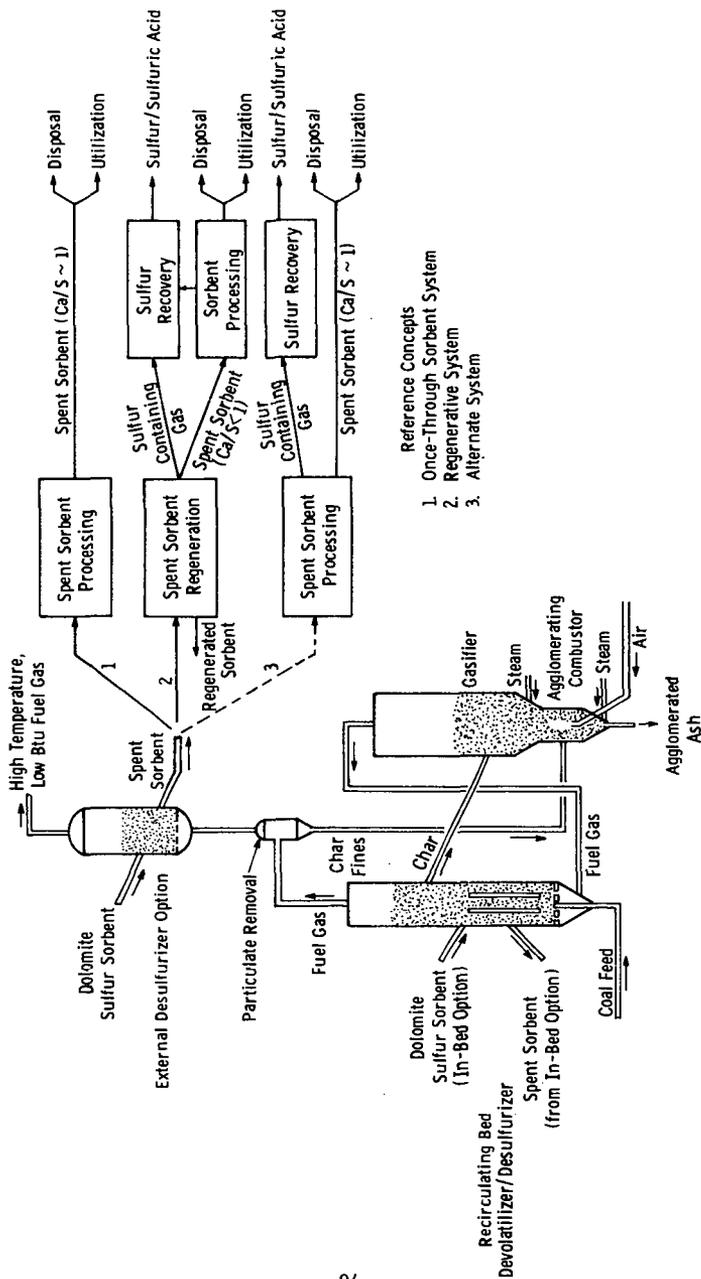


Fig. 1 —Westinghouse multistage fluidized bed gasification/desulfurization process utilizing calcium-based sulfur removal system

SULFUR REMOVAL

Laboratory and engineering studies are being carried out to evaluate two areas critical to sulfur removal: sulfur removal process options and sorbent selection. These efforts parallel development work planned for the process development unit related to these areas.

Process Options

The technical and environmental performance and economic aspects of sulfur removal process options are being evaluated in order to provide a basis for selection and to define process development requirements. Two major options have been identified: once-through sorbent operation versus regenerative sorbent operation and in situ (devolatilizer) desulfurization versus external desulfurization.

Both once-through sorbent and regenerative sorbent desulfurization behavior are being developed. The PDU is currently designed for once-through sorbent operation. Trade-offs between once-through and regenerative sulfur removal exist with factors such as sorbent consumption, sorbent attrition, trace element release, and system complexity and operability being important considerations.

Sorbent Selection

Both limestone (CaCO_3) and dolomite ($\text{MgCa}(\text{CO}_3)_2$) can be used as sulfur sorbents under full gasification conditions at high fuel temperatures, but laboratory studies show that there are several factors which restrict their use under specific design conditions, and which impact on both the desulfurization process, and the overall power generation plant.

Limestone reacts with hydrogen sulfide only when it has calcined, a kinetic rather than a thermodynamic restriction.⁽³⁾ For atmospheric pressure applications, calcined limestone should achieve 90% desulfurization of fuel gases at calcium to sulfur molar feed ratios of $\sim 1.8/1$.⁽⁴⁾ Recent fixed-bed tests by the Bureau of Mines confirm this projection.⁽⁵⁾ However for desulfurizing low Btu gas at pressure, calcium carbonate is the stable form of the reacting sorbent, and limestone is inactive.⁽⁶⁾

For dolomite, at Ca/S feed ratios of $< 1.2/1.0$, projections from laboratory data show that almost complete reaction of the calcium content may be attained while fixing 90% of the fuel sulfur in solid form, for particle sizes up to 2000 microns.⁽⁷⁾ For larger particle sizes reaction is apparently limited by diffusion of reactant into the solid. No significant variation was noted in testing dolomites ranging from the relatively pure massive-grained Canaan dolomite (Connecticut), through the sucrose-type dolomites (Glasshouse, Ohio), to the impure Tymochtee dolomite (Ohio).^(2c) Fluidized-bed tests by Conoco Coal Development Co.* have demonstrated the excellent sulfur capture abilities of dolomite with simulated fuel gases.⁽⁸⁾ The Bureau of Mines tests showed that half-calcined dolomite demonstrated improved sulfur removal at 1500°F over that noted at 1400°F.⁽⁵⁾ However when they increased the desulfurizing temperature to 1600°F, they noted a drastic loss of desulfurizing action as the dolomite decomposed to the fully-calcined state. While this test has not been simulated in laboratory tests, precalcined dolomites have shown similar sulfidation reaction rates to those noted with half-calcined dolomite. Further tests are evidently required to explore this discrepancy.

The major limitations on using dolomites arise from trace-element emissions, attrition rates, and suitability for processing by direct air oxidation for disposal.

One of the major concerns in operating a gas turbine with the low Btu gas is the extent to which corrosion and erosion will limit the lifetime of the metal alloys used in the blades and stators.^(2c) The alkali metals, particularly sodium, induce hot corrosion (accelerated oxidation or sulfidation attack of the metal) by depositing oxygen-excluding liquid films of sulfates on the metals. Dolomites contain sodium and potassium as impurities, and they are found both as clay mineral components, and as more volatile compounds - probably chlorides, in the carbonate rock. The range of these impurities in dolomites is enormous, e.g. Na (5-330 ppm), and K(5-6,500 ppm).^(2c) Recent studies

* Conoco Coal Development Co. and Consolidation Coal Co. are used in this paper. Consolidation Coal Co. is used when work was performed under that organizational name.

of the release of alkalis from dolomites into fuel gas have demonstrated that significant fractions of the alkali can enter the gas stream, and that this release is essentially complete within a short fraction of the expected sorbent residence times. (2c) The resulting alkali level in the turbine feed gas is substantially in excess of that permitted by current empirical specifications for oil-fired turbines (-10 ppb Na). There are several approaches which may be taken to avoid this problem. First of all, a low-alkali dolomite may be chosen as sulfur sorbent. This is likely to be the result of an unusually fortuitous selection of power plant site. Although the available analysis of dolomites show significant variations in alkali content within a particular geological stratum from quarry to quarry and from stratum to stratum within a quarry, the majority of the analyses are of sufficient vintage to be suspect. However we have noted a consistent increase in alkali content with increasing quarry depth, so that material quarried at a depth of 100 ft may contain one order of magnitude more alkali than that quarried near the surface. (9)

An alternative to selecting a "clean" dolomite, is to pre-heat the material to release the alkalis before using the stone as a sulfur sorbent. The bulk of the alkali release occurs within 20 minutes of heating the stone to ~870°C, and after this initial release the rate of alkali loss is extremely low. The third possibility is to add materials such as aluminosilicates to the sorbent bed, or at a particulate filtration stage to getter the alkalis. It should be emphasized that several critical questions cannot be satisfactorily answered without further research. The extent to which chlorine from the coal may strip alkalis from dolomite and coal char must be investigated. In addition the turbine tolerance to the combined presence of sodium and potassium requires further experimental and theoretical investigation. (2c) The chemical fate of minor elements such as the alkalis in coal gasification is not well known. Recent studies at the Bureau of Mines show considerable

release of chlorine to the gas phase - presumably as HCl. (2c) However the mass balance for alkalis in the input and output solids was not sufficiently precise to estimate the levels of alkali in the gas phase.

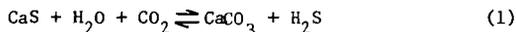
It should also be noted that the turbine tolerance to alkalis is theoretically a function of total chlorine (as HCl) levels in the gas phase. The combination of high chlorine and high alkali levels may avoid corrosive sulfate deposits. This apparent advantage will be limited by direct gaseous attack of the protective oxide scales on the turbine alloys.

SORBENT REGENERATION

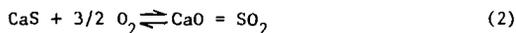
The consumption of sorbent by the power plant sulfur removal system may be minimized by utilizing a processing step to regenerate the utilized sorbent to an active form. Ideally the sorbent would be entirely reconstituted by the regeneration process, but in reality fresh sorbent will be required due to deactivation of the regenerated sorbent and attrition losses. Regeneration of the sulfided sorbent requires that the captured sulfur be converted to some other form, preferably elemental sulfur of commercial quality. The purge stream of spent sorbent must be processed to some environmentally acceptable or useful form. This combination of functions, sorbent regeneration-sulfur recovery-spent sorbent processing, must result in an integrated process which is compatible with the coal gasification process and is economically and environmentally acceptable.

Regeneration Process Options

A variety of potential regeneration process concepts have been evaluated for technical feasibility. Two concepts have been selected for further engineering assessment: (1) Sorbent regeneration by reaction of sulfided sorbent with steam and carbon dioxide to generate carbonated sorbent and a hydrogen sulfide gas stream; (2) sorbent regeneration by reaction of sulfided sorbent with oxygen to generate the oxide form of the sorbent and a sulfur dioxide gas stream. The chemical reactions are written, respectively.



and



Steam and CO₂ Regeneration Scheme

A schematic flow diagram for the sorbent regeneration system based on the steam and CO₂ regeneration reaction is shown in Figure 2. This process is also being evaluated by Consolidation Coal. (8)

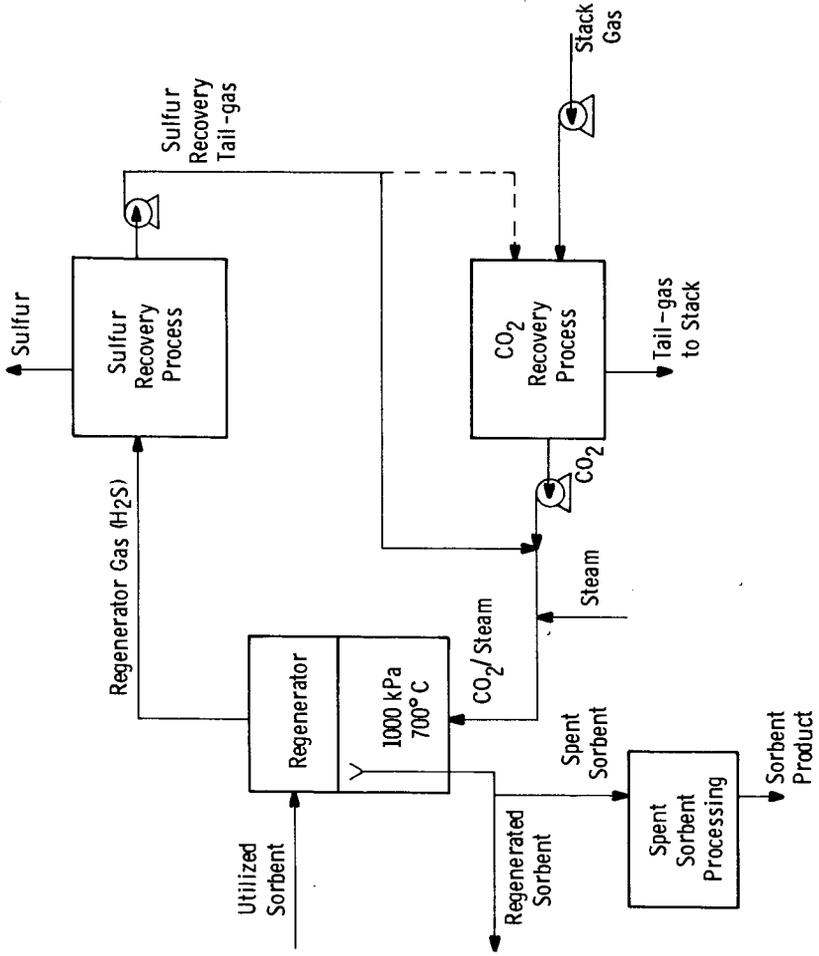


Fig. 2 — Sorbent regeneration by steam and CO₂ reaction

Three major components are involved in the sorbent regeneration system: the regenerator reaction vessel, the sulfur recovery process and the CO₂ recovery process. A number of commercial processes are available for sulfur recovery from H₂S gas streams. The specific process selection will depend largely on two factors - the level of H₂S in the regenerator gas and the optimum scheme for steam and CO₂ utilization. An H₂S volume percent of about 15% will permit the application of conventional Claus process technology. Lower H₂S concentrations will require either preliminary concentrating of the H₂S-gas, followed by Claus sulfur recovery, concentrating and recycle of the Claus plant tail-gas, or application of alternate sulfur recovery processes suitable for low H₂S concentrations such as the Stretford process (Ralph M. Parsons Co. and Union Oil Co. of California).

Make-up CO₂ for the regeneration reaction can be supplied by power plant stack gas purification. A portion of the sulfur recovery tail-gas may also require purification in order to maintain low levels of impurities (N₂, O₂, etc.) in the CO₂/steam reactant stream. Numerous commercial processes are available for CO₂ recovery - Selexol, Benfield, Catacarb, Sulfinol, and many others. The economics and environmental performance of each of these processes will differ for this application and require evaluation.

The single most important factor influencing the economics and performance of this regenerative scheme is the regenerator gas H₂S concentration. The size of the regenerator reaction vessel, the size and complexity of the sulfur recovery process, and the rate of steam consumption and auxiliary power usage all increase as the H₂S concentration is reduced. Estimates of the H₂S concentration based on reaction kinetics and thermodynamics are about 3-5 volume %.

Other factors such as regenerated sorbent activity, the required rate of sorbent circulation, the effect of the regeneration process on the power plant availability, etc., are also important to the process feasibility.

Oxygen Regeneration Scheme

A schematic flow diagram of the sorbent regeneration system based on the oxygen regeneration reaction is shown in Figure 3. An atmospheric pressure version of this process has been applied by Esso (U.K.) for their CAFB gasification process.⁽¹⁰⁾

This regeneration process is conceptually simpler than the steam/CO₂ regeneration process since only two major process components are involved: the regenerator reaction vessel and the sulfur recovery process. On the other hand, the oxygen regeneration process is necessarily a higher temperature regeneration scheme with the potential for greater sorbent deactivation. The regenerator could be operated at pressures of 200 to 1000 kPa (2 to 10 atmospheres) and temperatures of 1000 to 1100°C with SO₂ volume percents of 2 to 4 expected for the high pressure system and up to 10% for the low pressure system.

Sulfur recovery from dilute SO₂ streams is generally more expensive and complex than from dilute H₂S streams. The most highly commercialized sulfur recovery process for this application is the Allied Chemical direct reduction process (using methane or clean liquid fuels as reductant) which will work effectively on SO₂ streams down to about 4 volume % SO₂ depending upon the oxygen content of the gas.⁽¹¹⁾ For lower SO₂ concentrations a commercial concentrating step such as the Wellman-Lord process must be used. Other sulfur recovery processes applicable to SO₂ streams which are in early stages of commercialization are the Foster Wheeler RESOX process (which uses coal as the SO₂ reductant), the ASARCO-Phelps Dodge process, the Bureau of Mines Citrate process, the Westvaco activated carbon process, and the Stauffer Aquaclus process.

While the low pressure oxygen regeneration results in a much greater SO₂ concentration in the regenerator gas, the technological and reliability problems involved in circulating the hot sorbent between vessels with greatly different operating pressures may not be easily overcome. Again, as in the steam/CO₂ regeneration process,

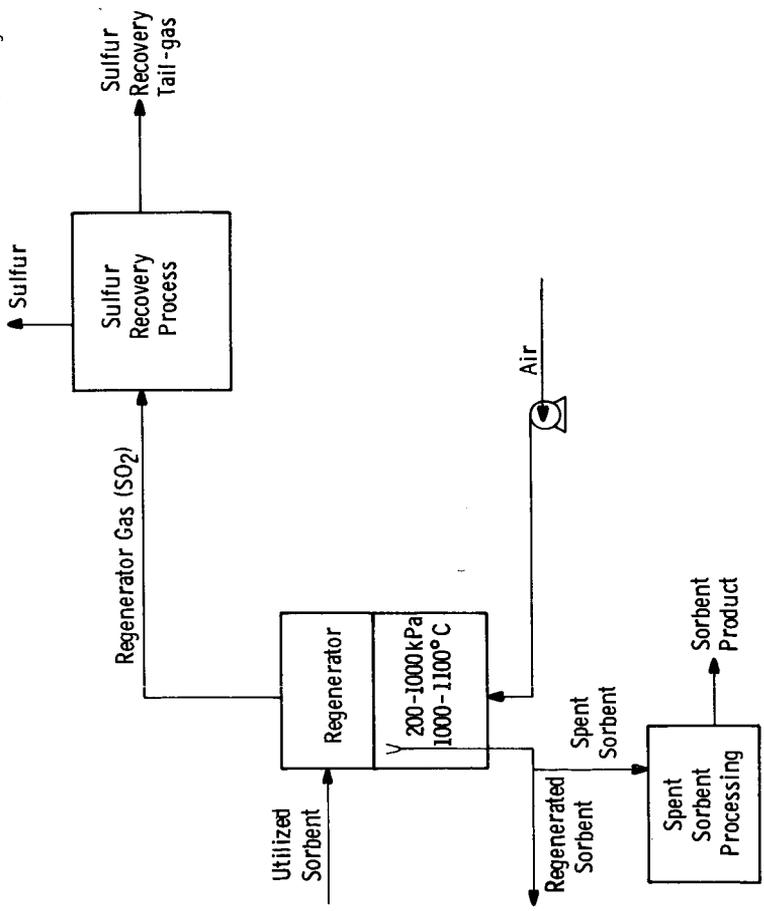


Fig. 3 - Sorbent regeneration by oxygen reaction

the concentration of the sulfur-bearing species in the regenerator gas has a dominant influence on the economics and performance of the regeneration system. Increased operating temperatures will provide greater SO_2 concentrations (thermodynamically) but may increase sorbent deactivation.

The overall economics, technical performance and environmental impact of these two sorbent regeneration concepts must be evaluated in order to determine the feasibility of sorbent regeneration, in order to select the most promising regeneration scheme and in order to identify the optimum components to be utilized in the regeneration scheme. The critical interfaces between the coal gasification system, the power generation system, the spent sorbent processing system and the sorbent regeneration system are being considered in the evaluation.

Regeneration Chemistry

It was noted by Mellor⁽¹²⁾ that the equilibrium $\text{CaS} + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{S}$ cannot be used to reform calcium carbonate, because of the low concentration of hydrogen sulfide produced. This problem may be overcome by carrying out the reaction at pressure.⁽¹³⁾ However the early work by Pell⁽¹⁴⁾ showed that calcium sulfide is rapidly deactivated, and TG studies show that only 20% of the calcium sulfide is readily converted to calcium carbonate after 10 cycles of sulfidation/regeneration, at 704°C.^(b)

An encouraging feature is that the rate of sulfidation decreases very slowly as the stone is recycled and the regenerated sorbent is almost as reactive as fresh stone.⁽⁶⁾

The initial rate of regeneration is very fast and is apparently limited by production of the equilibrium level of hydrogen sulfide, since the initial rate increases on dropping the temperature from 700°C to 650°C. However, when the regeneration has proceeded to a certain stage (50% after 2 cycles, or 20% after 10 cycles), the rate

falls off by more than one order of magnitude. At this stage the rate can be increased by increasing the reaction temperature, so that at 870°C, all the sulfide is readily regenerated. However, the equilibrium concentration of H_2S becomes so unfavorable that this is not a technically feasible solution.

The deactivation of calcium sulfide thus becomes a chemically limiting step in regeneration. An additional clue to the mechanism of deactivation is given by the fact that when calcium sulfide is prepared by reduction of calcium sulfate, at 820 or 850°C, for 2 hours, only 26% of the calcium sulfide is regenerable.⁽¹⁵⁾ This increased deactivation may be partly due to the longer residence time at higher temperatures than is customary in sulfidation reactions, since sulfidation takes about 15 minutes. Recent studies by Sun⁽¹⁶⁾ have shown that longer exposure at high temperatures (871°C) during sulfidation, reduces the extent of regeneration, as does increasing the temperature of sulfidation to 950°C, while lowering the sulfidation temperature to 750°C increases the extent of regeneration. The deactivation of the calcium sulfide is always accompanied by some growth of calcium sulfide particle size, and by extensive growth of magnesium oxide crystallites in proximity to the calcium sulfide as determined by X-ray diffraction line-widths.

It can be concluded that a continuous regeneration system must operate with a low sulfur differential between the calcium sulfide content of the desulfurizer and regenerator exit streams.

Squires⁽¹⁷⁾ has demonstrated that the extent of regeneration improves dramatically with partial pressures of steam of 15 atmospheres, and that 50% of the calcium sulfide is regenerable. While his sulfidation reaction conditions (700°C) may not have been severe enough to cause growth of the magnesium oxide around the calcium containing crystallites, the improved diffusivity of the reactant gases through the solid caused by raising the H_2O/CO_2 ratio may significantly improve the extent of regeneration before the reaction rate dwindles. Pell's

experiments carried out at a 1/1 ratio at 15 atm indicate little if any improvement over the TG value for extent of regeneration. The average extent of regeneration for 20 cycles is ~13%, so that each mole of calcium will remove 2.7 moles of sulfur via the regenerator, and one mole of sulfur via the spent sorbent stream.

The calcium to sulfur molar make-up feed rate required is therefore 0.25/1 unless attrition losses are greater than 5% of the total calcium per cycle, in which case reducing the attrition loss becomes more important than improving the regenerability of the stone. Consolidation Coal Co. (8) have reported attrition loss rates of less than 1% per cycle; however it is not known if such performance can be projected to large scale units.

SPENT SORBENT DISPOSITION

The once-through and regenerative process options will produce a dry, partially utilized dolomite or limestone with particles up to 6 mm in size. In addition, fine particles of sorbent (with some ash and char) will be collected in the gas particulate collection systems. The composition of the sorbent for disposition will depend on the characteristics of the original stone, the coal feed, the selection of the sorbent processing system, and the process operating conditions. The major compounds in the waste stone from the desulfurizer or regenerator utilizing dolomite are calcium carbonate (CaCO_3), magnesium oxide (MgO), and calcium sulfide (CaS). Trace elements from the sorbent and coal will also be present.

Direct disposal or utilization of this material is not considered to be an option which will be generally available. Thus, processing of the spent sorbent has been incorporated in the sulfur removal system. The ultimate selection and development of a spent sorbent processing scheme will depend on many factors related to the development of the desulfurization system and the regeneration system. These factors will determine the nature of the spent sorbent and the processing required for the spent sorbent processing system. Among the factors that will affect the disposition of the sorbent are the quantity of spent sorbent, its chemical characteristics, regulations, geographical location, and the market size in the case of utilization.

Processing

A variety of spent sorbent processing schemes have been identified which could potentially convert the spent sorbent produced in a once-through or regenerative operation into a material suitable

for direct disposal or utilization. (4,19) Processing alternatives have been developed to convert calcium-based sorbents containing calcium sulfide to environmentally acceptable forms for disposal or utilization. Work by Westinghouse on the CFB fluidized bed gasification/desulfurization process, under contract to EPA, has identified spent sorbent processing options. (4) Experimental programs are now being carried out as an extension of this work to permit technical and economic assessments of these processes. These tests will provide information directly applicable to the subject coal gasification/desulfurization process. Spent sorbent processing systems being considered include dry oxidation, oxidation plus carbonation, deadburning, slurry carbonation, dry sulfation, high temperature processing with coal ash, and low temperature processing with coal ash.

A dry oxidation process which converts the spent sorbent (calcium sulfide) from a once-through or regenerative operation into a calcium sulfate material has been selected as the base spent sorbent processing scheme. Experimental studies and process studies for the dry oxidation process are being performed as part of the current program.

Thermogravimetric studies of the direct oxidation of calcium sulfide to calcium sulfate have revealed some important features of the reaction which must be considered in process evaluation.

First, in most dolomitic stones, complete oxidation of the sulfided stone occurs rapidly in air at 800°C; while sulfided limestones containing more than 30 molar % CaS and the sulfides of large-grained dolomites are oxidized incompletely.

Secondly, the reaction is extremely exothermic, $\Delta H_{298} = -912 \text{ kJ mole}^{-1}$, and if the temperature of the reacting solid is permitted to rise to higher temperatures, sulfur dioxide will be

emitted by one of two mechanisms. In the first mechanism direct oxidation to the oxide may occur: $\text{CaS} + 3/2 \text{O}_2 \rightarrow \text{CaO} + \text{SO}_2$. However if low partial pressures of oxygen are developed in the system as a result of the primary reaction, then calcium sulfide and calcium sulfate interact to reject sulfur dioxide according to the reaction



By carrying out the oxidation reaction in a fluidized bed reactor at 800°C in excess air, both of these competing reactions may be avoided. In thermogravimetric tests at 800°C, sulfur dioxide transients in the exit gas stream were accompanied by temperature excesses. Typically 32 moles of cold air per mole of calcium are required for heat balance in a system operating at a 2/1 calcium to sulfur mole ratio in the desulfurizer. Because of the large excess of air entering the system, >3X stoichiometric, the particles should oxidize at much the same rate as they do in the TG apparatus; stone residence times greater than 30 minutes are projected to ensure that oxidation is almost complete (>90%).

The third feature of this reaction is that regenerated stone which has experienced multiple sulfidation/regeneration cycles is not completely oxidizable. A function of the calcium sulfide which is inert in the regeneration reaction is also inert in the oxidation reaction.

Based on the information available, the dry oxidation process is considered attractive for once-through operation with most dolomites. This process does not appear as attractive for once-through operation with limestones or for regenerative operation. The primary concern is the environmental impact from sorbent disposal. Further work is required to permit a comprehensive assessment of dry oxidation. Work is proceeding to investigate other processing options.

Disposal

The environmental impact of any disposed material is a function of its physical and chemical properties and the quantity involved. Two disposal alternatives will be investigated: land and ocean dumping. Environmental impact tests are planned to study the direct disposal of material from the spent sorbent processing system. These tests will be carried out using material produced in laboratory units to investigate the affect of operating conditions and in the process development unit to determine the environmental impact from material produced in the integrated process.

Westinghouse has carried out environmental impact tests on related materials as part of the CAFB fluidized bed gasification and the fluidized bed combustion programs being carried out under contract to EPA. (4,18;19,20) Leaching and activity tests have been developed at Westinghouse to assess the potential water contamination and heat release from disposing a spent bed limestone directly from a gasification process and from the spent limestone after further processing. These studies indicate the leachability and activity can be significantly reduced by further processing. Spent dolomite from fluidized bed combustion processes has also been tested⁽¹⁸⁾ which indicates that if the calcium sulfide in the dolomite can be converted to calcium sulfate through the dry oxidation process, the material will be environmentally acceptable.

Utilization

The direct disposal of sorbent may not be possible or permitted in all cases. Utilization of spent sorbent is an alternative which has the potential to provide technically and economically attractive by-product. Potential applications of processed or unprocessed spent sorbent include soil stabilization, land fill, concrete, refractory brick, gypsum, municipal waste treatment. Preliminary work has been carried out in this area. (4,20,21)

ASSESSMENT

High temperature sulfur removal with a fluidized bed coal gasification system appears attractive based on available information. A number of processing options are being developed which consider integration of the sulfur removal system with a low Btu gasification - combined cycle power plant and consider the total sulfur removal system from sorbent selection to sorbent disposition. Assessment of the sulfur removal system includes:

Sulfur Removal: Dolomites are the preferred sorbent for the Westinghouse coal gasification process. Sulfur removal efficiencies of 90% are projected with mean particle sizes between 1000 and 2000 μ and a calcium to sulfur molar ratio of 1.2/1.0 for a once-through system. Combined devolatilization/desulfurization is considered attractive but compatibility must be demonstrated. The external desulfurizer option offers an alternative with greater flexibility. There appear to be ample supplies of dolomite available.

Sorbent Regeneration: Two regeneration concepts have been selected for further study. Regeneration by carbon dioxide and steam is technically feasible and is the preferred option. Calcium to sulfur molar feed make-up is projected to be 0.25/1 based on attrition losses < 5% of the sorbent per cycle. Commercial technology is available for sulfur recovery from dilute H_2S or SO_2 gas streams and for CO_2 recovery. Advanced systems, which may reduce costs, are not being incorporated into the current development effort.

Spent Sorbent Disposition: In general, spent sorbent processing will be required for once-through or regenerative operation due to the calcium sulfide present in the sorbent. Alternate processing schemes are under investigation to permit disposal or utilization of the material.

A dry oxidation process is attractive for once-through operation with most dolomites. Preliminary oxidation tests and environmental impact tests indicate this processing option will be economic and environmentally acceptable. Preliminary tests on related materials indicates utilization of the spent sorbent may be practical.

Sorbent Selection: General factors to be considered in the selection of a sorbent are the desulfurization performance, the sorbent regenerability, the spent sorbent properties, sorbent attrition behavior and trace metals release behavior. Sodium, potassium, and chlorine release is of particular importance to control gas turbine corrosion. Trace metals release to the fuel gas may be controlled by selecting a "pure" sorbent, pretreating the sorbent or utilizing a getter in the fuel gas cleaning system. Available data indicate the trace elements can be controlled to meet turbine protection requirements. Further work is required to specify the preferred method of operation.

A once-through sulfur removal system utilizing dolomite with a dry oxidation spent sorbent processing system has been selected for the reference design. Further development evaluation of the technical performance, economics, and environmental impact of the alternative sulfur removal systems under consideration must be carried out to select the most promising system. The integration of the alternative processing schemes into an optimum high temperature sulfur removal system which is compatible with the coal gasification power plant is the object of the development effort.

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