Manganese-Based Sorbents for Coal Gas Desulfurization

Lee D. Gasper-Galvin (LGASPE@METC.DOE.GOV; 304-285-4832)
Edward P. Fisher (EFISHE@METC.DOE.GOV; 304-285-4011)
Morgantown Energy Technology Center

William J. Goyette (410-789-8800, x167)
Chemetals

Introduction

Manganese-based sorbents have previously been investigated for sulfur removal from coal gases at high temperatures, e.g., 800 °C (1,472 °F) and above, and with simulated low-Btu fuel gas or mixtures of H_2S and H_2 in N_2 (Turkdogan and Olsson, 1978; Hepworth and Slimane, 1994). The special emphasis on higher temperatures was because manganese oxide is one of the few metal oxides that have stability and coal gas desulfurization potential at such temperatures.

Some studies have been performed at lower temperatures, e.g., 400 to 800 °C (752 to 1,472 °F) (Wakker and Gerritsen, 1990a, 1990b); these researchers showed that increasing H_2 and CO increases the sulfur capacity of a sorbent containing Mn oxide and alumina, while increasing H_2O decreases the sulfur capacity. Thermodynamic studies (Westmoreland, et al. 1976) suggest that Mn-based sorbents may perform much better in the range of 400 to 800 °C (752 to 1,472 °F) than at higher temperatures. Hepworth and Slimane (1994) also showed a graph of calculated equilibrium levels of H_2S in the presence of temperatures from 700 to 1,200 °C (1,292 to 2,192 °F) for different types of coal gas. The graph indicated that the lowest equilibrium H_2S levels were obtained in the presence of oxygen-blown Shell gas at the lowest temperatures. Thermogravimetric analysis studies by Westmoreland, et al. (1977) showed that among sorbents consisting of the oxides of Mn, V, Ca, and Zn, the Mn oxide showed the highest reaction rate over the temperature range 300 to 800 °C (572 to 1,472 °F).

Since overall sorbent performance is a combination of the effects of thermodynamics, kinetics, and gas-solid mass transfer resistance, it seems reasonable from the information cited above that an Mn-based sorbent would perform very well in a highly reducing Shell gas at lower temperatures. The present study shows the effect of temperature, inlet H_2S concentration, and type of coal gas (air-blown KRW gas versus oxygen-blown Shell gas) on the performance of Mn-based sorbent. The sorbent used for these studies was CST-939 from Chemetals (Baltimore, Maryland). The CST-939 is a proprietary sorbent containing essentially 96 percent MnO, and has previously been marketed as guard bed material for use downstream from hydrodesulfurization units and upstream from reformers in petrochemical refining.

Objectives

The intent of this study is to perform a preliminary screening on a particular Mn-based sorbent, CST-939 (from Chemetals), for hot gas desulfurization. The purpose of the preliminary screening is to determine which temperature and type of coal gas this sorbent demonstrates the greatest capacity and efficiency for sulfur removal.

Approach

The first two sets of experiments, tests CST1 and CST2, were conducted with simulated KRW gas containing 2,000 ppmv H_2S and 871 and 343 °C (1,600 and 650 °F), respectively. Due to the tremendous capacity of the sorbent, these experiments required as long as 75 hours to achieve breakthrough (breakthrough is defined as 200 ppmv H_2S in the outlet gas). Therefore, the later experiments were conducted with simulated KRW gas (or Shell gas) containing 30,000 ppmv H_2S to decrease the time required for breakthrough. A set of six experiments, three with KRW gas and three with Shall gas, were conducted for 1.5 cycles each at temperatures of 343, 538, and 871 °C (650, 1,000, and 1,600 °F). A fresh sample of the sorbent was used for each set of experiments.

During one of the early experiments (test CST2) using 2,000 ppmv H_2S, the regeneration temperature was ramped from 343 °C (650 °F) to 871 °C (1,600 °F) to determine the lowest temperature that may be sufficient for regeneration with 50 mol percent air/50 mol percent steam. The extent of regeneration was indicated by the amount of SO_2 given off at each temperature. Sulfur dioxide as high as 3.0 volume percent was given off after 1/2 hour on-stream at 343 °C (650 °F), as shown by gas chromatographic analysis, but the concentration then dropped off rapidly and regeneration was not sustained at this temperature. A relatively small amount of SO_2 was released at 538 °C (1,000 °F). The rate of regeneration finally increased at 649 °C (1,200 °F), at which temperature concentrations as high as 23.8 percent by volume SO_2 were measured. The additional SO_2 that was released at 760 °C (1,400 °F) was minimal. Finally, when the sorbent bed was raised to a temperature of 871 °C (1,600 °F), significant quantities of SO_2 were released, giving a concentration as high as 2.2 percent by volume. Since $MnSO_4$ decomposes in air at an atmospheric pressure of 850 °C (1,562 °F), it is not surprising that additional sulfur was released after heating the sorbent to 871 °C (1,600 °F). It was concluded that 871 °C (1,600 °F) would be the best temperature for air-steam regeneration of the sorbent.

During the second sulfidation of the CST2 series of experiments described above, it was noted that a significant amount of SO_2 was released during the first hour on-stream. This indicated that regeneration was not complete, even after using the air-steam mixture at 871 °C (1,600 °F). Another set of experiments (CST3) was conducted in which the first regeneration was conducted with air-steam at 871 °C (1,600 °F) and the second regeneration was performed in the same manner, except the oxidative regeneration step was followed by a reductive regeneration step. Reductive regeneration was carried out with simulated KRW gas without H_2S for 11 hours. The result of the reductive regeneration was that no SO_2 was detected during the first 2-1/2 hours on-stream and no higher than 3.0 ppmv was detected afterward.

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Thus, it could be seen that a reductive regeneration step was helpful. For the remaining experiments, a simplified reductive regeneration was used, as described in the Experimental Methods section.

Experimental Methods

A schematic diagram of the experimental apparatus is shown in Figure 1. The apparatus consisted of a gas-mixing system, a fixed-bed reactor, a water-cooled condenser with a water knock-out pot, an ice water-cooled condenser with a water knock-out pot, a gas sampling system, and a tail-gas cleanup system. The gas mixture feed to the reactor simulated the partially quenched exit gas of an air-blown KRW fluidized-bed coal gasifier or an oxygen-blown Shell entrained-bed coal gasifier, with the molar compositions given in Table 1. Gases were supplied from gas cylinders and the flow rates were controlled and monitored through MKS Model 1159B mass flow controllers with two MKS Model 247C four-channel digital readouts, except for the nitrogen purge gas, which was metered through a Matheson Model FM-1050-VIA, 603 tube rotameter. After the gases were mixed in a manifold, they were fed into the fixed-bed reactor. Steam was introduced by feeding a predetermined amount of water into the gas stream via an ISCO Model 100D metering pump.

One-Inch Sorbent Screening Unit
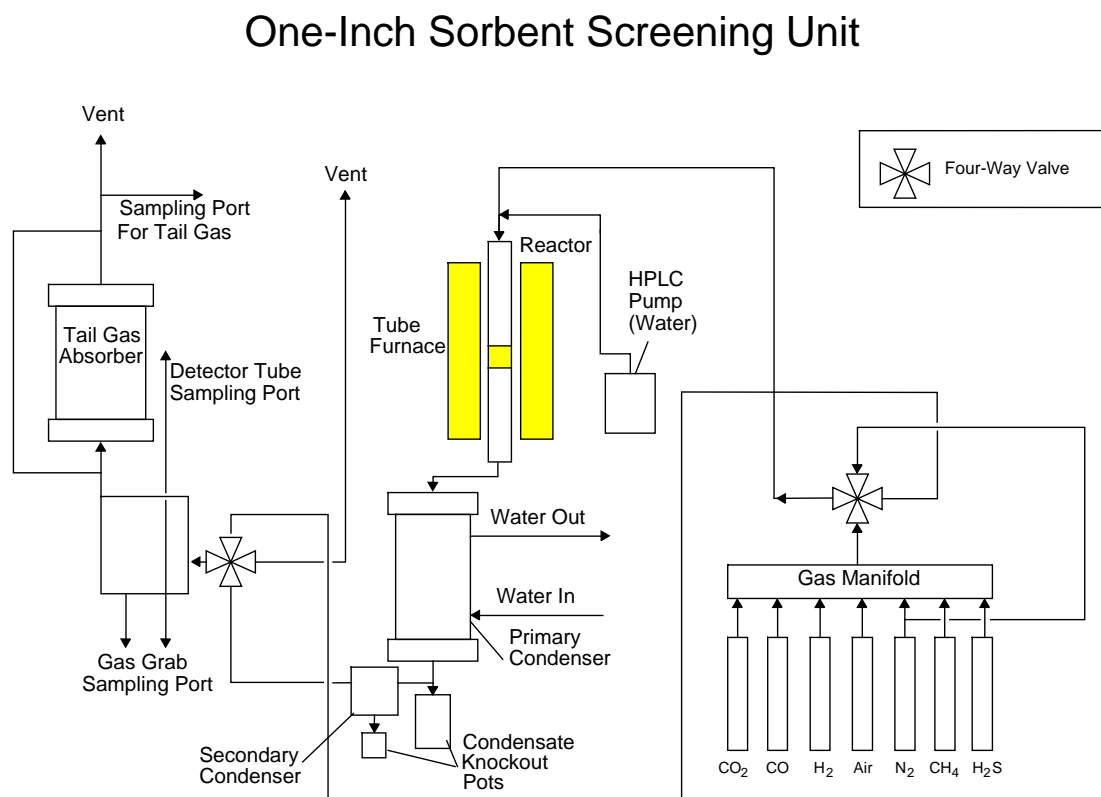
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Figure 1

Table 1. Simulated Gas Composition

Shell Gas	Percent	KRW Gas	Percent
Carbon Dioxide	2.0	Carbon Dioxide	11.0
Carbon Monoxide	64.1	Carbon Monoxide	12.5
Hydrogen Sulfide	3.0	Hydrogen Sulfide	3.0
Methane	0.0	Methane	1.0
Hydrogen	27.3	Hydrogen	13.8
Steam	2.0	Steam	19.0
Nitrogen	Balance	Nitrogen	Balance

The reactor consisted of an alonized 316-stainless steel (SS) tube, with a 2.54-cm (1-inch) outside diameter (OD), a 0.165-cm (0.065-inch) wall thickness, and 114.3-cm (45-inch) length. Alonization of the reactor was necessary to minimize the corrosion of the stainless steel by H_2S, particularly in the presence of high-temperature steam. The reactor was placed vertically in a Lindberg tubular electric furnace.

The gas mixture was preheated as it passed through the top half of the reactor tube. The temperatures of the gas at the inlet and the center of the reactor bed were measured by Omega K-type quick-connect thermocouples located along the central axis. The thermocouples were connected to an Omega Model 199A digital readout via an Omega Model OSW3-20-PG rotary selector switch. The reactor inlet and outlet pressures were measured with Matheson Model 63-5651 308 kPa (30 psig) test gauges. The reactor was designed to withstand a pressure of 308 kPa (30 psig) and a temperature of 982 °C (1,800 °F). The over-temperature circuit on the tube furnace was set for 927 °C (1,700 °F).

The sorbent sample was placed in the center of the reactor and the bed height was 7.6 cm (3 inches). The sorbent bed was supported on an alonized, 316 SS perforated plate with a layer of glass wool to catch any fines that might be produced from the bed. The gas lines between the reactor outlet and the condenser inlet were heated via Thermolyne heavy Samox-insulated heating tapes regulated with Omega 6200 temperature controllers and were insulated with a Fiberfax blanket to prevent steam condensation in the gas lines. The exit gas from the reactor was filtered with a Balston Model B49 filter unit containing a Balston Model 050-11-BQ filter tube, cooled in two condensers (a primary condenser that was water-cooled, followed by a secondary condenser that was ice water-cooled), and sampled for gas analysis. The tail gas was sent through an absorber (316 SS, 8.9-cm [3.5-inch] OD, schedule 40 pipe, 41.9 cm [16.5 inches] long) containing a zinc-based sorbent to remove the sulfurous gases before discharge to the atmosphere. The condensates from the two condensers were caught in their respective water knock-out pots located below the condensers. The water knock-out pots consisted of 1.3-cm (0.5-inch) OD, 0.089-cm (0.035-inch) wall, 25.4-cm (10-inch) long 316 SS tubes.

The conditions for oxidative regeneration and reductive regeneration are shown in Table 2. The test matrix, with actual run numbers, sulfidation conditions, and the number of sulfidation/regeneration cycles, is given in Table 3. Gastec precision gas detector tubes were used to determine the H_2S and SO_2 concentrations in the inlet and outlet gas streams to plus or minus 25 percent. All gaseous components (other than water vapor) were analyzed by gas chromatography of gas grab samples and/or via an on-line VG Prima 600 mass spectrometer. Sulfidation was stopped when the hydrogen sulfide concentration of the effluent gas reached 1,000 ppmv for sulfidations run with KRW gas and 400 ppmv for sulfidations run with Shell gas. Following sulfidation, the reactor was purged with nitrogen to flush out the reducing gas. The oxidative regeneration with air-steam was stopped when the SO_2 concentration of the effluent gas was below 50 ppmv. Reductive regeneration was conducted for 4 hours unless the combination of ppmv H_2S plus ppmv SO_2 dropped below 50 ppmv prior to 4 hours on-stream, at which time the regeneration was stopped. A fresh load of sorbent was subjected to each set of sulfidation/regeneration conditions to establish its sulfur sorption capacity and efficiency. Some experiments were repeated to verify the results, particularly for cases in which any operating difficulties were encountered.

Table 2. Regeneration Conditions

Oxidative		Reductive	
Temperature	1,600 °F	Temperature	1,600 °F
Pressure	15 psig	Pressure	15 psig
Composition:		Composition:	
Air	50%	Hydrogen	25%
Steam	50%	Nitrogen	75%

Table 3. Sorbent Test Matrix

Test Number	Coal Gas/H_2S Concentration	Temperature/Cycles
CST1	KRW/0.2%	871 °C/1.5
CST2	KRW/0.2%	343 °C/1.5
CST3	KRW/3.0%	871 °C/2.5
CST4	KRW/3.0%	871 °C/1.5
CST5	KRW/3.0%	538 °C/1.5
CST6	Shell/3.0%	343 °C/~1.0
CST7	Shell/3.0%	538 °C/1.5
CST8	Shell/3.0%	871 °C/1.5
CST9	Shell/3.0%	343 °C/1.5
CST10	KRW/3.0%	343 °C/1.5
CST11	Shell/3.0%	871 °C/1.5

Sorbent samples were analyzed for total sulfur content and crush strength. Sulfur content was determined using a LECO analyzer. Crush strengths were obtained by compressing the

sorbent extrudates between the two flat surfaces of a Chatillon crush strength tester until the point of breakage.

Results and Discussion

Selected H_2S breakthrough curves are shown in Figures 2 through 5. These graphs show the effect of temperature in simulated KRW gas, inlet H_2S concentration in simulated KRW gas, type of simulated gas mixture (i.e., KRW or Shell gas), and the effect of temperature in simulated Shell gas, respectively. Each of these graphs will be discussed in more detail below. The data shown are the result of detector tube or mass spectrometer analysis of the outlet H_2S concentration.

The H_2S breakthrough curves from test series CST1 and CST2, shown in Figure 2, illustrates the dramatic effect of temperature on sulfur removal efficiency and capacity. These tests were conducted with simulated KRW gas containing 2,000 ppmv of H_2S, at 871 °C (1,600 °F), and 343 °C (650 °F), respectively. The final letter of each test number indicates whether it was a first or second sulfidation, e.g., CST1A was the first sulfidation of test series CST1, while CST1C was the second sulfidation of the same test series (CST1B, which is not shown, was the first regeneration). It is apparent from Figure 2 that the CST-939 sorbent performed poorly at 871 °C (1,600 °F) in the presence of simulated KRW gas. However, at 343 °C (650 °F), it performed quite satisfactory during the first sulfidation, yielding a pre-breakthrough H_2S concentration of approximately 40 to 60 ppmv for nearly 60 hours on-stream. With breakthrough defined as the point at which the outlet concentration of H_2S reaches 200 ppmv, then breakthrough occurred at approximately 75 hours on-stream. The second sulfidation, however, broke through at 41 hours on-stream and significant quantities of SO_2 (usually > 100 ppmv) were released during the first 30 hours on-stream. This early breakthrough and SO_2 release suggests there may have been a problem with regenerability. However, many sorbents do not show stable performance until the third or fourth cycle and, therefore, a multicycle test would be required to establish the extent of regenerability of the sorbent under these conditions.

Figure 3 shows the comparison of series CST1, with an inlet concentration of 2,000 ppmv H_2S, and series CST4, with 30,000 ppmv H_2S, conducted with simulated KRW gas at 871 °C (1,600 °F). As expected, the higher concentration shows more rapid breakthrough.

The dependence of sorbent performance on the type of simulated coal gas is shown in Figure 4. These experiments were conducted at 538 °C (1,000 °F) with 30,000 ppmv H_2S inlet concentration. The CST5 series was run with simulated KRW gas, and the CST7 series was run with simulated Shell gas. It is clearly seen that both the efficiency and the capacity of the sorbent are considerably better in the presence of Shell gas. This is in agreement with what had been (1) predicted by the equilibrium calculations of Hepworth and Slimane (1994), and (2) implicated by experiments on the effect of increasing H_2 and CO, while decreasing H_2O, by Wakker and Gerritsen (1990). While the sorbent performance in Shell gas, showing a pre-breakthrough concentration of 50 ppmv or less of H_2S, would be acceptable for most
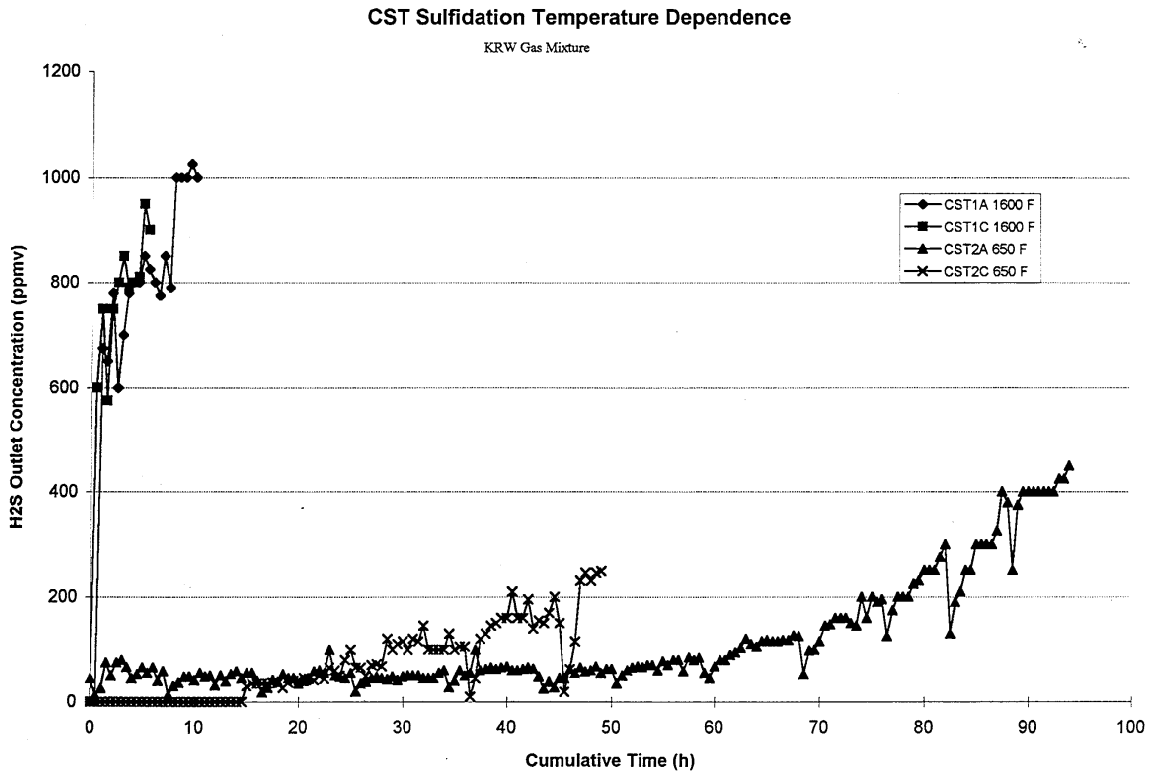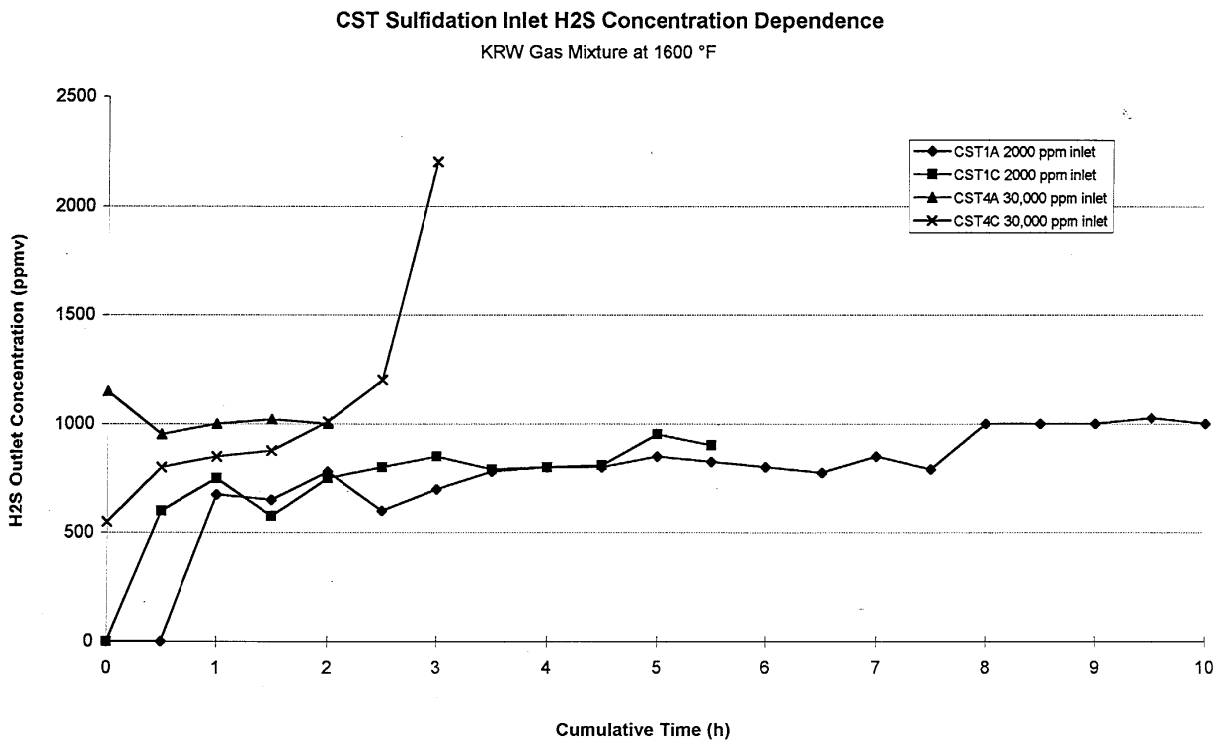
CST Sulfidation Temperature Dependence

KRW Gas Mixture

Figure 2

CST Sulfidation Inlet H2S Concentration Dependence

KRW Gas Mixture at 1600 °F

Figure 3

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CST Sulfidation Dependence on Type of Simulated Gas

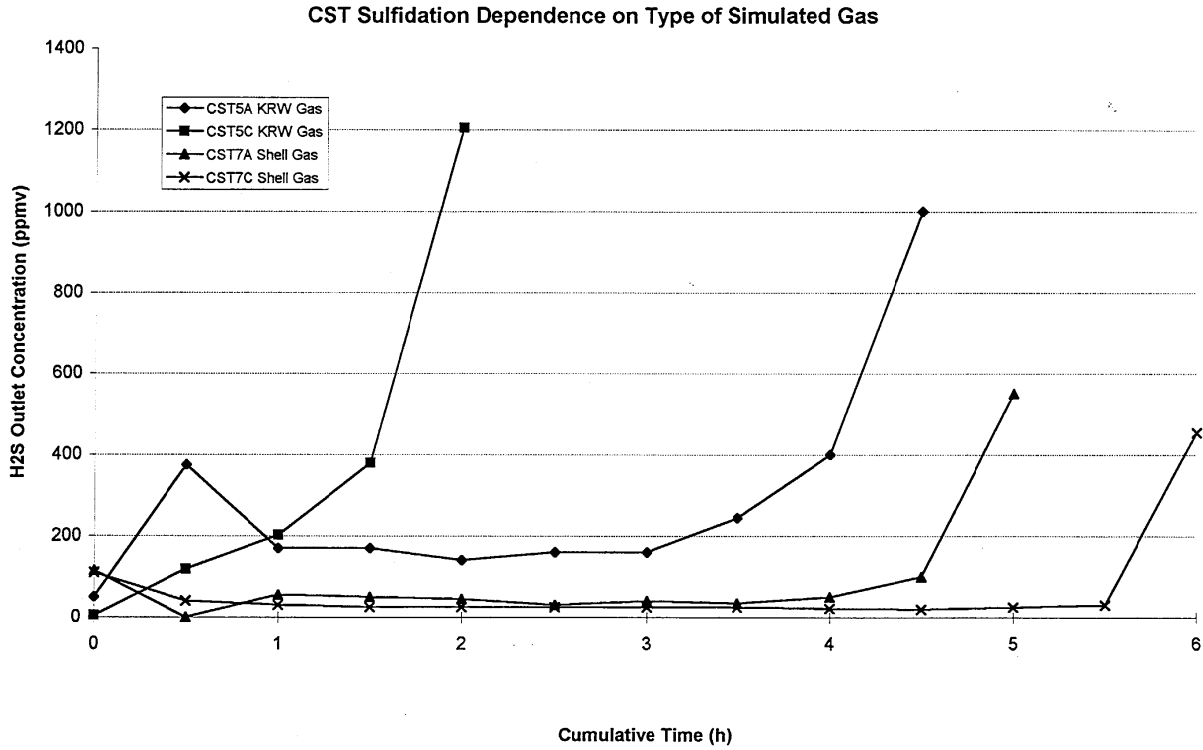Figure 4

CST Temperature Dependence in Simulated Shell Gas
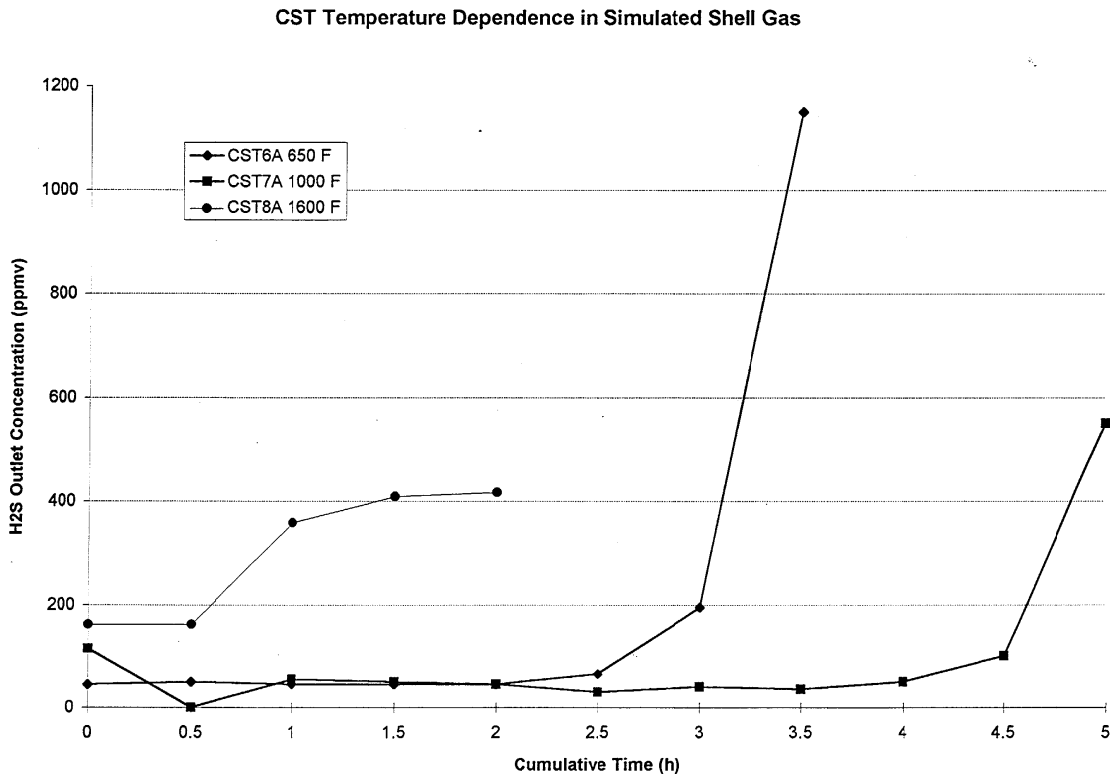

Figure 5

IGCC applications, the performance in KRW gas, with approximately 180 ppmv H_2S in the outlet gas, would be unacceptable.

Figure 5 shows the temperature dependence of sorbent performance in simulated Shell gas during the first sulfidation at 343, 538, and 871 °C (650, 1,000, and 1,600 °F). All measured concentrations of H_2S during the experiment at 871 °C (1,600 °F) were unacceptably high. However, the sorbent performed quite well at the lower temperatures of 343 and 538 °C (650 and 1,000 °F), with pre-breakthrough H_2S concentrations of approximately 50 ppmv. These data suggest that 538 °C (1,000 °F) may be the best operating temperature, since the break-through time at this temperature was 50 percent longer. Caution should be used in this inter-pretation, however, because many sorbents do not show their stable performance until the third cycle of sulfidation/regeneration.

Table 4 shows the sulfur loading of each sorbent after being removed from the reactor, through test CST8. The loading was determined by LECO analysis for total sulfur content. Note that the sulfur loadings for CST7 and CST8, which were conducted with simulated Shell gas, were significantly higher than those for CST4 and CST5, which were run with simulated KRW gas under otherwise similar conditions. This is consistent with the related breakthrough curve results.

Table 4. Sorbent Sulfur Loading

Sorbent Type	Sulfur Loading (%)
CST1A-C	0.76
CST2A-C	10.75
CST3A-E	9.39
CST4A-C	6.76
CST5A-C	7.02
CST6A-B	1.78
CST7A-C	21.27
CST8A-C	14.85
by Leco analysis	

The crush strength (in lb/pellet) for the fresh sorbent and reacted samples through test CST8 are shown in Table 5. The values given are the average from testing 15 pellets, with the standard deviation given in square brackets. It is important to note that in spite of the sub-stantial amounts of sulfur loaded, the crush strength was not significantly less than that of the fresh sorbent, and in many cases was significantly greater.

Table 5. Crush Strength

Sorbent Type	Crush Strength [std. dev.]
CST-939 (fresh)	10.4 [3.0]
CST1A-C	17.7 [7.0]
CST2A-C	9.4 [5.1]
CST3A-E	13.6 [6.8]
CST4A-C	16.2 [7.0]
CST5A-C	12.4 [4.6]
CST6A-B	11.8 [5.2]
CST7A-C	33.5 [10.4]
CST8A-C	16.7 [7.9]

Conclusions

The following conclusions were made from the data collected on the CST-939 sorbent:

- The sorbent efficiency and capacity are much greater at 343 °C (650 °F) than at 871 °C (1,600 °F).

- The sorbent efficiency and capacity are much greater in the presence of the more highly-reducing Shell gas than with the less-reducing KRW gas.

- The sorbent showed tremendous capacity for sulfur pickup, with actual loadings as high as 21 weight percent.

- Oxidative regeneration at 871 °C (1,600 °F) appeared to decompose sulfate; however, unusually high SO_2 release during the second sulfidations and/or reductive regenerations indicated incomplete regeneration.

- The average crush strength of the reacted sorbent did not indicate any loss of strength as compared to the fresh sorbent.

- Superior sorbent performance was obtained in the presence of simulated Shell gas at 538 °C (1,000 °F).

Future Work

Future work will include a 10-cycle test of the CST-939 sorbent with simulated Shell gas at 538 °C (1,000 °F) to test for sorbent regenerability and longer term durability.

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