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A REGENERABLE SORBENT INJECTION/FILTRATION PROCESS FOR H₂S REMOVAL FROM HOT GAS

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ABSTRACT

The operational characteristics of a hot gas desulfurization process involving regenerable sorbent injection and its subsequent collection with a ceramic filtration device were studied utilizing a bench-scale transport reactor. Hydrogen sulfide removal from simulated hot gas was evaluated as a function of both zinc oxide-based sorbent physical and chemical characteristics and various process parameters. In addition, the sorbent capture efficiency and regenerability of the ceramic filtration device were evaluated, and regeneration of sulfided sorbents via injection into an oxidizing gas was studied. For both sorbent sulfidation and spent sorbent regeneration, gas-solid reaction occurred both in the duct and within layers of partially reacted sorbent captured by the ceramic filter. Very high sulfur removal efficiencies were obtained only in highly reducing hot gas compositions at or above about 700°C, using stoichiometric ratio (defined as ZnO/H₂S ratio) values of about 1.5, and sorbent particles of about 20 μm or less in diameter. Under such conditions, the experimental data indicated that reaction of H₂S with zinc vapor formed by reduction of zinc oxide contributed appreciably to sulfur removal. Negligible zinc loss from the hot zone of the reactor was detected, apparently due to rapid formation of zinc sulfide product layers on zinc oxide particles. The ceramic filtration devices captured 100% of all sorbent particles and were fully regenerable over periods of several tens of injection/backpulse cleaning cycles. Spent sorbent could be fully regenerated rapidly at 850°C without problems due to exotherm generation.

INTRODUCTION

Development of reliable hot gas desulfurization processes, required for ultimate commercialization of advanced coal-fired power generation systems, has been a very active area of investigation for nearly two decades. A number of specific desulfurization schemes that use regenerable mixed metal oxide sorbents (generally zinc-based) have progressed to the demonstration stage at a fairly large scale. However, these schemes employ "conventional" gas-solid reactor configurations (e.g., fixed bed, moving bed, or fluidized bed) that have in common long-term reliability concerns associated with sorbent stability. In particular, zinc loss from sorbents due to reduction and subsequent vaporization, mechanical attrition leading to unacceptably high flow resistance in sorbent beds, and sintering/sulfate

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formation during spent sorbent regeneration are issues that have not been thoroughly resolved for conventional hot gas desulfurization processes. Most efforts to improve this situation have centered on tailoring the properties of the sorbent materials.

An alternative approach to mitigate the long-term reliability concerns associated with current hot gas desulfurization schemes involves adoption of novel gas-solid reactor schemes that can more easily accommodate the intrinsic deficiencies of the regenerable sorbent materials. One such process is the combined sorbent injection/filtration scheme shown conceptually in Figure 1. This desulfurization process involves the sequential steps of: (i) injection of finely divided sorbent into the hot gas; (ii) sorbent reaction with H_2S and collection in a ceramic filtration device, (iii) backpulsing of the ceramic filter to recover spent sorbent; (iv) injection of spent sorbent into an oxidizing gas followed by a second filtration step to regenerate the sorbent; and (v) backpulse recovery and subsequent transport of the regenerated sorbent to the start of the process cycle.

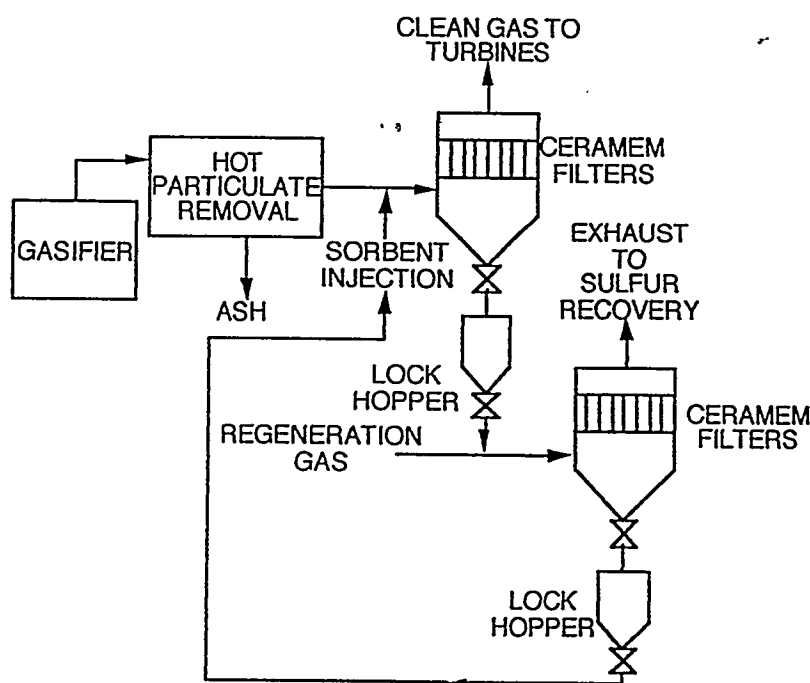


Figure 1. Conceptual Schematic of the Sorbent Injection/Filtration Process

Previously presented research related to this process has included: (a) initial feasibility experiments that demonstrated nearly 100% H_2S removal for practical stoichiometric Zn/S ratios and 100% sorbent capture efficiency for the ceramic filters [1]; and (b) study of the sulfidation reaction kinetics of the process using a laminar flow "quenching" reactor. [2] This paper summarizes the results of broader studies of the operational characteristics of the entire process using a bench-scale transport reactor. A full account of this experimental program

has recently been provided in a final project report to DOE. [3]

EXPERIMENTAL DETAILS

Bench-Scale Transport Reactor

A flow schematic of the bench-scale transport reactor is shown in Figure 2. This reactor was used for both H_2S removal and spent sorbent regeneration tests. Simulated hot gas of varying compositions (for sulfidation tests) or nitrogen-diluted air (for regeneration tests) was fed into a 36 in. long, 1.5 in. diameter quartz tube enclosed within a three-zone high-temperature furnace, sealed with water-cooled end caps. The furnace was calibrated to maintain a 24 in. long nearly isothermal ($\pm 20^\circ C$) reaction zone. A 1.5 in. diameter, 6 in. long CeraMem gas particulate filter [4] was placed at the outlet end of the isothermal zone, and held in place using a compressed wrapping of fibrous ceramic mat material. Fine particulate sorbents were introduced into the hot zone of the reactor through a 0.25 in.

diameter quartz tube that was concentric with the larger tube; the position of this "sorbent feed tube" could be adjusted within the reactor to vary the residence time of sorbent in the free-flowing hot gas. The feed rate of sorbent into the reactor was controlled using a precisely regulated and calibrated particle feeder: either a rotary-brush dispersion feeder (Model P-RBG-1000, Amherst Process Systems, Hadley, MA) or one utilized and described previously [1,2] were used in these tests. (Contrary to the depiction in Figure 2, most of the testing was performed with the reactor in a "down-flow" direction, i.e., with the reactor inlet at top, to prevent larger sorbent particles from falling backwards out of the reaction zone.) The reactor also was equipped with hardware to allow off-line hot backpulse cleaning immediately after sorbent sulfidation or regeneration tests to remove captured sorbent from the ceramic filter. A GC equipped with a flame photometric detector was utilized to measure inlet and outlet H₂S or SO₂ concentrations.

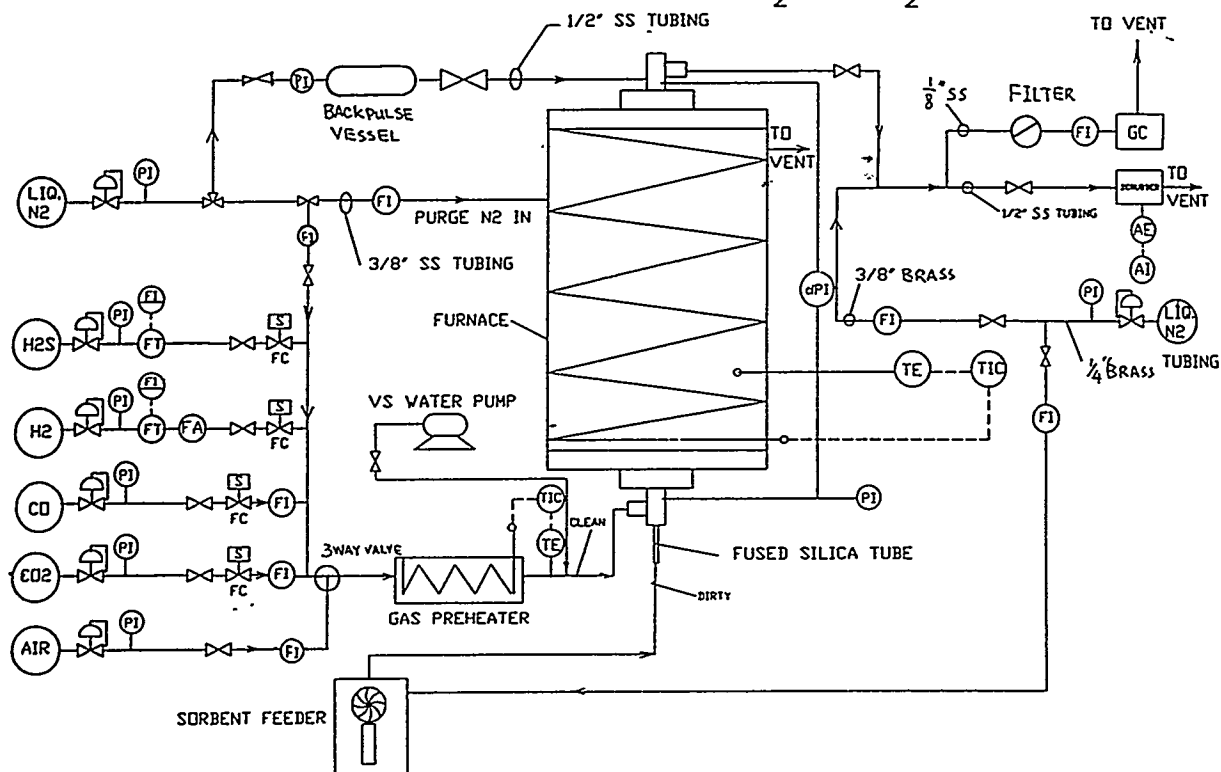


Figure 2. Flow Schematic of the Bench-Scale Transport Reactor

Sorbent Materials

Table 1 lists the three zinc-based sorbent materials studied in these tests.

TABLE 1. Physical and Chemical Properties of Zinc-Based Sorbents

	J. Matthey ZnO	RTI ZT-4	U.C. L-3140
ZnO/TiO ₂ Molar Ratio	---	1.5	2.0
Particle Size Range	2 to 5 μm	35 to 75 μm	3 to 100 μm^*
BET Surface Area	2.9 m ² /g	3.5 m ² /g	3.6 m ² /g
Particle Structure	Individual particles/small aggregates	Hard, porous aggregates	Hard, porous aggregates

* Size-classified into several narrow-sized lots

These included a commercial fine zinc oxide powder from Johnson Matthey, type ZT-4 zinc titanate sorbent prepared by Research Triangle Institute for fluidized bed desulfurization applications [5], and type L-3140 zinc titanate sorbent obtained from United Catalysts, Inc. Table 1 lists some important physical and chemical characteristics of these materials. The L-3140 sorbent was size-classified into a number of narrow particle size fractions to allow evaluation of particle size effects in the reactor.

RESULTS

Hydrogen Sulfide Removal Studies

Results shown below are for a highly reducing synthetic hot gas of composition: 14.8% H₂, 15.5% CO, 7.0% CO₂, 0.4% H₂S, < 0.1% H₂O, balance N₂. Experiments performed with less reducing hot gas compositions resulted in very long injection periods required to reach high steady-state levels (e.g. > 95%) of H₂S removal. This general result that H₂S removal rates were enhanced as the reduction power of the hot gas increased was consistent with a primary reaction mechanism consisting of rapid zinc oxide reduction, followed by zinc vaporization and subsequent sulfidation in the gas phase, as demonstrated in previously presented studies.[1,2]

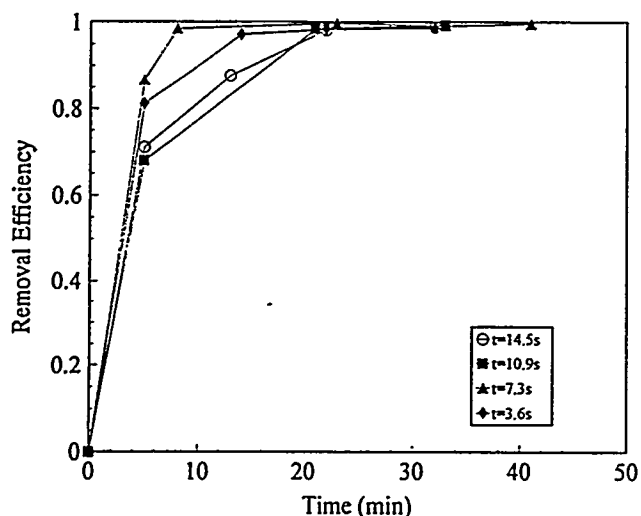


Figure 3. Effect of Residence Time in Flow Zone on H₂S Removal Efficiency

Figure 3 shows the H₂S removal efficiency attained as a function of sorbent injection time for various residence times of ZnO sorbent in the reaction zone between the sorbent injection point and the front face of the ceramic filter. (This data was acquired for Zn/S = 1.5, T = 750°C, and bulk hot gas flow velocity = 4.2 cm/sec. The sorbent injection position was varied to change residence time.) Two facts, (i) the lack of any significant functionality between this residence time and the rate of increase of removal efficiency, and (ii) the result that at least seven minutes of injection is required to attain high removal of H₂S, are

strong evidence that most of the removal occurred due to reaction with partially sulfided sorbent captured on the ceramic filter surfaces. This result is consistent with previous studies that examined the reaction rate of zinc-based particle sulfidation by H₂S [2,6]. Similar trends were obtained when residence time was changed by varying the total gas flowrate while keeping the sorbent injection point in a fixed position in the reaction zone. In addition, when the ceramic filter was moved out of the reactor's hot zone, sulfur removal efficiencies were dramatically reduced due to quenching of the sulfidation reaction.[3]

At otherwise identical process conditions, the rate of H₂S removal was most dependent on a particular sorbent material's particle size, but apparently was not strongly sensitive to other sorbent physical or chemical characteristics. Figure 4 shows the H₂S removal efficiency attained as a function of sorbent injection time for various narrow-size distribution, size-classified lots of the L-3140 sorbent. Removal efficiencies were effectively identical for sorbents with particle sizes of about 20 μm or less (including the Johnson-Matthey ZnO sorbent), and decreased

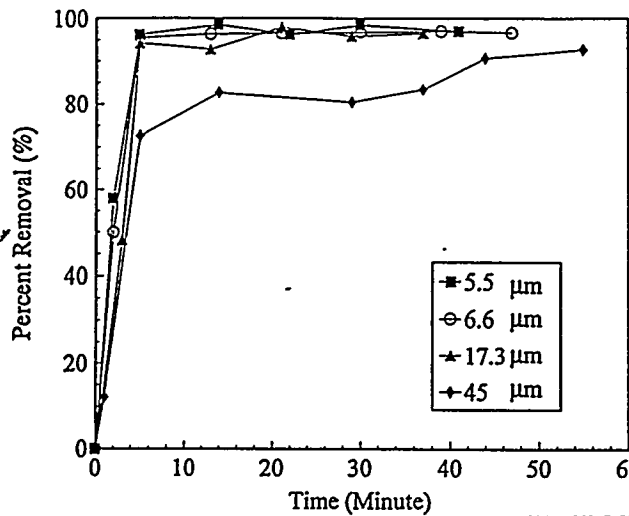


Figure 4. Effect of Sorbent Average Particle Size on H₂S Removal Efficiency (750°C, L-3140 sorbent, 5 cm/sec, Zn/S = 1.5)

removal efficiencies, presumably due to formation of solid sulfide layers around unreacted oxide particle cores, resulting in diffusional limitations to further reaction.

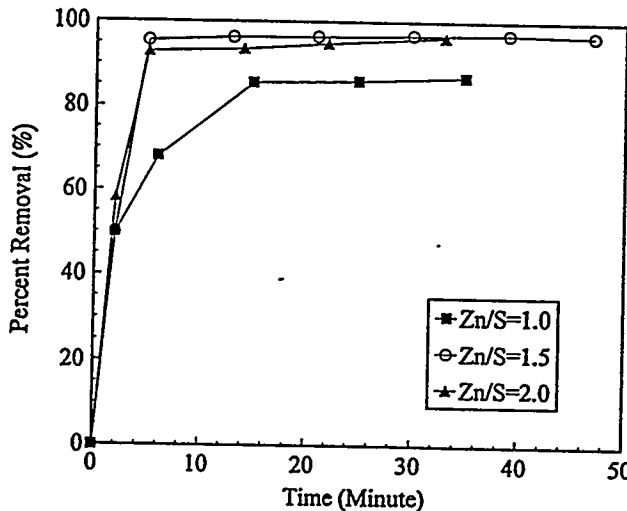


Figure 5. Effect of Zn/S Stoichiometric Ratio on H₂S Removal Efficiency (750°C, 5 cm/s)

Of note also is the fact that negligible enhancement in the time necessary to achieve high steady-state H₂S removal was achieved by raising the reactor temperature to 850°C. This result is also suggestive of diffusional limitations through solid reaction products, but may also be dependent on other kinetic factors.

The apparent requirement for relatively high reactor temperatures to achieve practical sulfidation rates in this reaction scheme runs counter to the current desire to reduce desulfurization reactor temperatures prompted by concerns over the cost and durability of components required to construct large-scale desulfurization reactors. For the sorbent injection/filtration process to be viable for such large-scale use given this constraint, it would be necessary to employ other sorbent materials that have appreciably faster reaction kinetics at lower temperatures (e.g., 600°C or lower). Study of such materials was not within the scope of this project, however.

for larger average particle sizes (including the ZT-4 sorbent). Calculated surface reaction rates for the different sorbents indicated that reactivity of the zinc titanate sorbents was roughly equivalent to that of ZnO, as expected from previous studies.[2,6]

Figure 5 shows the H₂S-removal efficiency attained as a function of sorbent injection time for the 6.6 μm average particle size fraction of the L-3140 sorbent as a function of the stoichiometric ratio, defined as Zn/S derived from the molar flow rates of H₂S and ZnO into the reactor. This data shows that excess sorbent must be injected to reach high sulfur

Somewhat surprisingly, for very high stoichiometric ratios, observed sulfur removal trends were no better than for moderately high values of this parameter.

The effect of temperature on H₂S removal trends is shown in Figure 16 for the 6.6 μm average particle size fraction of the L-3140 sorbent, in test runs at Zn/S = 1.5 and bulk flow velocities of about 5 cm/s.

These data show very clearly that the sulfidation reaction is highly thermally activated; apparently, reaction temperatures of at least 700°C are required to attain high sulfur removal rates after reasonably short injection periods.

Sulfided Sorbent Regeneration Studies

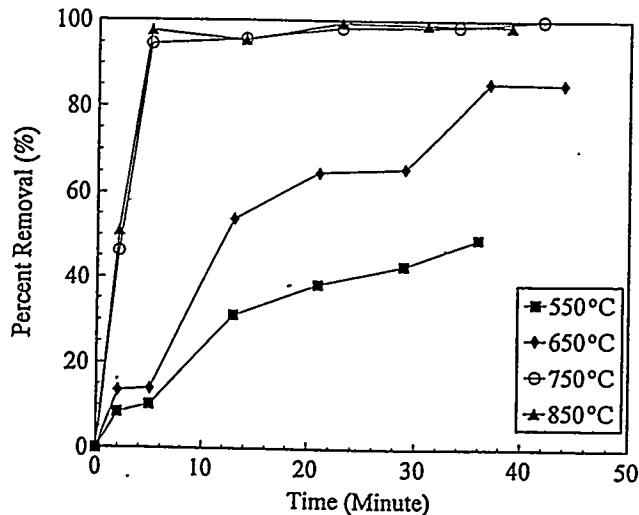


Figure 6. Effect of Reaction Temperature on H_2S Removal Efficiency ($Zn/S = 1.5$, 5 cm/s)

Regeneration of sulfided zinc oxide sorbent was evaluated as a function of temperature, residence time, oxygen concentration in the regeneration gas, and Zn/O_2 ratio. Figure 7 shows the efficiency of ZnS conversion to ZnO as a function of injection time and regeneration temperature, using gas containing 3% oxygen. As expected, increasing reaction temperature resulted in increasingly rapid regeneration. Over 96% conversion could be obtained at 850°C within two minutes when using gas containing 5% O_2 . Furthermore, this was achieved without generation of an appreciable exotherm typically encountered when beds of sorbent are regenerated in this fashion.

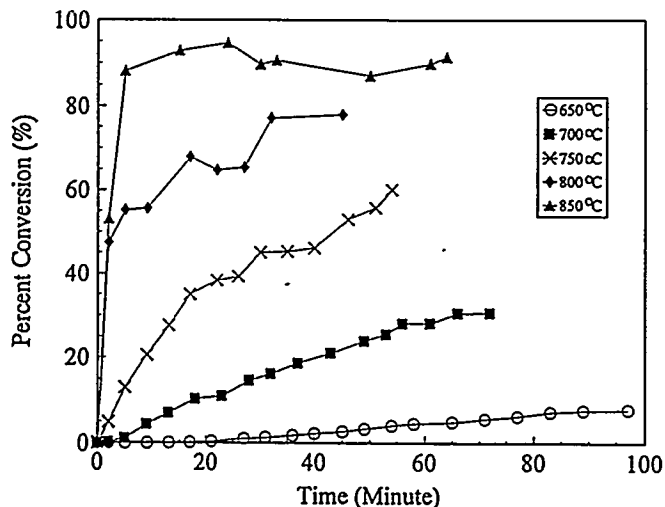


Figure 7. Regeneration of Sulfided ZnO as a Function of Time and Temp. in 3% O_2

Removal of the ceramic filter after more than twenty sulfidation experiments in highly reducing gas, followed by examination and extraction of the quartz tube area located on the outlet side of the filter showed only very small amounts of zinc deposition (presumably from metallic zinc vapor that passed through the filter and subsequently condensed).

Ceramic Filter Performance

Off-line backpulsing of the ceramic filter after every sulfidation or regeneration experiment resulted in complete removal of captured particles and full recovery of filter baseline flow resistance, as long as backpulsing was conducted at 300°C or higher. Use of colder backpulse gas resulted in incomplete filter cleaning. Modified EPA Method 5 particulate testing confirmed that no detectable particulates passed through the ceramic filter.

REFERENCES

1. D.L. Roberts and R.A. Abrams, in D.L. Bonk (ed.), Proc. of the Coal-Fired Power Systems '93 Mtg., Rpt. No. DOE/METC-93/6131, 1993, pp. 245-254.
2. K. Ishikawa et al., Sulfidation and Reduction of Zinc Titanate and Zinc Oxide Sorbents for Injection in Gasifier Exit Ducts, in Proc. of the 12th Annual Pittsburgh Coal Conference, PETC, 1995.
3. R.J. Higgins, W. Ji, and R.L. Goldsmith, Report No. DOE/ER/81364-7, 1996.
4. D.L. Roberts et. al., pp. 539-540 in Ref. 1.
5. S.K. Gangwal and R.P. Gupta, pp. 146-157 in Ref. 1.
6. S. Lew, A.F. Sarofim, and M. Flyttzani-Stephanopoulos, Ind. Eng. Chem. Res., 31 (8), 1992, p. 1890.