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INVESTIGATION ON DURABILITY AND REACTIVITY OF PROMISING METAL OXIDE SORBENTS DURING SULFIDATION AND REGENERATION

Technical Progress Report for the Period
April 1 to June 30, 1998

Final Report

By
K. C. Kwon

August 1998

Work Performed Under Contract no DE-FG21-94MC31206–15

For
U.S. Department of Energy
Federal EnergyTechnology Center
Morgantown, West Virginia

By
Tuskegee University
Tuskegee, Alabama

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ABSTRACT

Hot-gas desulfurization for the integrated gasification combined cycle (IGCC) process has been investigated by many researchers to remove effectively hydrogen sulfide with various metal oxide sorbents at high pressures and high temperatures. Metal oxides such as zinc titanate oxides, zinc ferrite oxide, copper oxide, manganese oxide and calcium oxide, were found to be promising sorbents in comparison with other removal methods such as membrane separations and reactive membrane separations. Some metal oxide sorbents exhibited the quite favorable performance in terms of attrition resistance and sulfur capacity. Experiments on removal reaction of H_2S from coal gas mixtures with formulated metal oxide sorbents were conducted in a batch reactor or a differential reactor.

The objectives of this research project are to formulate promising metal oxide sorbents for removal of sulfur from coal gas mixtures, to find initial reaction kinetics for the metal oxide-hydrogen sulfide heterogeneous reaction system, to obtain effects of hydrogen, nitrogen and moisture on dynamic absorption and equilibrium absorption at various absorption temperatures. Promising durable metal oxide sorbents with high-sulfur-absorbing capacity were formulated by mixing active metal oxide powders with inert metal oxide powders, and calcining these powder mixtures.

The Research Triangle Institute (RTI), a sub-contractor of this research project, will also prepare promising metal oxide sorbents for this research project, plan experiments on removal of sulfur compounds from coal gases with metal oxide, and review experimental

results.

EXECUTIVE SUMMARY

The main objectives of this research project are to formulate durable metal oxide sorbents of high-sulfur-absorbing capacity by a physical mixing method, to investigate effects of hydrogen, moisture, temperature, concentrations of H_2S, and residence time of reaction gas mixtures on equilibrium absorption as well as initial dynamic absorption of H_2S into sorbents, and to evaluate effective diffusivity of H_2S through sorbent particles, using a batch reactor and a differential reactor.

A cylindrical rod model was developed to evaluate intraparticular diffusivity of H_2S into a sorbent, using experimental data from a batch reactor. A reaction rate equation in terms of disappearance of H_2S was developed with experimental data on initial reaction rates. The initial reaction rates were obtained from experimental data of concentrations of H_2S vs. reaction durations, using the batch reactor.

The 1.64 cm^3 differential micro reactor was fabricated with a titanium grade-2 tube to investigate initial dynamic absorption as well as equilibrium absorption of H_2S into sorbents. Concentrations of H_2S in gas samples from the differential micro reactor were analyzed with an electronic balance. The 35 cm^3 micro batch reactor was fabricated with 316 stainless steel. Concentrations of H_2S in gas samples from the micro batch reactor were analyzed with a gas chromatograph.

INTRODUCTION

Coal is the most plentiful energy resource in the United States and continues to be the major fuel utilized by electrical power plants. The coal resources will become more attractive for chemical feedstocks as well as sources of liquid and gaseous fuels, as petroleum resources become more depleted.

Coal is a very complex and heterogeneous material. Effective utilization of coal requires an understanding of the formation, structure, and purification of coal. Raw coal consists of minerals and organic matter. Coal minerals include primarily pyrites, silicate (quartz, clays) and various minor minerals, whereas organic matter is composed of carbon, oxygen, hydrogen, nitrogen and sulfur. Sulfur in coal is present as organic sulfur, pyritic sulfur and sulfate sulfur. Sulfur occurring in the form of relative coarse pyrite particles is removed largely by density separation, but very finely disseminated pyrite and organic sulfur cannot be removed in this way.

Sulfur products in combustion not only pollute the environment, but also are detrimental to combustion systems because of the corrosive action of their combustion products. In gasification process, coal is reacted with steam and air or oxygen to produce a medium to high calorific value fuel gas. The fuel gas can be subsequently combusted in a gas/steam turbine combined cycle (IGCC). These IGCC-based power generation options offer much higher thermodynamic cycle efficiencies that promise to reduce all forms of pollutants released from a coal conversion process through a lower fuel consumption and the use of more energy efficient high pressure and/or temperature unit operations for the removal of environmental pollutants. Among these options, integrated gasification combined cycles (IGCC) are relatively well studied.

Removal of hydrogen sulfide from hot coal gases produced in integrated gasification combined cycle power generation systems by metal oxide sorbents is required to protect downstream combustion turbines from being corroded with sulfur compounds. Removal of sulfur compound from coal gas products is investigated by using various metal oxide sorbents, and membrane separation methods. Current research results show that removal of sulfur with metal oxide sorbents appears to be the most promising method among others.

Main requirements of these metal oxide sorbents are durability and high sulfur-loading capacity during absorption-regeneration cycles. Spalling of sulfur-loaded fixed-bed metal oxide sorbents occurs during the regeneration of sulfur-loaded metal sorbents. The main causes of spalling of sorbents appear to be temperature rises of sulfur-loaded sorbents due to tremendous exothermic heat of reaction, and sulfate formation during regeneration processes. Sulfate products occupy more space than sulfide products in pores of sorbents, and result in significant structural stresses of metal sorbents.

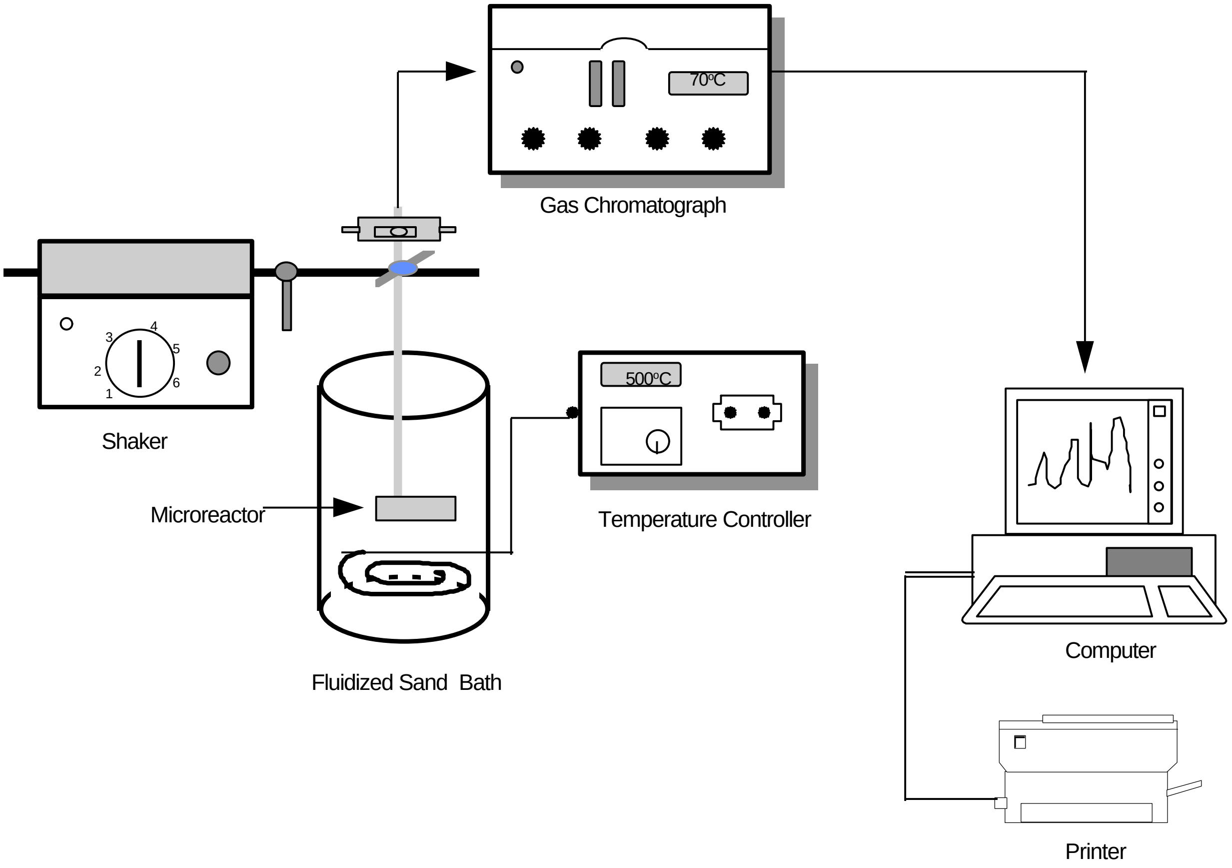
Research activities and efforts of this research project were concentrated on formulating metal oxide sorbents, conducting experiments on equilibrium absorption as well as initial dynamic absorption of hydrogen sulfide into formulated sorbents, studying effects of temperature, moisture, and hydrogen on initial dynamic absorption as well as equilibrium absorption of H_2S into sorbents, and evaluating intraparticular diffusivity of H_2S into sorbents in a batch reactor as well as a differential reactor.

EXPERIMENTAL SETUP/PROCEDURE

Micro Batch Reactor

A 35 cm^3 316 SS batch reactor (see Figures 1 and 2) was fabricated with Swagelok fittings, which will provide tight sealing for batch reaction experiments. A fresh metal oxide sorbent with promising formulas and simulated coal gases containing hydrogen sulfide are introduced in a batch reactor. The batch reactor, loaded with the fresh sorbent and the simulated coal gas mixture, is submerged in a fluidized sand bath to maintain the heterogeneous reaction system at a desired reaction temperature. Fine metal oxide sorbents will be used to increase outer surface of sorbent particles. The batch reactor, loaded with a mixture of fresh sorbent and simulated coal gas mixtures, is shaken in a constant-temperature fluidized sand bath to reduce effects of mass transfer of hydrogen sulfide to sorbent particles. The sulfidation reaction is terminated at a desired reaction time. Conversions of sorbents are analyzed with a gas chromatograph.

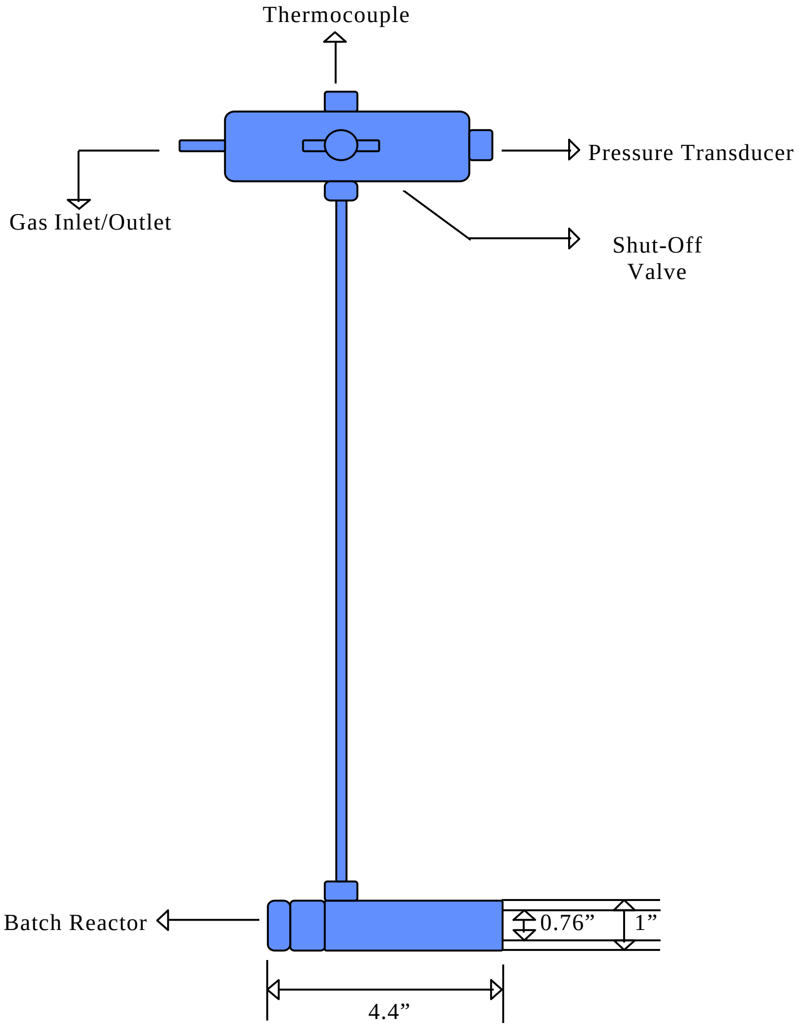
Figure1. Batch Reactor System



Differential Reactor

A differential reactor mainly consists of one 10-cm-long ¼-inch titanium grade-2 tubing and two 1/4” external column end fittings. A differential reactor assembly mainly consists of four mass flow meters for gases, one differential reactor, one preheater, one high pressure liquid pump for water, one four-way switch valve, one muffle furnace, three filters for gases, four check valves, and one water collection bottle (see Figure 3). Fresh formulated metal oxide sorbents in the form of 1-mm cylindrical rod were crushed to obtain 100 - 200 mesh (74 –140 µm) particles. The differential reactor was loaded with 0.1-g 74-140 µm sorbent particles. The reactor, loaded with the sorbent particles, was placed inside the muffle furnace to be heated at a desired temperature. Nitrogen was introduced into the sorbent-loaded reactor during preheating the reactor. When the temperature of the reactor was raised at a desired temperature, a reaction mixture was introduced into the reactor for a desired reaction duration, by switching nitrogen with a simulated coal gas mixture. Absorption amounts of hydrogen sulfide into the sorbent were analyzed with an electronic balance. The range for the space (residence) time of the simulated coal gas mixture in the reactor was 0.072 - 0.36 s (500 - 100 cc/min) under the reaction conditions.

Figure 2. Batch Reactor Assembly



Formulation of Metal Oxide Sorbents

Metal oxide sorbents were formulated with zinc oxide powder as an active sorbent ingredient, bentonite and kaolin as binding materials and titanium oxide as a supporting metal oxide. This pasty mixture was extrudated 1-mm cylindrical rods. The viscosity of the pasty mixture appeared to be sensitive to amounts of water as well as amounts of binding materials added to a powder mixture at room temperature. Homogeneous mixing of these pasty slurry mixtures seemed to be very critical in producing duplicate formulations of sorbents. The formulated metal oxide sorbents were calcined for 0.5 - 4 hours at 800 - 900^{o}C (see Table 1). Detailed formulations of sorbents as well as effects of additives on improving absorption capacities of formulated sorbents were discussed in the appendix of the final report, which was written in a separate volume.

Figure 3. A Differential Reactor Assembly

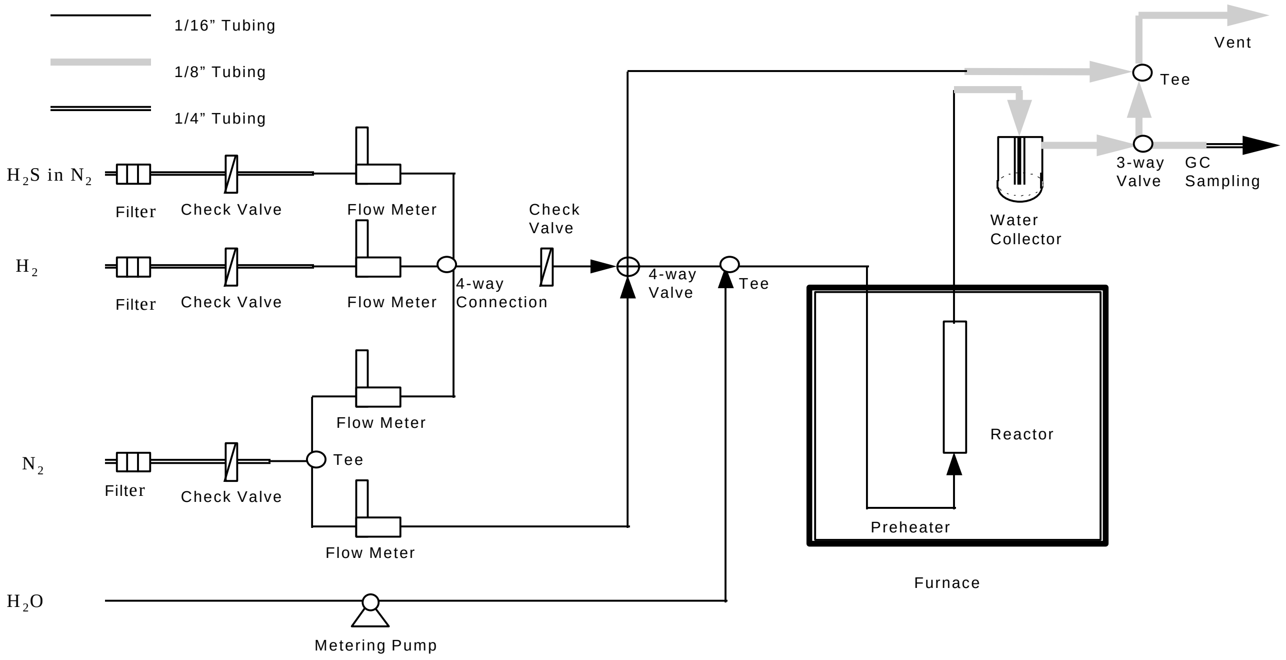


Table 1. Formulation of metal oxide sorbents.

	TU-1	TU-19	TU-28	TU-24	TU-25	TU-188
ZnO, g	1.7	1	1	1.8	0.5	1.7
TiO_2, g	2	2	2	1.2	2.5	2
Bentonite, g	0.3	0.15	0.1	0.15	0.15	
Kaolin						0.1
Calcination Temperature, ^oC		800	830	800	830	860
Calcination Duration, min	800	100	100	100	100	90
Bulk Density of Sorbent, g/cm^3	1.73	1.73		1.73		2.09
Specific Pore Volume, cm^3/g	0.36	0.36		0.36		0.42

Table 2. Experimental conditions for the reaction of hydrogen sulfide with sorbents in a batch reactor.

Reactor Volume, cm^3:	35
Temperature, ^oC:	350 - 550
Pressure, psia	363 - 479
Reaction Time, min:	1 - 60
Particle Size	1 mm cylindrical rod or 74 –140 μm
Amount of Sorbent, g	0.05 - 0.4
Initial Partial Pressure of Hydrogen at 25^{o}C, psia:	14.7 -24.7
Initial Amount of Water, g:	0.05 - 0.12
Initial Concentration of H_2S, ppm	9107
Initial Partial Pressure of Nitrogen at 25^{o}C, psia:	140 -150

Table 3. Experimental conditions for the reaction of hydrogen sulfide with sorbents in a differential reactor.

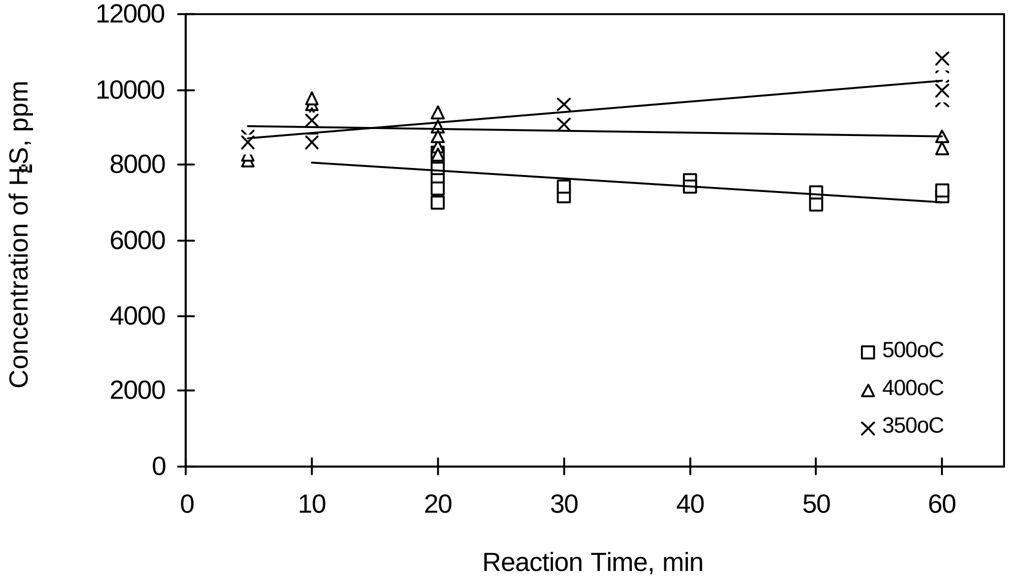
Reactor Volume, cm^3:	1.6
Temperature, ^oC:	530
Pressure, psia	105
Reaction Time, s:	5-120000
Space Time under the absorption conditions, s:	0.072 - 0.36
Gas Flow Rate at room temperature, cc/min	100 - 500
Particle Size	74 –140 µm
Amount of Sorbent, g	0.1
Hydrogen, vol %	10 - 40
Moisture, vol %	0 - 10
Concentration of H_2S, ppm	2500-7500
Nitrogen, vol %	10 - 80

RESULTS AND DISCUSSION

Batch Reactor Experiments

Experiments on reactivity of hydrogen sulfide with the 316 SS batch reactor wall, using a simulated coal gas mixture consisting of 9107-ppm hydrogen sulfide (0.005 g; 1 w%), 0.085-g water (15.84 w%), 0.0029-g hydrogen (0.58 w%), and 0.4046-g nitrogen (81.34 w%), were carried out, as shown in Figure 4. Absorption of hydrogen sulfide on the reactor wall increases with absorption temperatures. Absorption of H_2S into the 316 SS wall increases with absorption time above 400^{o}C. Absorption of H_2S into the 316 SS wall does not take place, and previously-absorbed H_2S appears to be released from the 316 SS wall at 350^{o}C. These experimental data were incorporated in calculating absorption of H_2S into formulated sorbents.

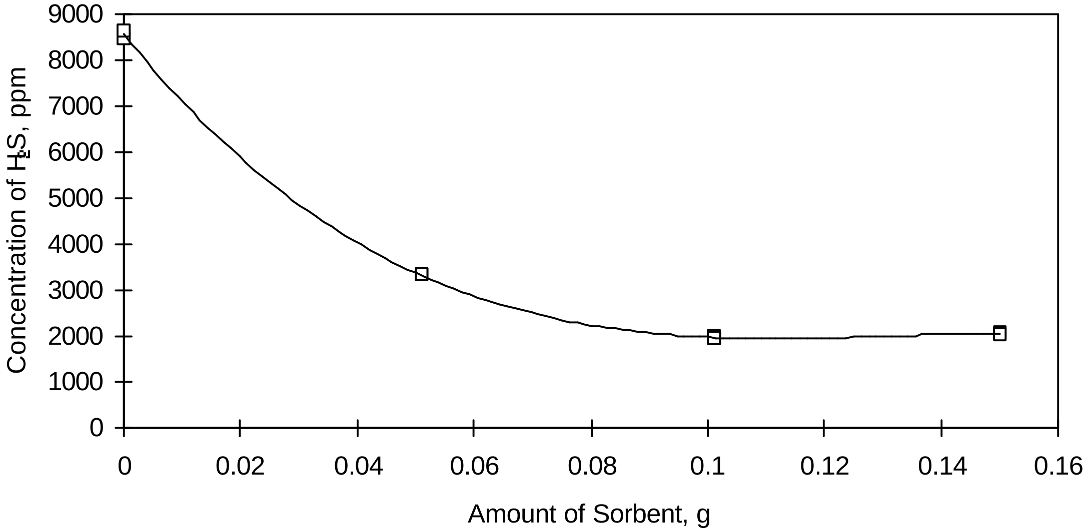
Figure 4 Reactivity of 316 stainless steel with the initial concentration 9107-ppm H_2S and 0.085-g moisture at various temperatures.



ZT-4 Sorbent

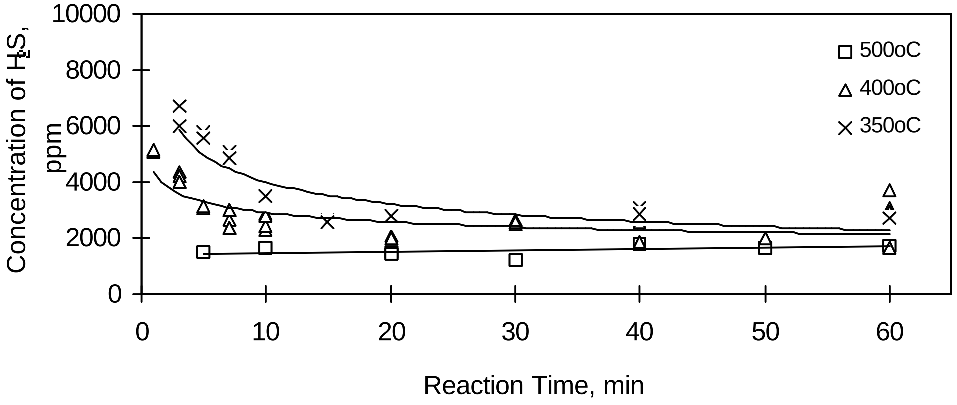
A series of experiments on effects of ZT-4 sorbent amounts on removal of H_2S were carried out for 10 min at 500^oC (Figure 5). The ZT-4 sorbent was formulated by the Research Triangle Institute (RTI). Removal of H_2S increases with amounts of the sorbent, but appears to level off above 0.1-g sorbent.

Figure 5. Effects of ZT-4 sorbent amounts on removal of H_2S with the initial concentration 9107-ppm H_2S and 0.085-g moisture for 10 min at 500 ^oC.



Reactivity of ZT-4 sorbent with H_2S was examined at various temperatures (Figure 6). Reactivity of the sorbent with H_2S increases with reaction temperatures. Equilibrium removal of H_2S increases with reaction temperatures, and requires longer reaction times with lower reaction temperatures.

Figure 6. Reactivity of 0.1-g ZT-4 sorbent with 0.085-g moisture and the initial concentration 9107-ppm H_2S at various temperatures.



Effects of moisture on reactivity of ZT-4 sorbent with H_2S were investigated at 350^oC

(Figures 7 and 8). Increased moisture increases removal of H_2S below equilibrium absorption, as shown in Figure 7. Equilibrium absorption of H_2S appears to be independent of moisture amounts, as shown in Figure 8. This fact may indicate that moisture does not affect equilibrium absorption for the absorption of H_2S into ZT-4 sorbent at 350°C.

Figure 7 Effects of moisture on reactivity of 0.1-g ZT-4 sorbent with the initial concentration 9107-ppm H_2S for 3 min at 350°C.

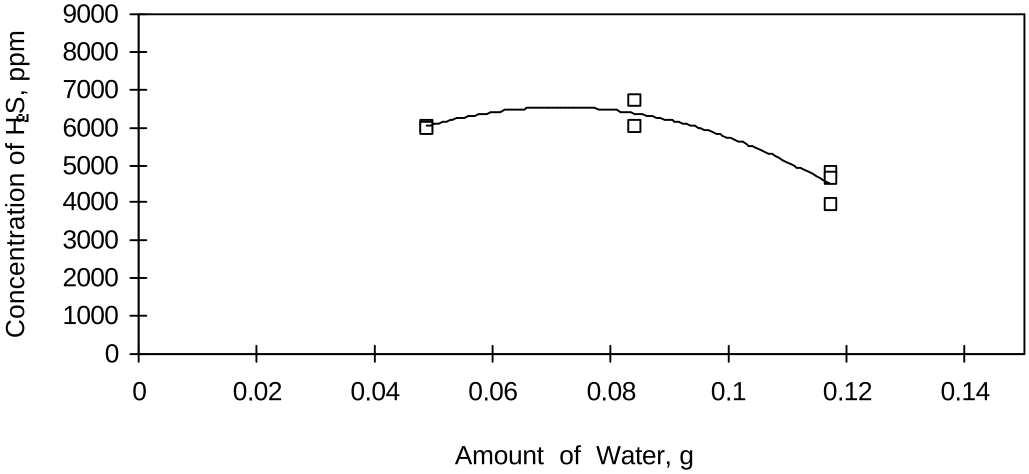
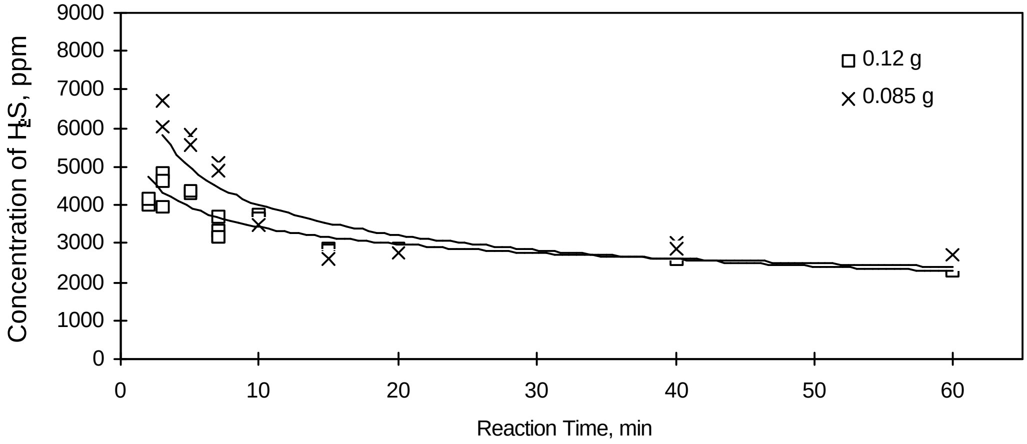
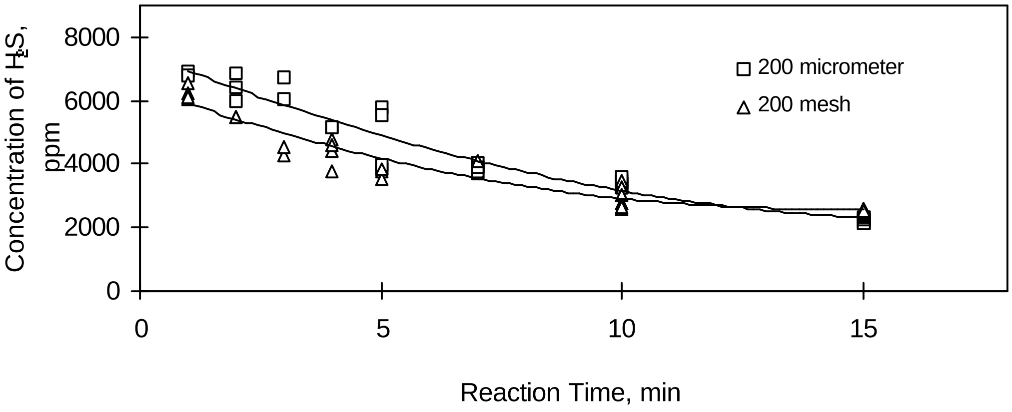


Figure 8. Effects of moisture on reactivity of 0.1-g ZT-4 sorbent with the initial concentration 9107-ppm H_2S and various moisture amounts at 350°C.



Effects of particle sizes of ZT-4 sorbent on removal of H_2S were examined at 350°C, as shown in Figure 9. The minus-200-mesh sorbent removes more H_2S than the 200-μm sorbent below equilibrium absorption. Equilibrium absorption of H_2S is not affected by particle sizes. This observation may suggest that absorption of H_2S into the sorbent is initially controlled by surface reaction at the outer surface of the sorbent particles, whereas intraparticular mass transfer of H_2S into pores of the sorbent is a limited step in the absorption of H_2S into the sorbent for an extended absorption duration at 350°C.

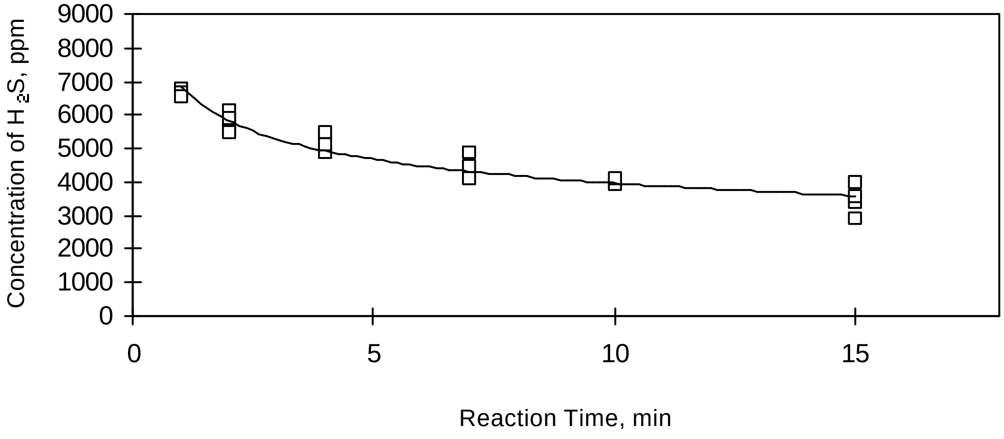
Figure 9. Effects of particle sizes on reactivity of 0.1-g ZT-4 sorbent with the initial concentration 9107-ppm H_2S and 0.085-g moisture at 350 °C.



TU-1 and TU-19 Sorbents

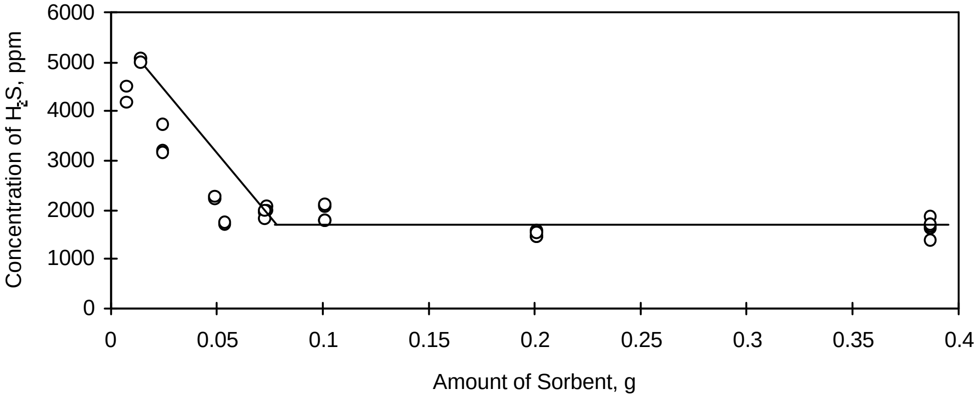
Reactivity of TU-1 sorbent, the first metal oxide sorbent formulated, was tested at 350°C (see Figure 10). The 1/16"-cylindrical-rod TU-1 sorbent, consisting mainly of zinc oxide and titanium oxide, was formulated with a physical mixing method. Absorption of H_2S into the sobent also increases with absorption times, as shown in Figure 10.

Figure 10. Reactivity of 0.1-g TU-1 sorbent with the initial concentration 9107-ppm H_2S and 0.085-g moisture at 350°C and various reaction times.



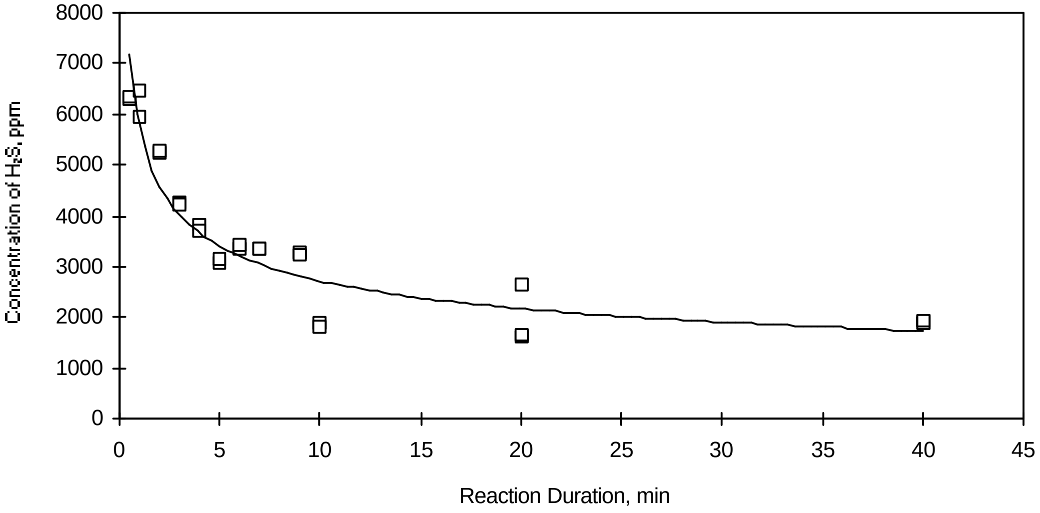
A series of experiments on effects of TU-19 sorbent amount on the removal of H_2S were carried out for 60 min at 500°C (see Figure 11). The removal of H_2S increases with the amounts of the sorbent, but appears to level off above 0.05-g sorbent.

Figure 11. Effects of TU-19 sorbent amounts on removal of H_2S in the presence of the initial concentration 9107-ppm H_2S and 0.085-g moisture for 1 hour at 500^{o}C.

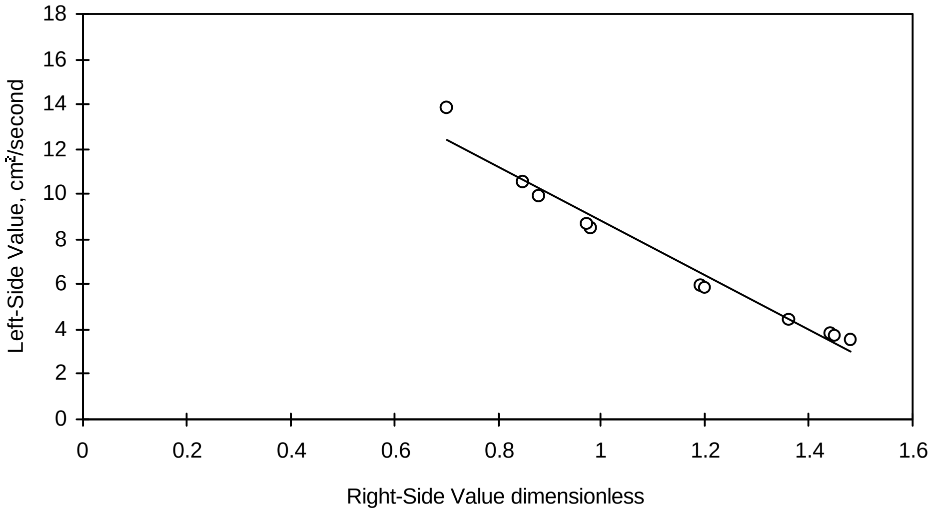


Reactivity of 0.1-g TU-19 sorbent was investigated in the presence of the initial concentration 9107-ppm H_2S and 0.085-g moisture at 500^{o}C and various reaction times (Figure 12). These experimental data showed that most absorption of H_2S into the sorbent occurs during the first 5-min reaction time.

Figure 12. Reactivity of 0.1-g TU-19 sorbent with the initial concentration 9107-ppm H_2S in the presence 0.085-g moisture at 500oC and various reaction times.



Intraparticular diffusivity of H_2S through the TU-19 sorbent in the form of 1-mm cylindrical rod was evaluated at 500^{o}C, using the following cylindrical rod model. The model was developed with the unreacted core assumption and the quasi steady state assumption. Left-side values of the equation 1 and right-side values of the equation 1 were obtained with experimental data, shown in Figure 12. Left-side values of the equation 1 were plotted against the right-side values of the equation 1 (Figure 13). Intraparticle diffusivity was determined from the slope of this plot. The intraparticle diffusivity of H_2S was found to be 2.018×10^{-3} cm^2/s at 500^{o}C.



Figuree 13. Left-side values vs. right-side values of the cylindrical rod model for the determination of intraparticle diffusivity through the TU-19 sorbent.

$$\ln(\tfrac{r}{R})r\tfrac{dr}{dt} = D_e(\tfrac{B}{b})(1+Ar^2) + \text{constant} \qquad (1)$$

$$r = (R^2 - (\tfrac{C_{AO}-C_A}{bpLr_B})V)^{0.5} \qquad (2)$$

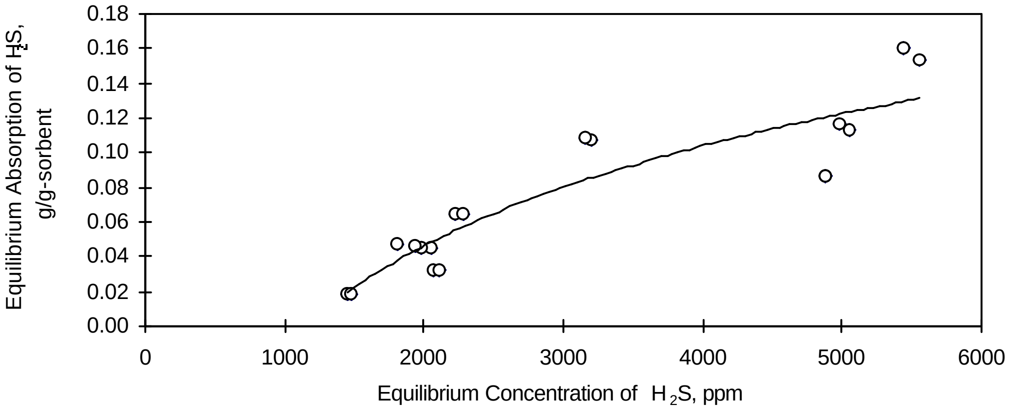
$$B = \tfrac{C_{Ao}}{r_B} - \tfrac{bV_B}{V} \qquad (3)$$

$$A = \tfrac{bpL}{BV} \qquad (4)$$

where r: radius of an unreacted core
R: radius of cylindrical sorbent
t: reaction time
V_B: volume of cylindrical sorbent
L: Length of a cylindrical-rod sorbent
ρ_B: density of a cylindrical-rod sorbent
D_e: intraparticle diffusivity
V: reactor volume
b: equilibrium absorption
C_{AO}: initial concentration of H_2S
C_A: concentration of H_2S

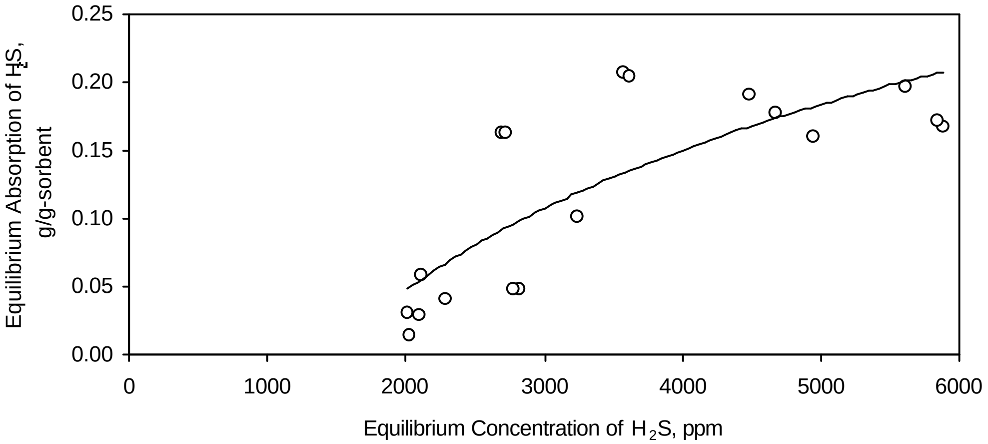
Equilibrium absorption of H_2S into the TU-19 sorbent was investigated at various equilibrium concentrations of H_2S and 500°C. Equilibrium absorption of H_2S into the TU-19 sorbent are 0.02 - 0.16 g-H_2S/g-sorbent in the presence of 14.7-psia H_2 and 0.085-g moisture. Equilibrium absorption of H_2S into the TU-19 sorbent increases with concentrations of H_2S at 500°C and 450 psia (see Figure 14).

Figure 14. Equilibrium absorption of H_2S into TU-19 sorbent in the presence of 14.7-psia H_2 (room temperature) and 0.085-g moisture at 500 °C.



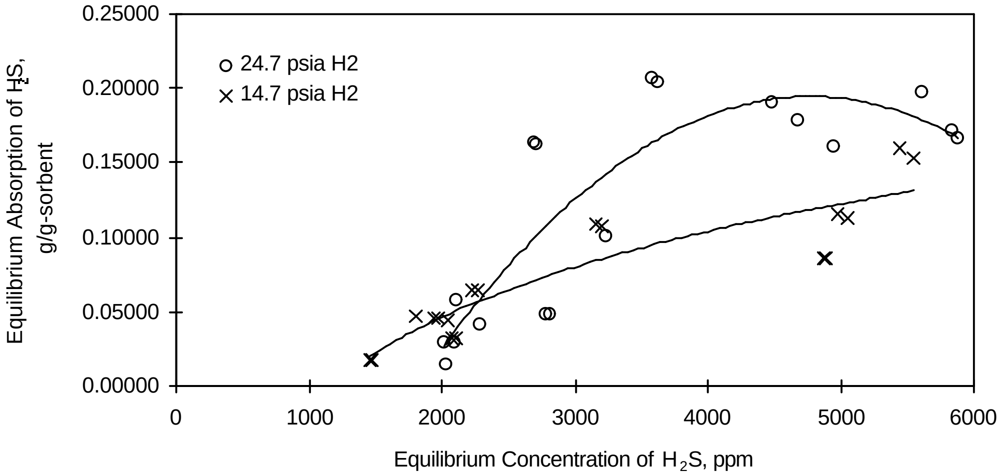
Equilibrium absorption of H_2S into the TU-19 sorbent are 0.03 - 0.20 g-H_2S/g-sorbent in the presence of 24.7-psia H_2 and 0.085-g moisture. These data may indicate that equilibrium absorption values at higher hydrogen partial pressures are higher than those at lower hydrogen partial pressures. Equilibrium absorption of H_2S into the TU-19 sorbent increases with concentrations of H_2S (see Figure 15). These high absorption values may show that a portion of H_2S is absorbed into the inert sorbent matrix of the TU-19 sorbent.

Figure 15. Equilibrium absorption of H_2S into TU-19 sorbent in the presence of 24.7-psia H_2 (room temperature) and 0.085-g moisture at 500 °C.



Equilibrium absorption of the TU-19 sorbent in the presence of 24.7-psia H_2 (room temperature) is compared with that in the presence of 14.7-psia H_2. Equilibrium absorption of the TU-19 sorbent in the presence of 24.7-psia H_2 is higher than that in the presence of 14.7-psia H_2 (see Figure 16). This observation may indicate that partial pressure of hydrogen appears to affect significantly equilibrium absorption of H_2S into the sorbent.

Figure 16. Effects of H_2 pressure on equilibrium absorption of H_2S into TU-19 sorbent in the presence of 0.085-g moisture at 500 °C.



The equilibrium absorption curve of the TU-19 sorbent is quite different from that of the TU-28 sorbent in the presence of 24.7-psia H_2 and 0.085-g moisture at 500°C (see Figures 17 and 18). This fact may suggest that formulation procedures and methods affect equilibrium absorption capacity of sorbents.

Figure 17. Equilibrium absorption of H_2S into TU-28 sorbent in the presence of 24.7-psia H_2 (room temperature) and 0.085-g moisture at 500 °C.

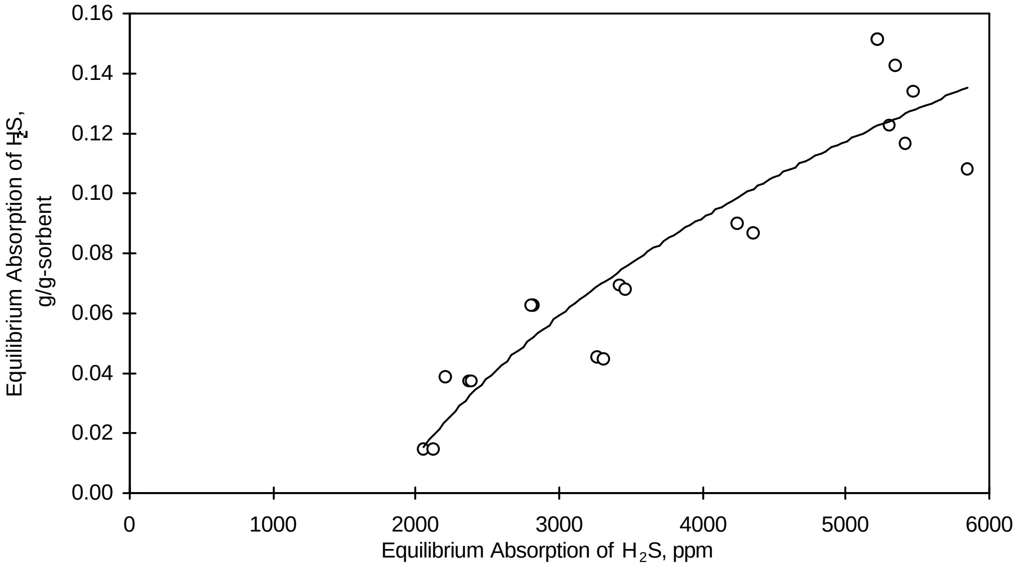
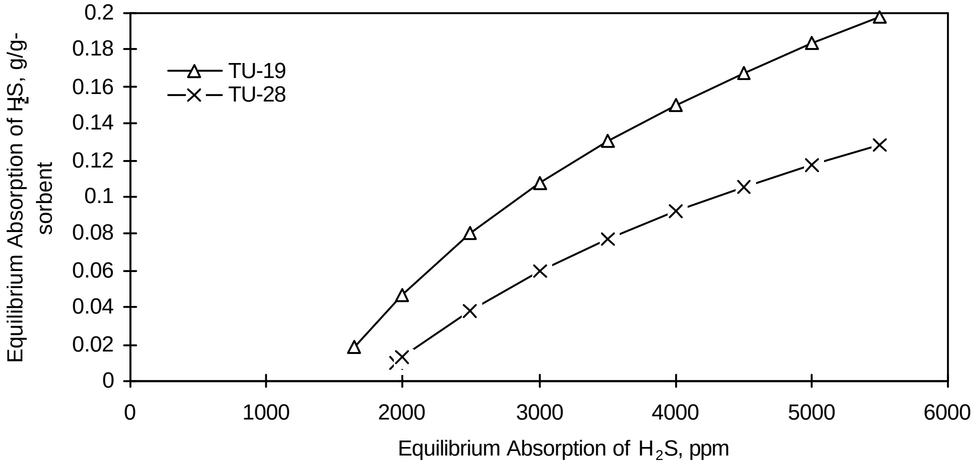


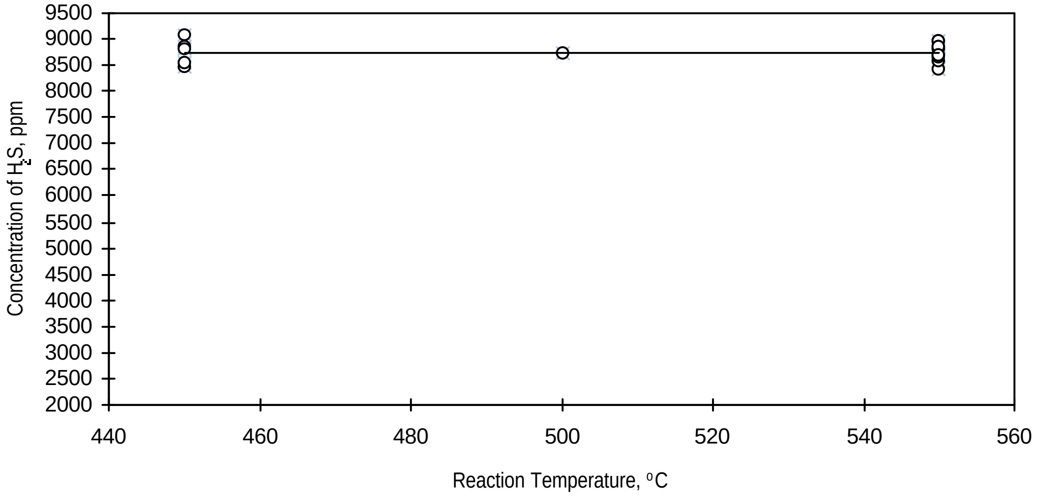
Figure 18. Effects of formulation procedures on equilibrium absorption of H_2S into sorbents with 24.7-psia H_2 and 0.085-g moisture at 500 °C.



TU-25 Sorbent

Reactivity of H_2S with the reactor wall was investigated in the absence of sorbents for 1 min at 450 -550°C. The concentration of H_2S was decreased from the initial concentration 9107 ppm to 8700 ppm for the 1 min reaction duration, as shown in Figure 19. These experimental data were incorporated in calculating reaction rates of H_2S with the formulated sorbents as well as dynamic absorption of H_2S into the formulated sorbents.

Figure 19. Reactivity of H_2S with the reactor wall in the presence of initial concentration 9107-ppm H_2S, and initial 14.7-psia H_2 for 1 min at various temperatures.



Effects of hydrogen partial pressures on reactivity of the 100-200 mesh TU-25 sorbent were investigated in the presence of 0.085-g moisture for 1 min at 500°C, as shown in Figure

20. Reaction rates of H_2S with the TU-25 sorbent increase with amounts of the sorbent. Reactivity of the TU-25 sorbent with H_2S in the presence of the initial 14.7-psia hydrogen is higher than that in the presence of the initial 24.7-psia hydrogen. These data may suggest that hydrogen itself affects initial reaction rates of H_2S with the formulated TU-25 sorbent.

Figure 20. Effects of hydrogen pressures on reactivity of 100-200 mesh TU-25 sorbent with H_2S in the presence of 0.085-g moisture for 1 min at 500°C.

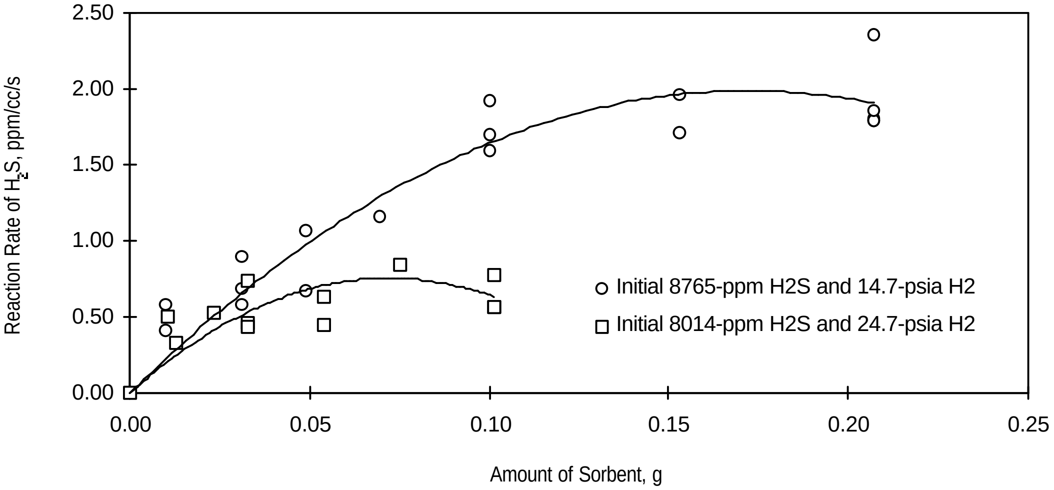
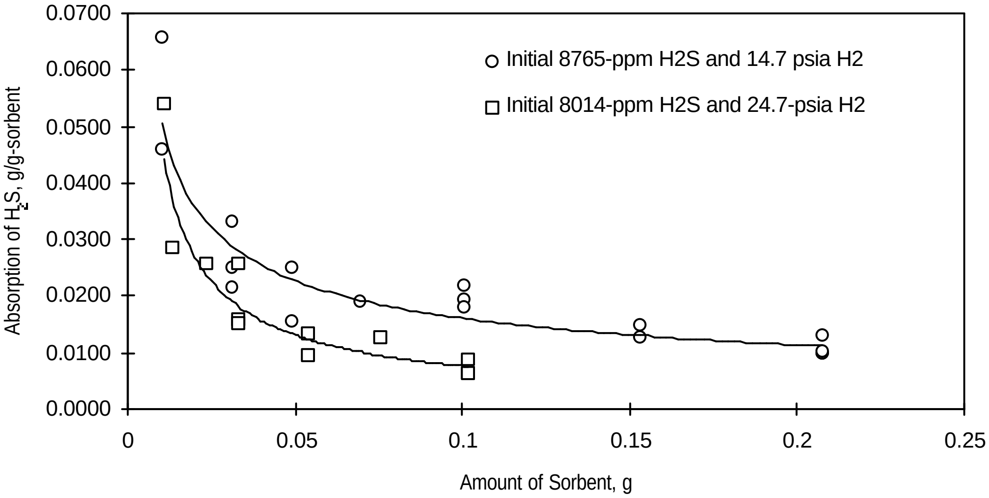


Figure 21 Effects of hydrogen partial pressure on absorption of H_2S into TU-25 sorbent in the presence of 0.085-g moisture for 1 min at 500°C

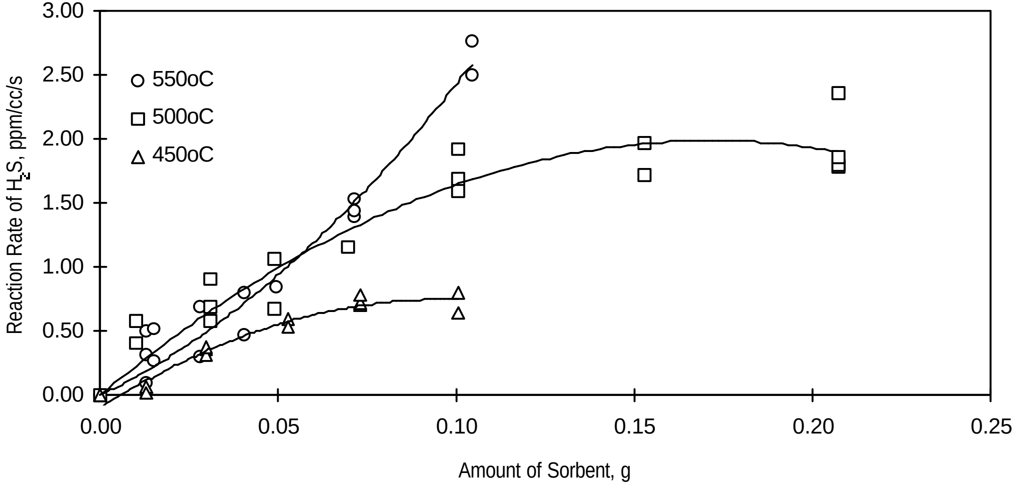


Effects of hydrogen partial pressures on dynamic absorption of H_2S into the 100-200 mesh TU-25 sorbent were investigated in the presence of 0.085-g moisture for 1 min at 500°C, as shown in Figure 21. Dynamic absorption of H_2S into the TU-25 sorbent in the presence of the initial 14.7-psia hydrogen is higher than that in the presence of the initial 24.7-

psia hydrogen. Dynamic absorption of H_2S into the sorbent decreases with increased quantities of the sorbent. This observation may indicate that dynamic absorption of H_2S into the sorbent is affected by partial pressures of hydrogen as well as amounts of the sorbent.

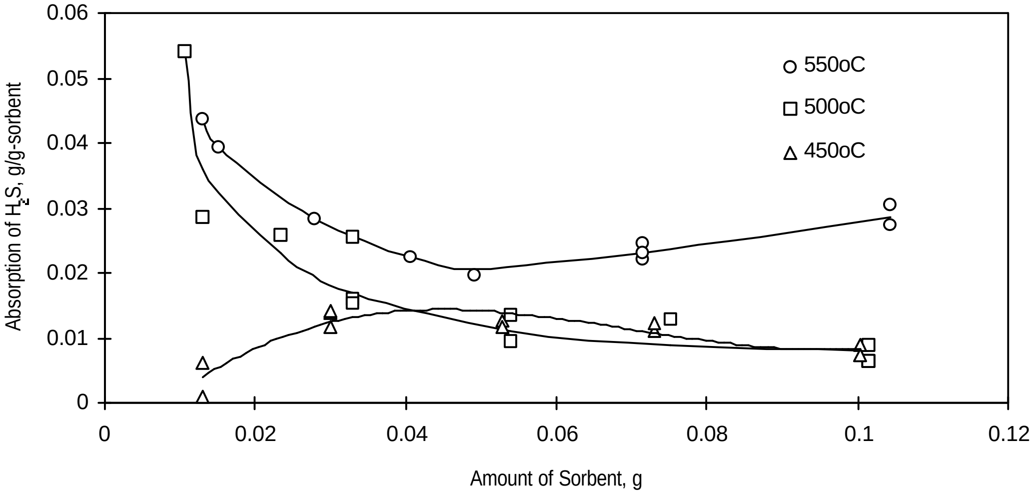
Various amounts of 100-200 mesh TU-25 sorbent were reacted with H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 1 min at various temperatures to identify effects of reaction temperatures on reactivity of H_2S with the TU-25 sorbent, as shown in Figure 22. Reactivity of H_2S with the TU-25 sorbent increases with reaction temperatures, as expected. Reaction rates of H_2S with the TU-25 sorbent increase with increased quantities of the sorbent up to 0.1-g sorbent. However, reaction rates of H_2S with the TU-25 sorbent for 1 min at 500°C appear to level off above 0.1-g sorbent, as observed from the previous experimental results.

Figure 22. Effects of temperatures on reactivity of 100-200 mesh TU-25 sorbent with initial 8675-ppm H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 1 min.



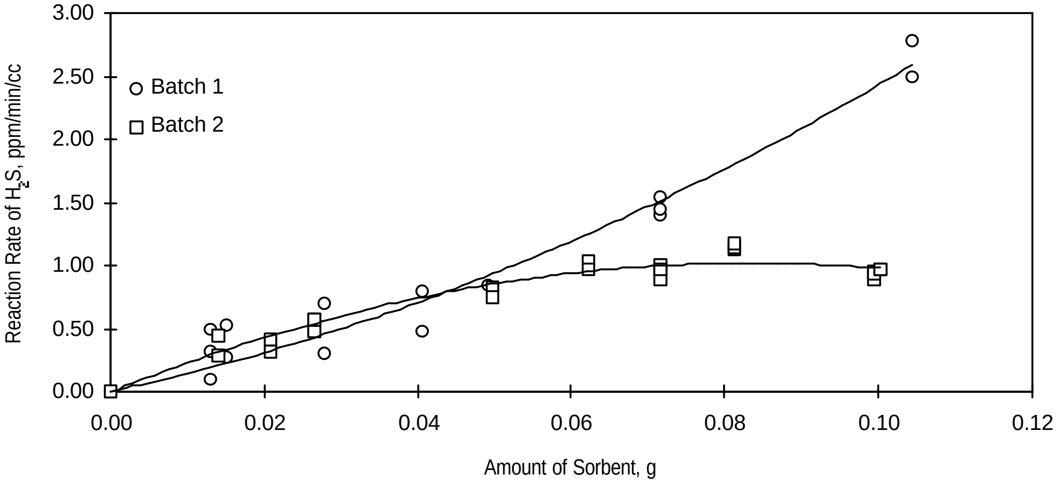
Effects of temperatures on dynamic absorption of H_2S into the TU-25 sorbent were investigated, as shown in Figure 23. Dynamic absorption of H_2S into the sorbent was calculated from changes in concentrations of H_2S in the reactor. Dynamic absorption of H_2S appears to be dependent on amounts of the sorbent as well as absorption temperatures. Dynamic absorption of H_2S increases generally with increased reaction temperatures. Dynamic absorption of H_2S into the TU-25 sorbent decreases with increased quantities of the sorbent for the 1-min reaction duration at the reaction temperature range of 500°C - 550°C up to 0.04-g sorbent. Dynamic absorption of H_2S into the sorbent for the 1-min reaction duration at 550°C appears to be almost same as that at 500°C up to 0.04-g sorbent.

Figure 23. Effects of temperatures on absorption of H_2S into TU-25 sorbent in the presence of initial 14.7-psia H_2 and 0.085-g moisture for 1 min.



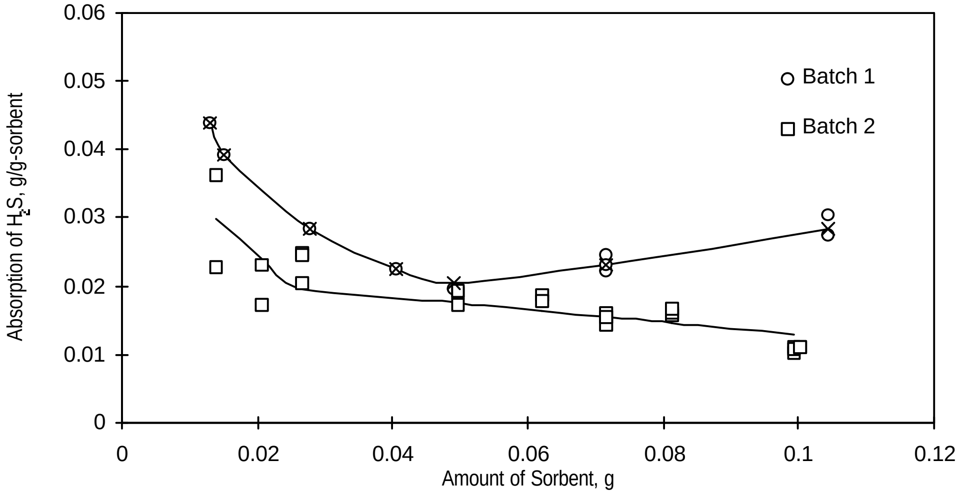
Dynamic absorption of H_2S into the TU-25 sorbent increases with increased quantities of the sorbent for the 1-min reaction duration at 450°C up to 0.04-g sorbent (see Figure 23). Dynamic absorption of H_2S into the sorbent for the 1-min reaction duration at 450°C appears to be almost same as that at 500°C above 0.04-g sorbent. Dynamic absorption of H_2S into the TU-25 sorbent increases with increased quantities of the sorbent for the 1-min reaction duration at 550°C above 0.04-g sorbent. These observations may suggest that mechanisms on absorption of H_2S into the TU-25 sorbent are dependent on absorption temperatures.

Figure 24. Reproducibilty of formulation of TU-25 sorbent by comparing its reactivity with H_2S in the presence of 0.085-g moisture and14.7-psia hydrogen for 1 min at 550°C.



Reproducibility of formulating the TU-25 sorbent was examined by comparing its reactivity with H_2S in the presence of 0.085-g moisture and 14.7-psia hydrogen for 1 min at 550°C, as shown in Figure 24. The reactivity of the sorbent appeared to be independent of batch processing at below 0.04-g sorbent, while the reactivity of the sorbent from the batch 1 was higher than that from the batch 2 above 0.04-g sorbent. These data may indicate that reproducibility of formulation for the TU-25 sorbent is very poor.

Figure 25. Reproducibility of formulation for TU-25 sorbent by comparing its absorption with H_2S in the presence of initial 14.7-psia H_2 and 0.085-g moisture for 1 min at 550°C.



Reproducibility of formulation for the TU-25 sorbent was examined by comparing dynamic absorption of H_2S into the sorbent in the presence of 0.085-g moisture and 14.7-psia hydrogen for 1 min at 550°C, as shown in Figure 25. Dynamic absorption of H_2S into the sorbent from the batch 1 processing appeared to be higher than that from the batch 2.

TU-24 Sorbent

The 100-200 mesh TU-24 sorbent was reacted with H_2S for short reaction durations at various reaction temperatures, as shown in Figure 26. Reactivity of the sorbent increases with increased reaction temperatures. Reaction rates of H_2S with the sorbent increase with increased amounts of the sorbent. These observations may indicate that reactivity of H_2S with the TU-24 sorbent is a function of reaction temperatures and amounts of the TU-24 sorbent.

Dynamic absorption of H_2S into the TU-24 sorbent increases with increased dynamic absorption temperatures, and decreases with increased amounts of the TU-24 sorbent for the 1-min absorption duration, as shown in Figure 27. These experimental data may suggest that dynamic absorption of H_2S into the sorbent is dependent on absorption temperatures as well as amounts of the TU-24 sorbent. These observations also were found from the previous experiments on equilibrium absorption of H_2S into formulated sorbents.

Figure 26. Effects of temperatures on reactivity of 100-200 mesh TU-24 sorbent with H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen for 1 min.

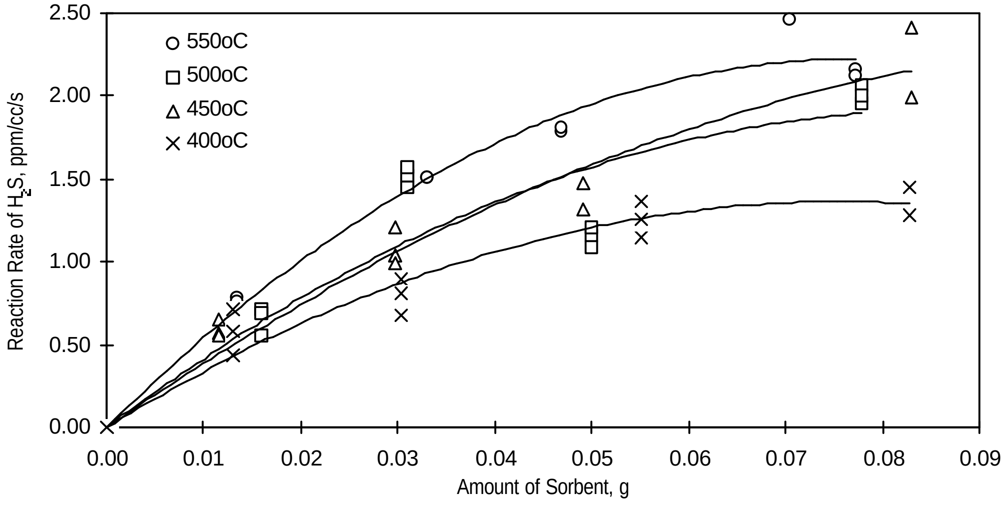
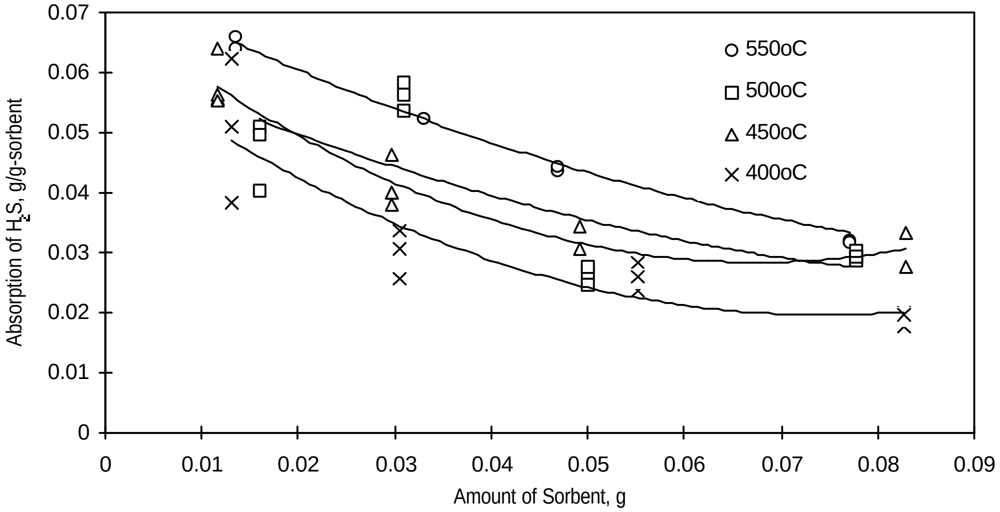
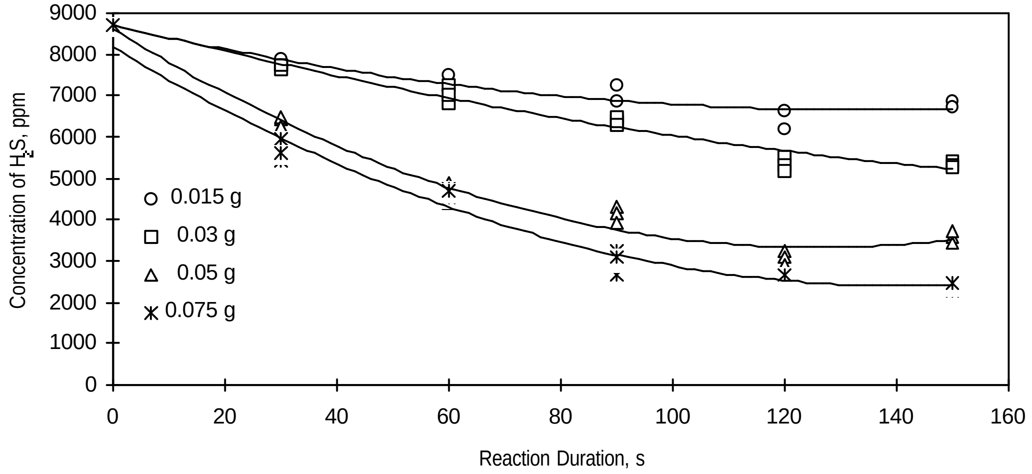


Figure 27. Effects of temperatures on absorption of H_2S into TU-24 sorbent in the presence of initial 14.7-psia H_2 and 0.085-g moisture for 1 min.



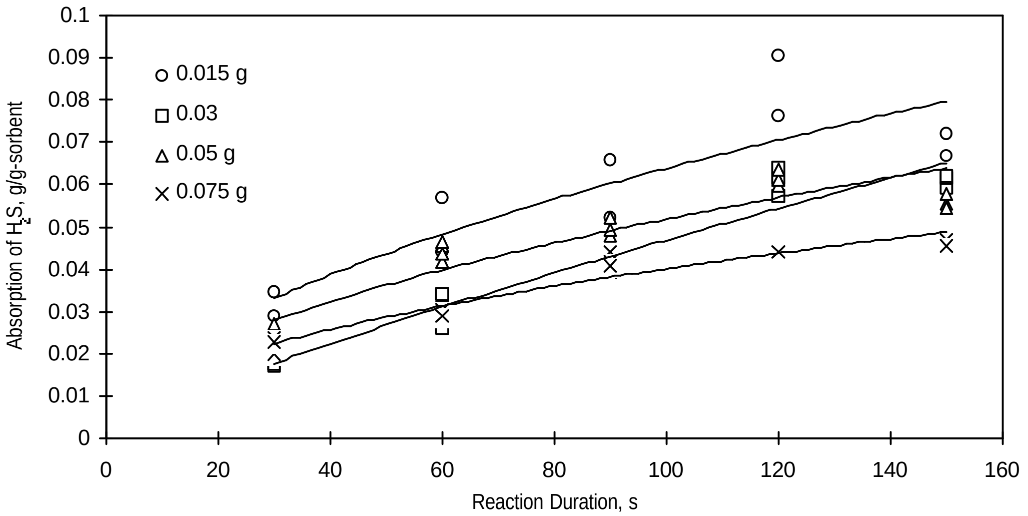
The TU-24 sorbent was reacted with the 8700-ppm initial concentration H_2S in the presence of initial 14.7-psia H_2 and 0.085-g moisture for 30 -150 seconds at 500°C, as shown in Figure 28. Concentrations of H_2S decrease with increased reaction durations as well as increased amounts of the sorbent. These facts may suggest that reaction rates of H_2S with the TU-24 sorbent may be dependent on reaction durations as well as quantities of the TU-24 sorbent.

Figure 28. Changes in concentration of H_2S in the reaction with TU-24 sorbent in the presence of initial 14.7-psia hydrogen and 0.085-g moisture at 500°C.



Dynamic absorption of H_2S into the TU-24 sorbent at 500°C increases with increased reaction durations and decreased quantities of the sorbent, as shown in Figure 29.

Figure 29. Effects of sorbent amounts on absorption of H_2S into TU-24 sorbent in the presence of initial 14.7-psia H_2 and 0.085-g moisture at 500°C.



Reaction rates of H_2S with the TU-24 sorbent at 500°C were obtained from the experimental data of H_2S concentrations at various reaction durations, as shown in Figure 30. Reaction rates of H_2S with the TU-24 sorbent at 500°C increase with increased amounts of the sorbent, and decrease with increased reaction durations.

Figure 30. Reactivity of 100-200 mesh TU-24 sorbent with initial 8702-ppm H_2S in the presence of 0.085-g moisture and initial 14.7-psia hydrogen at 500°C.

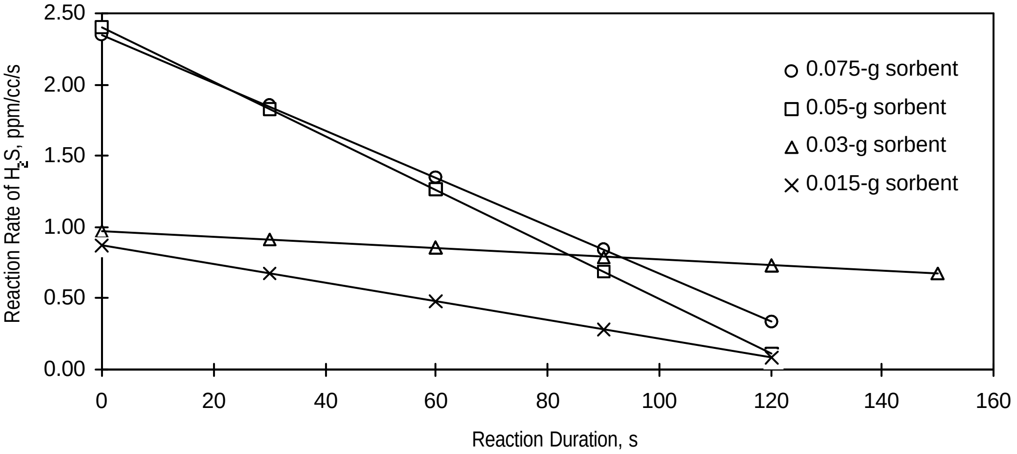
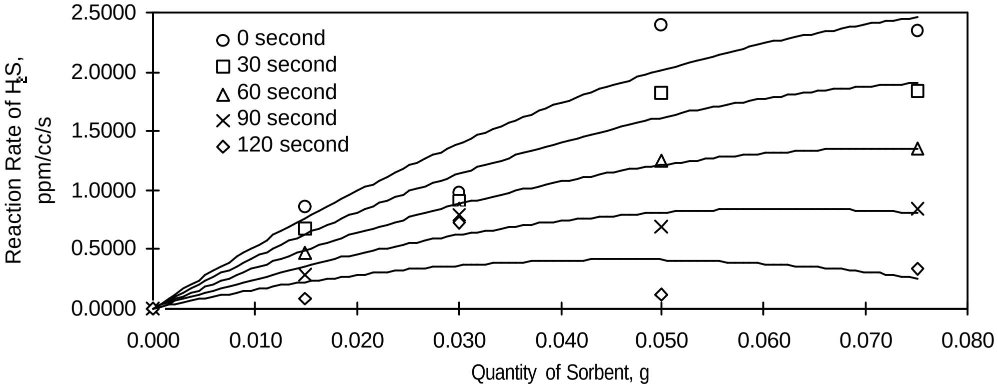


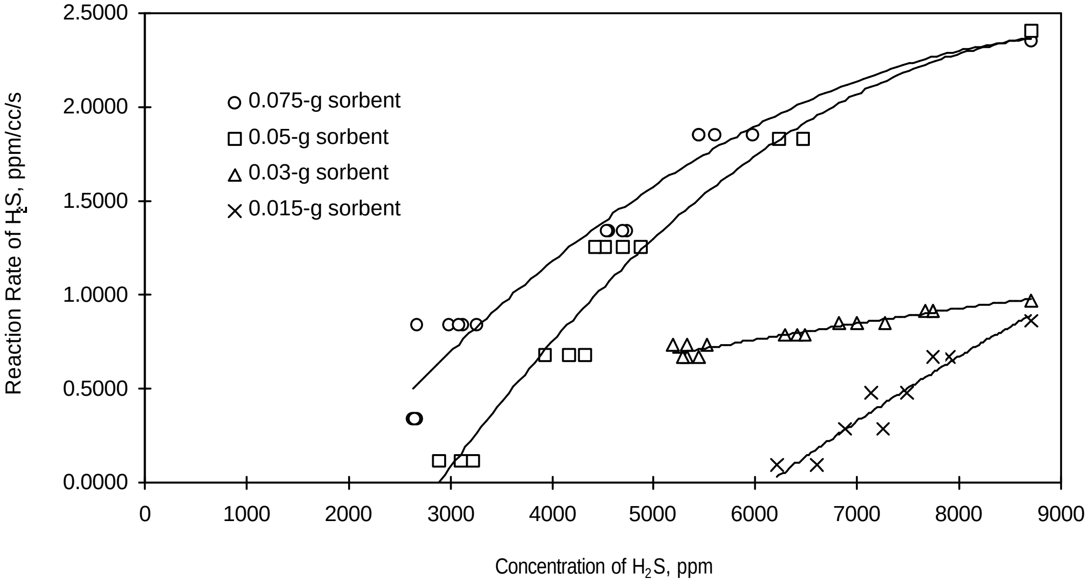
Figure 31 shows that reaction rates of H_2S with the 100 - 200 mesh TU-24 sorbent increase with increased quantities of the sorbent and decreased reaction durations. Figure 32 shows that reaction rates of H_2S with the TU-24 sorbent increase with increased quantities of the sorbent as well as increased concentrations of H_2S.

Figure 31. Reaction rates of H_2S with 100-200 mesh TU-24 sorbent in the presence of initial 14.7-psia H_2 and 0.085-g moisture at 500°C and various quantities of the sorbent.



The following reaction rate equation may be proposed, since reaction rates of H_2S with TU-24 sorbent are dependent on concentrations of H_2S and quantities of the sorbent, as shown in Figures 31 and 32.

Figure 32. Reaction rates of H_2S with 100-200 mesh TU-24 sorbent in the presence of initial 14.7-psia H_2 and 0.085-g moisture at 500°C.



$$-r_A = k_A C_A^{\alpha} M_S^{\beta} \qquad (5)$$

where $-r_A$: reaction rates of H_2S, g-mole/cm^3/s
C_A: concentrations of H_2S, g-mole/cm^3
M_S: quantities of sorbents, g/cm^3
k_A: reaction rate constant in terms of disappearance of H_2S, cc$^{(\alpha+\beta-1)}$/g$^{\beta}$/g-mole$^{(\alpha-1)}$/s
α: reaction order with respect to concentrations of H_2S
β: reaction order with respect to quantities of sorbents
cc: cm^3

The equation (5) is linearized by applying a logarithm to the both sides of the proposed reaction rate equation. The following linearized equation is obtained to evaluate k_A, α and β.

$$\ln(-r_A) = \ln(k_A) + \alpha\ln(C_A) + \beta\ln(M_S) \qquad (6)$$

The experimental data of H_2S concentrations at various reaction durations are applied to equation (6), and then the reaction rate equation constant k_A and the reaction orders such as α and β are obtained using the multiple linear regression method as well as the Gauss-Seidel method, as shown in equation 3.

$$-r_A = 9908 C_A^{1.5165} M_S^{1.1397} \qquad (7)$$

The reaction rate constant k_A in terms of disappearance of H_2S was found to be 9908 cm$^{4.9686}$/g$^{1.1397}$/g-mole$^{0.5165}$/s at the reaction temperature 500°C. The reaction order α with respect to concentrations of H_2S was found to be 1.5165, while the reaction order β with respect to quantities of the TU-24 sorbent was found to be 1.1397.

Differential Reactor

A series of experiments on absorption of H_2S into the sorbent were carried out for 5 – 150 seconds at 105 psia and 530°C to find effects of H_2S concentrations on initial reaction of H_2S with the sorbent. The concentrations of moisture and hydrogen are maintained at 10-vol % and 15 vol %, respectively. The concentrations of hydrogen sulfide in the simulated coal gas mixture are 2500 –7500 ppm. Absorption of H_2S decreases with increased concentrations of H_2S for short absorption durations of 5 – 150 seconds (see Figure 33). These observations may indicate that hydrogen sulfide absorbed into the porous matrix of the sorbent retards transfer of H_2S into micro pores of the sorbent with increased concentrations of H_2S.

A series of experiments on absorption of H_2S into the sorbent were carried out for 5 – 150 seconds at 105 psia and 530°C to find effects of moisture concentrations on initial reaction of H_2S with the sorbent. The concentrations of H_2S and hydrogen are maintained at 5000 ppm and 15 vol %, respectively. The concentrations of moisture in the simulated coal gas mixture are 0 – 10 vol %. Initial absorption of H_2S into the sorbent increases with increased concentrations of moisture for short absorption durations of 5 – 150 seconds (see Figures 34 and 35). These facts may indicate that moisture, ligher than H_2S, enhances mobility of H_2S through the porous matrix of the sorbent.

Figure 33. Effects of concentrations of H_2S on its absorption into 0.1-g TU-188 sorbent with 10 vol % moisture and 15 vol % H_2 at 300 scc/min gas flow rate and 530°C.

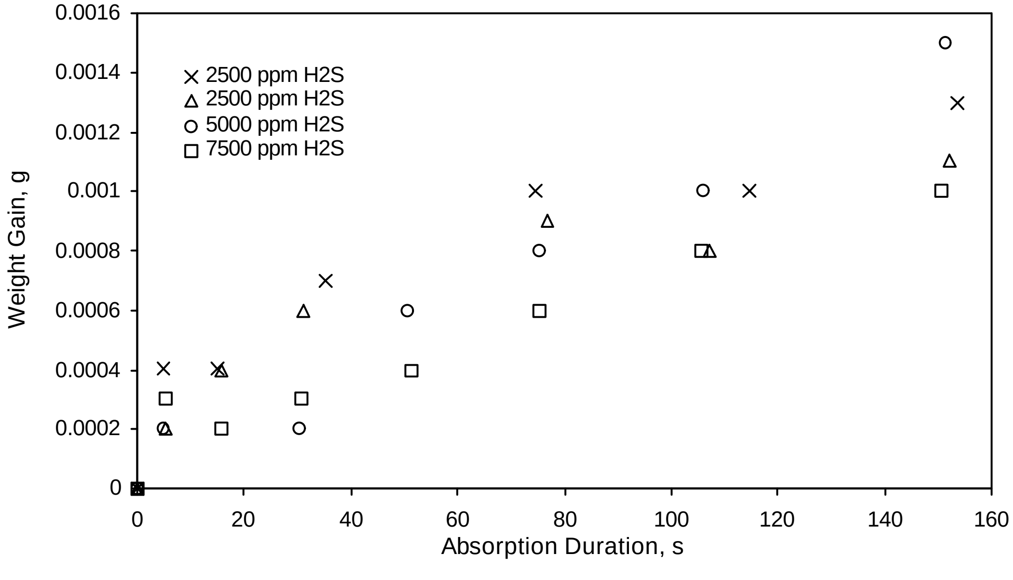
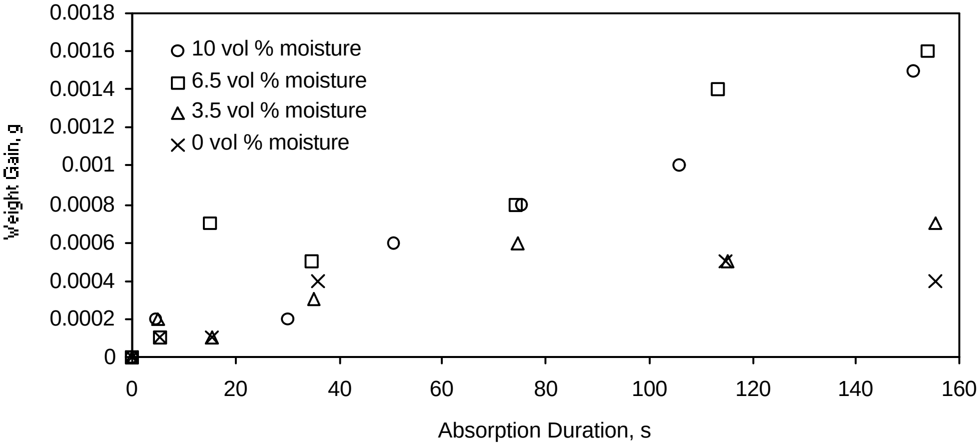


Figure 34. Effects of moisture on absorption of 5000-ppm H_2S into 0.1-g TU-188 sorbent with15 vol % H_2 and 300 scc/min gas flow rate at 530°C.



A series of experiments on absorption of H_2S into the sorbent were carried out for 5 – 150 seconds at 105 psia at 530°C to find effects of hydrogen concentrations on initial reaction of H_2S with the sorbent. The concentrations of H_2S and moisture are maintained at 5000 ppm and 10 vol %, respectively. The concentrations of hydrogen in the simulated coal gas mixture are 0 - 33 vol %. Initial absorption of H_2S into the sorbent increases with increased concentrations of hydrogen for short absorption durations of 5 – 150 seconds at 300 scc/min total gas flow rate as well as 100 scc/min total gas flow rate (see Figures 36 and 37). These results may suggest that a reducing gas such as hydrogen increase active surface area accessible to H_2S by the reaction of hydrogen with the porous metal oxide matrix of the sorbent and enlarging pore diameters of the sorbent.

Figure 35. Effects of moisture on absorption of 5000-ppm H_2S on 0.1-g TU-188 sorbent with 300 scc/min gas flow rate and 15 vol % H_2 at 530°C.

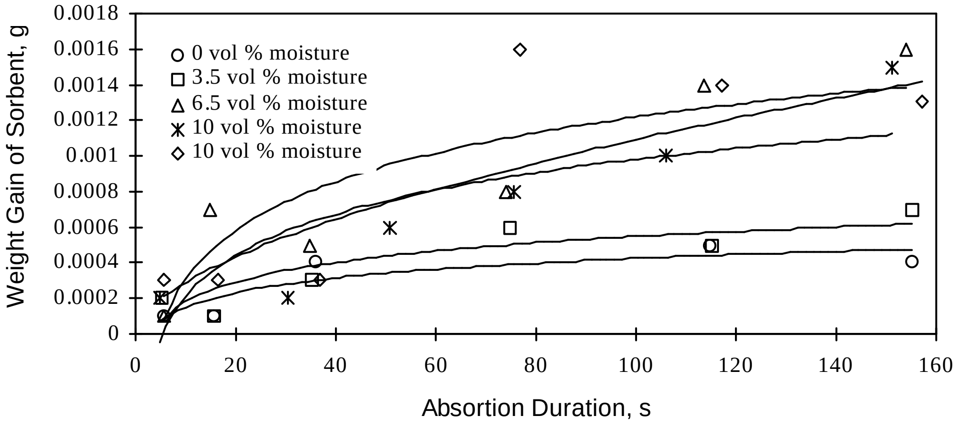
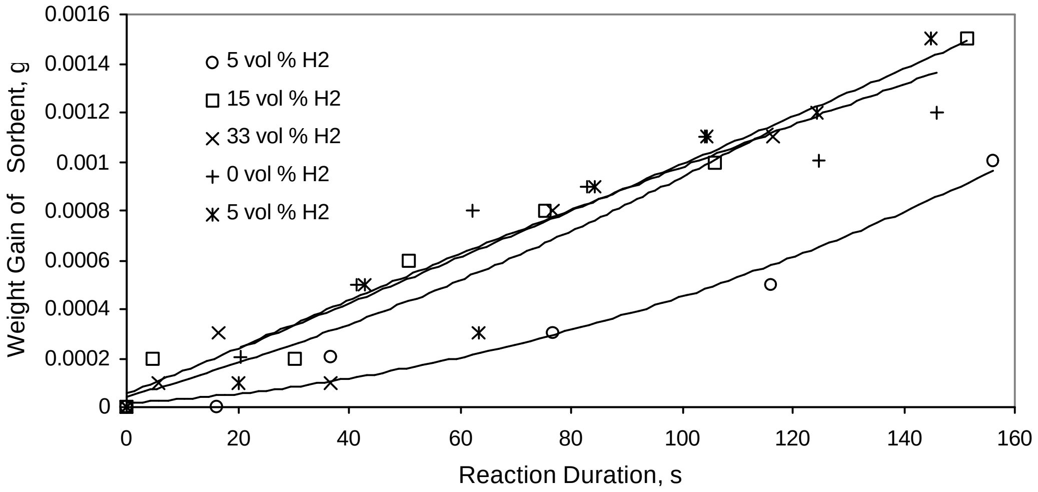


Figure 36. Effects of hydrogen on absorption of 5000-ppm H_2S into 0.1-g TU-188 sorbent with 10 vol % moisture and 300 scc/min gas flow rate at 530°C.



Effective Intrapaarticular Diffusivity

A series of experiments on absorption of H_2S into the sorbent were carried out for 30 – 12000 seconds at 105 psia and 530°C to find effects of hydrogen concentrations on effective diffusivity of H_2S with the sorbent. The concentrations of H_2S and moisture are maintained at 5000 ppm and 10 vol %, respectively. The concentrations of hydrogen in the simulated coal gas mixture are 10 – 40 vol %. The total gas flow rate of gas is maintained at 100 scc/min. The experimental data, shown in Figure 38, were applied to the unreacted core model (see Equation 8) to find the effective diffusivity of hydrogen sulfide into the sorbent.

Figure 37. Effects of hydrogen on absorption of 5000-ppm H_2S into 0.1-g TU-188 sorbent with 10 vol % water and 100 scc/min gas flow rate at 530°C.

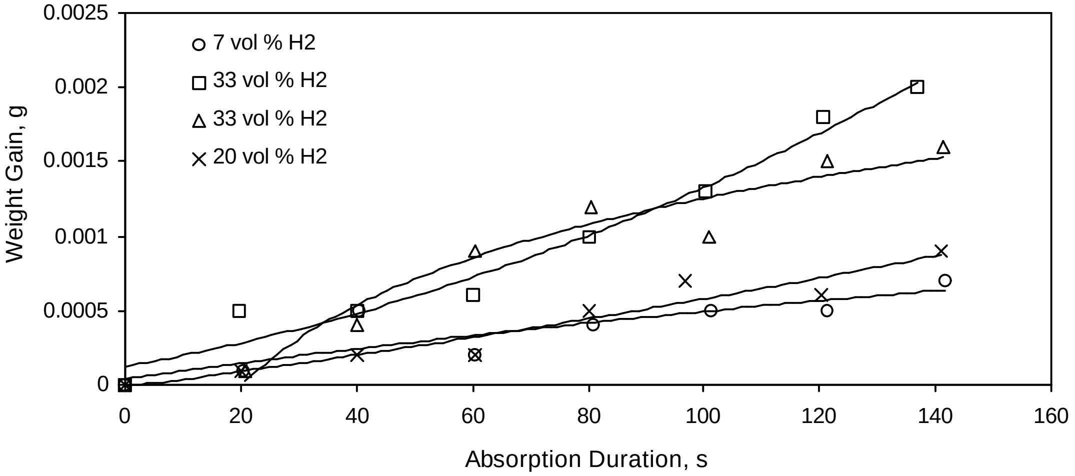
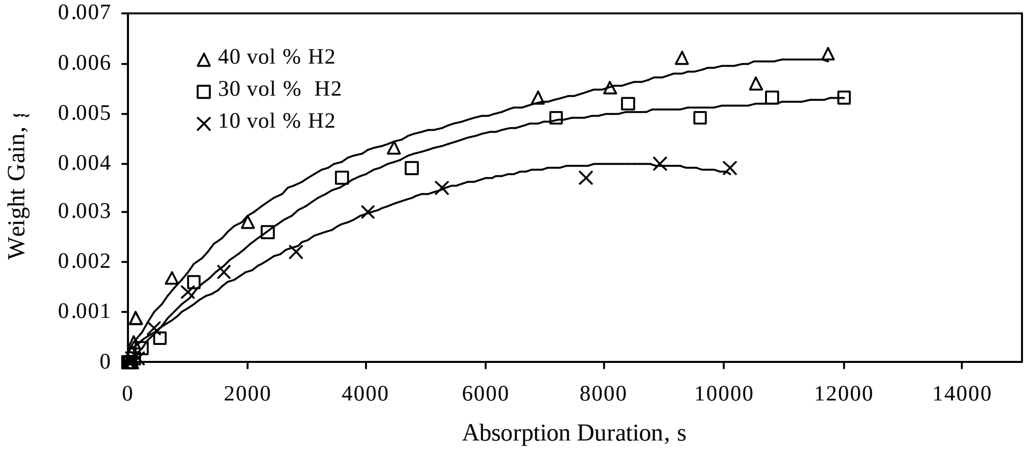


Figure 38. Effects of hydrogen on absorption of 5000-ppm H_2S into 0.1-g TU-188 sorbent with 10 vol % water and 100 scc/min gas flow rate at 530 °C.



$$\left[\ 1-3\left(\frac{r_C}{R}\right)^2+2\left(\frac{r_C}{R}\right)^3\ \right]=\frac{6bdC_{Ag}}{r_B R^2}t \qquad (8)$$

where r_C: radius of the unreacted core.
R: geometric average radius of a particle.
b: stoichiometry.
δ: effective diffusivity
C_{Ag}: concentration of an active gas
ρ_B: bulk density of particles
t: reaction duration

The effective diffusivity of H_2S into the Tu-188 sorbent is 0.51×10^{-3} cm^2/s in the presence of 10-vol % hydrogen. The effective diffusivity of H_2S into the sorbent is 0.31×10^{-3} cm^2/s in the presence of 30-vol % hydrogen. The effective diffusivity of H_2S into the sorbent is 0.24×10^{-3} cm^2/s in the presence of 40-vol % hydrogen. The magnitude of these diffusivity values of H_2S are agreeable with the value obtained from the unreacted-core cylindrical rod model, where the experimental data were obtained from the 35-cc batch reactor at 500°C. These experimental data indicate that hydrogen concentrations affect significantly intraparticle diffusivity of H_2S into the sorbent (see Figure 39).

A series of experiments on absorption of H_2S into the sorbent were carried out for 30 – 25000 seconds at 105 psia and 530°C to find effects of hydrogen concentrations on equilibrium absorption of H_2S with the sorbent. The concentrations of H_2S and moisture are maintained at 5000 ppm and 10-vol %, respectively. The equilibrium absorption of hydrogen sulfide in the sorbent increases with increased hydrogen concentrations (see Figures 38 and 40). These experimental results may explain that a reducing gas such as hydrogen increases absorption capacity of the sorbent by the reaction of hydrogen with the porous metal oxide matrix of the sorbent. The reaction of hydrogen with the sorbent may result in increasing pore sizes as well as active surface areas of the sorbent in favor of absorption of H_2S. These observations appear to be agreeable with those shown in Figures 36 and 37.

Figure 39. Left-side values of the unreacted core model against absorption durations.

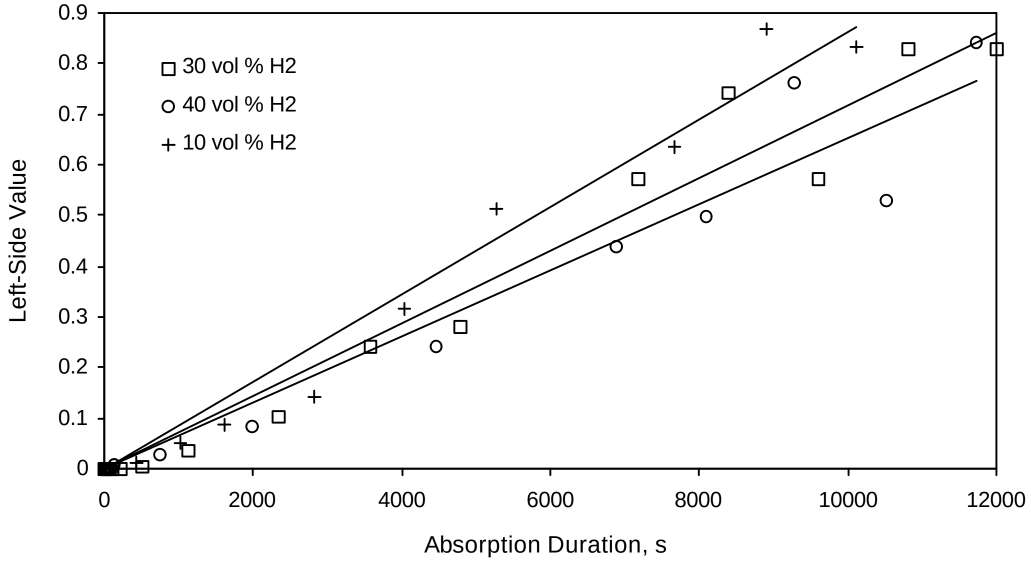
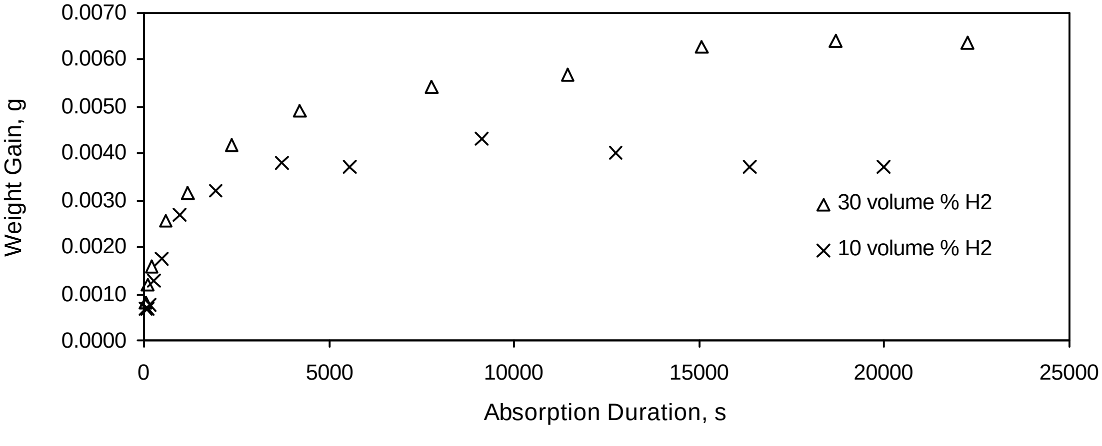


Figure 40. Effects of hydrogen on absorption of 5000-ppm H_2S into 0.1-g TU-188 sorbent with 10-volume % moisture and 300 scc/min gas flow rate at 530°C



Space Time

A series of experiments on effects of space (residence) times on dynamic absorption of H_2S into the sorbent were conducted at the 100 scc/min (0.36 s residence time) and the 300 scc/min (0.12 s residence time). Decreased residence time results in increased dynamic absorption of H_2S into the sorbent. These observations may suggest that transfer rate of H_2S

from the reactive gas mixture toward the surface of the porous solid sorbent particles affect significantly dynamic absorption of H_2S into the sorbent. These data may indicate that space times do not affect equilibrium absorption capacity of the sorbent in the presence of H_2S as an absorbed reactive gas (see Figure 41).

Figure 41. Effects of residence time of gas on absorption of 5000-ppm H_2S into 0.1-g TU-188 sorbent with 10 vol % moisture at 530 ^{o}C.

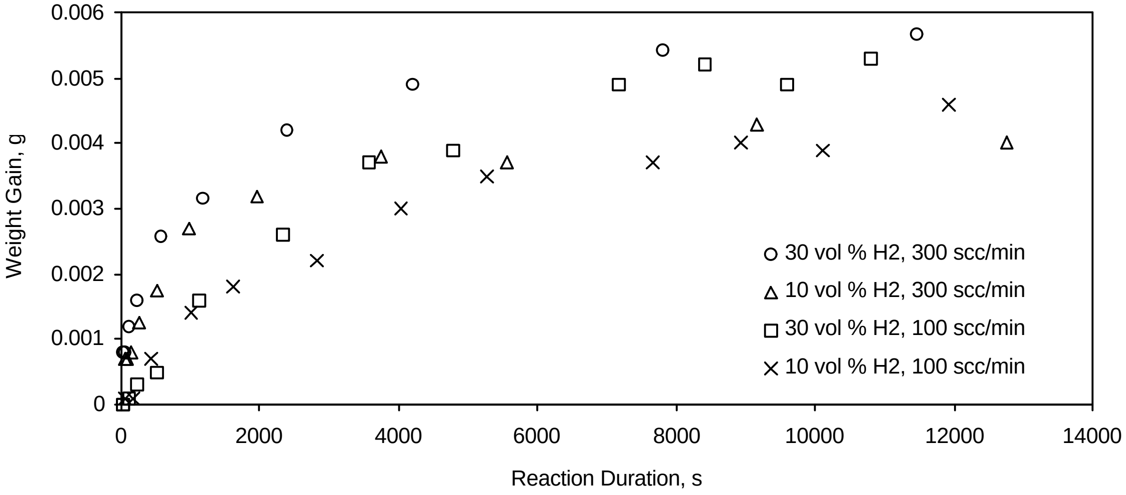
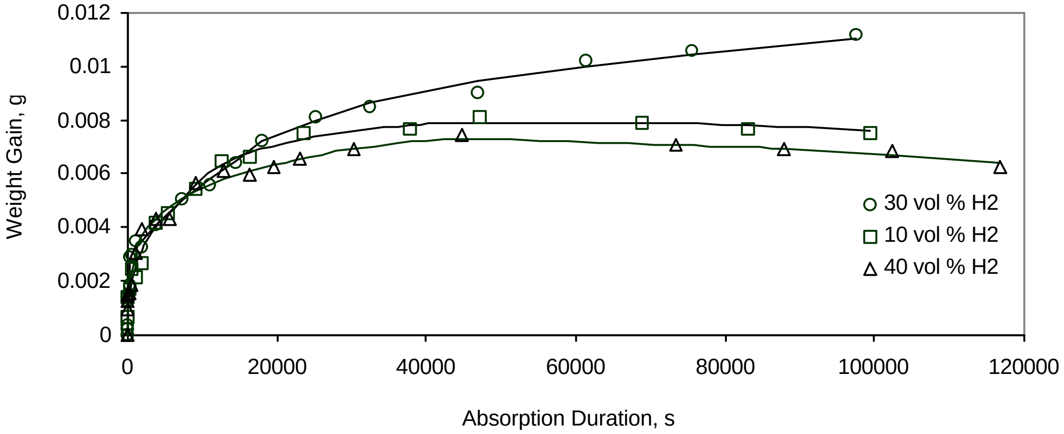


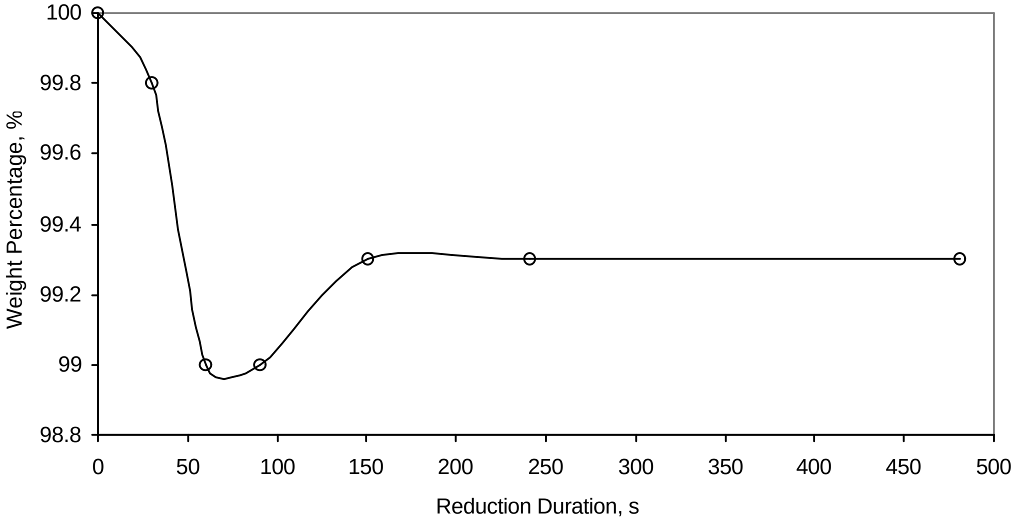
Figure 42. Effects of hydrogen on equilibrium absorption of 2500-ppm H_2S into 0.1-g TU-188 sorbent with the 10-volume % moisture at 530 ^{o}C.



Effects of Hydrogen

A series of experiments on equilibrium absorption of H_2S into the sorbent were carried out for 5 – 120000 seconds at 105 psia and 530^{o}C to find effects of hydrogen concentrations on equilibrium absorption of H_2S into the sorbent in the presence of 10-vol % moisture and 2500-ppm H_2S. Absorption of H_2S appear to either decrease or increase with increased concentrations of H_2S for long absorption durations (see Figure 42). Absorption of H_2S into the sorbent in the presence of 30-vol % hydrogen increases with increased absorption duration for the 28-hr absorption duration. These observations suggest that equilibrium absorption of H_2S into the sorbent can not be reached for the 28-hr absorption duration. Absorption of H_2S into the sorbent in the presence of 10-vol % hydrogen decreases slightly with increased absorption duration for the 28-hr absorption duration. These observations may inidicate that molecular hydrogen reduces the porous matrix of the metal oxide sorbent for the 28-hr absorption duration.

Figure 43. Weight loss of 0.1-g TU-188 sorbent in reduction reaction with hydrogen in the absence of H_2S at 300 scc/min gas flow rate and 530 ^{o}C.



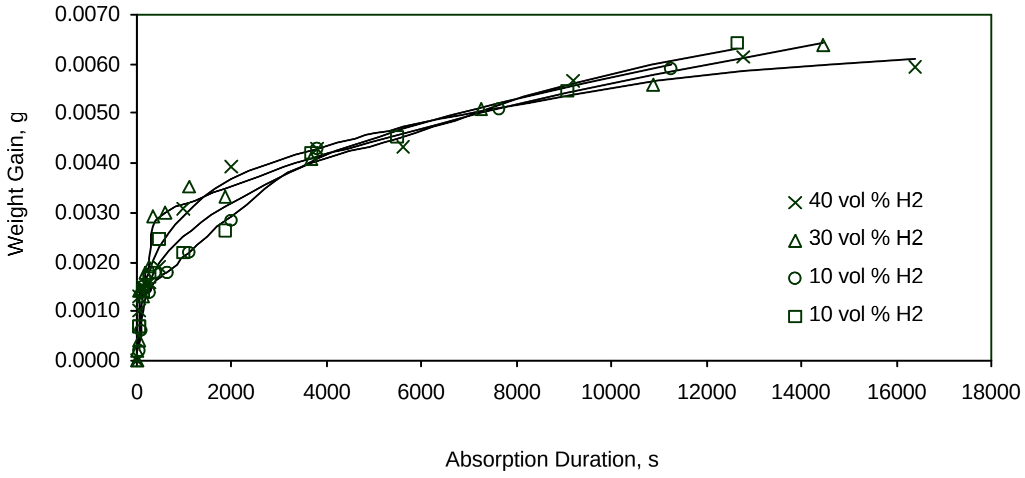
Reduction Reaction with Hydrogen

A series of reduction experiments were carried out in the presence of 10 vol % H_2, 10 vol % moisture, and 80 vol % N_2 for 30 – 24000 seconds at 105 psia and 530^{o}C to understand reduction reaction of the sorbent with wet hydrogen. The weight of the sorbent decrease significantly for the reduction duration of 8 min (see Figure 43). All the experiments on absorption of H_2S into sorbents were conducted with the sorbent reduced with hydrogen under the same experimental conditions as those of absorption experiments.

Surface Reaction Control and Pore Diffusion Control

A series of experiments on absorption of H_2S into the sorbent were carried out for 30 – 15000 seconds at 105 psia and 530^{o}C to investigate reaction mechanisms on the gaseous H_2S-solid metal oxide heterogeneous reaction system. The weight gain of the sorbent increases drastically during the initial absorption stage, and then increases slowly with increased absorption duration (see Figure 44). The transitional reaction control from the surface reaction control to the pore diffusion control appears to be pronounced with increased concentrations of hydrogen in the simulated wet coal gas mixtures.

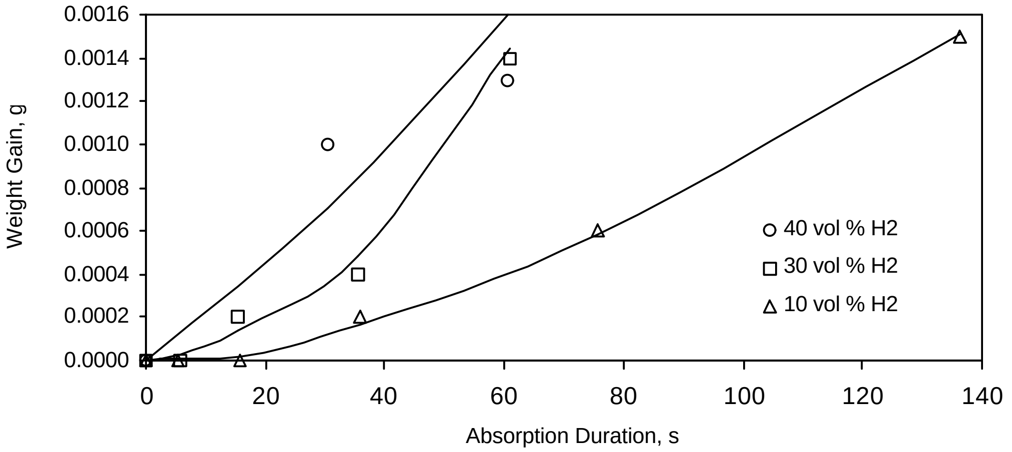
Figure 44. Effects of hydrogen on transition of reaction control in the absorption of 2500-ppm H_2S into 0.1-g TU-188 sorbent with the 10-volume % moisture at 530 ^{o}C.



Effects of Hydrogen on Surface Reaction

A series of experiments on absorption of H_2S into the sorbent were carried out for 6 – 140 seconds at 105 psia at 530^{o}C to investigate effects of hydrogen on initial absorption of H_2S into the solid sorbent (see Figure 45). Initial surface reaction of wet H_2S with the solid sorbent increases with increased concentrations of hydrogen. These facts may indicate that concentrations of hydrogen affects significantly the initial surface reaction control.

Figure 45. Effects of hydrogen on initial absorption of 2500-ppm H_2S into 0.1-g TU-188 sorbent with the 10-volume % moisture at 530 ^{o}C.



A series of experiments on absorption of H_2S into the sorbent were carried out for 6 – 950 seconds at 105 psia and 530^{o}C to find effects of temperature on initial dynamic absorption of H_2S with the sorbent. The concentrations of both moisture and hydrogen are maintained at 10-vol %. The concentration of hydrogen sulfide in the simulated coal gas mixture is 2500 ppm. Absorption of H_2S decreases generally with increased absorption temperature for short absorption durations of 5 – 950 seconds (see Figure 46). These observations may indicate that reduction reaction of the metal oxide sorbent with hydrogen may be dominant over absorption reaction of the metal oxide sorbent with hydrogen sulfide at increased absorption temperature.

Figure 46. Effects of temperature on absorption of 2500-ppm H_2S into 0.1-g TU-188 sorbent in the 10-volume % moisture and 10-volume % hydrogen at the 0.072-s space time.

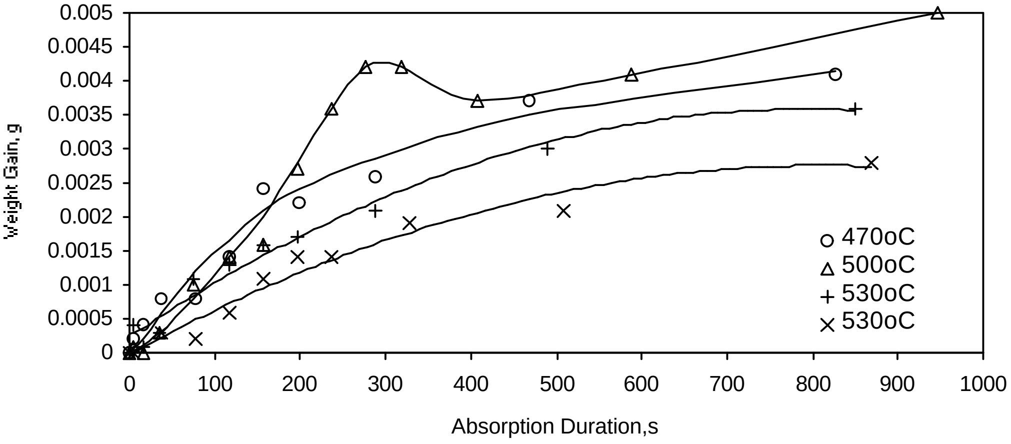
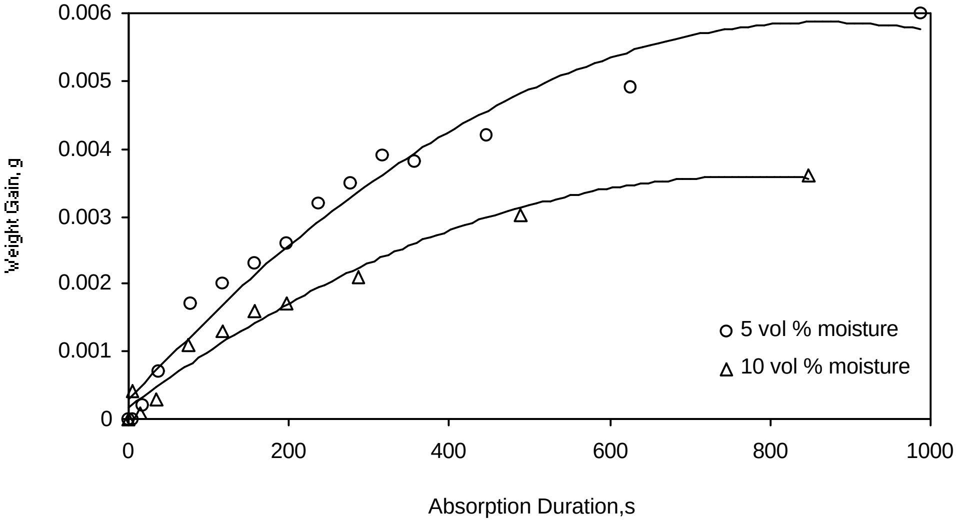
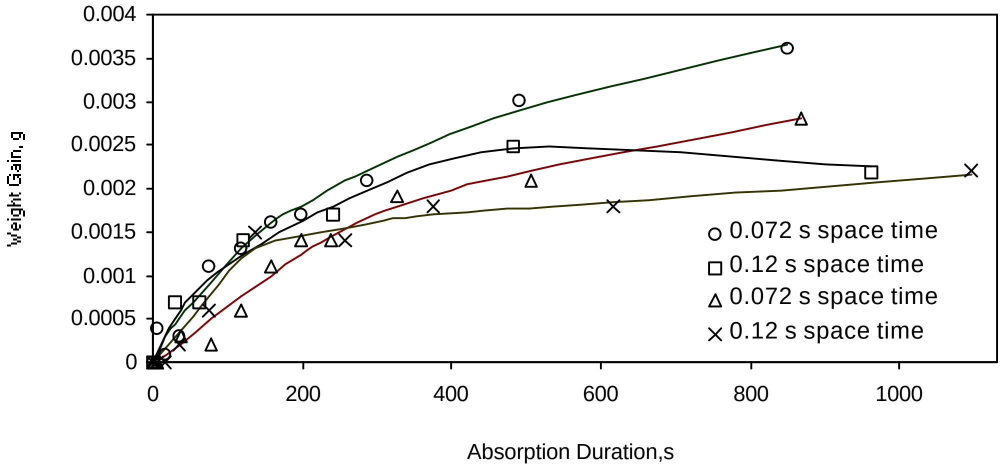


Figure 47. Effects of moisture on initial absorption of 2500-ppm H_2S into 0.1-g TU-188 sorbent with10-volume % hydrogen at the 0.072-s space time and 530 ^{o}C.



A series of experiments on absorption of H_2S into the sorbent were carried out for 6 – 970 seconds at 105 psia and 530^{o}C to find effects of moisture on initial dynamic absorption of H_2S with the sorbent. The concentrations of H_2S and hydrogen are maintained at 2500 ppm and 10 vol %, respectively. The concentrations of moisture in the simulated coal gas mixture are 5 – 10 vol %. Initial absorption of H_2S into the sorbent increases with decreased concentrations of moisture for short absorption durations of 5 – 970 seconds (see Figure 47). These facts may indicate that moisture, ligher than H_2S, retard initial surface reaction of the metal oxide sorbent by oxygen dissolved into distilled water. Distilled water fed into the reactor is evaporated in the preheater.

Figure 48. Effects of space time on initial absorption of 2500-ppm H_2S into 0.1-g TU-188 sorbent with10-volume % hydrogen and 10 vol % moisture at the 0.072-s space time and 530°C.



A series of experiments on effects of space (residence) times on initial dynamic absorption of H_2S into the sorbent were conducted for the reaction duration of 6 – 1100 seconds at the 300 scc/min (0.12 s residence time) and the 500 scc/min (0.072 s residence time). Space time does not affect significantly initial dynamic absorption of H_2S into the sorbent under these absorption conditions. These observations may suggest that transfer rate of H_2S from the reactive gas mixture toward the outer surface in the macro porous matrix of the solid sorbent particles does not affect significantly initial dynamic absorption of H_2S into the sorbent under these absorption conditions (see Figure 48).

CONCLUSIONS

The following conclusions are drawn, based on experimental data generated from a batch reactor as well as a differential reactor, and their interpretations.

- The cylindrical rod model was developed with the unreacted core assumption and the quasi steady state assumption to determine intraparticle diffusivity of hydrogen sulfide into metal oxide sorbents. The intraparticle diffusivity of H_2S into the 1-mm TU-28 sorbent was found to be 2.018×10^{-3} cm^2/s at 500°C.

- Equilibrium absorption of H_2S into the TU-19 sorbent increases with concentrations of H_2S. Partial pressures of hydrogen appear to affect significantly equilibrium absorption of

H_2S into the sorbent.

- The reaction rate equation in terms of disappearance of H_2S for 30 -150 seconds at 500°C was developed with the experimental data in order to determine a reaction rate constant in terms of disappearance of H_2S, a reaction order with respect to concentrations of H_2S, and a reaction order with respect to quantities of the solid 100 - 200 mesh TU-24 sorbent. The reaction rate constant in terms of disappearance of H_2S was found to be 9908 $cm^{4.9686}/g^{1.1397}/g\text{-}mole^{0.5165}/s$ at the reaction temperature 500°C. The reaction order with respect to the concentration of H_2S was found to be 1.5165, while the reaction order with respect to the quantity of the TU-24 sorbent was found to be 1.1397.

- Effects of hydrogen partial pressures on reactivity of the 100-200 mesh TU-25 sorbent were investigated in the presence of 0.085-g moisture for 1 min at 500°C. Reactivity of the TU-25 sorbent with H_2S was found to be significantly affected by partial pressures of hydrogen. Dynamic absorption of H_2S into the sorbent also is affected by partial pressures of hydrogen. Dynamic absorption of H_2S into the 100-200 mesh TU-25 sorbent decreases with increased sorbent quantities and decreased reaction temperatures.

- Hydrogen sulfide absorbed into the porous matrix of the sorbent retards transfer of H_2S into micro pores of the sorbent with increased concentrations of H_2S.

- A reducing gas such as hydrogen increases active surface area accessible to H_2S by the reaction of hydrogen with the porous metal oxide matrix of the sorbent and enlarging pore diameters of the sorbent.Hydrogen concentrations affect significantly intraparticle diffusivity of H_2S into the sorbent. A reducing gas such as hydrogen increases absorption capacity of the sorbent by the reaction of hydrogen with the porous metal oxide matrix of the sorbent. The reaction of hydrogen with the sorbent may result in increasing pore sizes as well as active surface areas of the sorbent in favor of absorption of H_2S. Concentrations of hydrogen affects significantly the initial surface reaction of the solid metal oxide sorbent with wet hydrogen.

- Equilibrium absorption of H_2S into the sorbent can not be reached in the presence of 30-vol % hydrogen for the 28-hr absorption duration. Equilibrium absorption of H_2S into the sorbent in the presence of 10-vol % hydrogen decreases slightly with increased absorption duration for the 28-hr absorption duration. These observations may inidicate that molecular hydrogen reduces the porous matrix of the metal oxide sorbent for the 28-hr absorption duration.

- The transitional reaction control from the surface reaction control to the intraparticular pore diffusion control appears to be pronounced with increased concentrations of hydrogen in the simulated wet coal gas mixtures.

- The weight of the sorbent in the absence of H_2S decrease significantly in the reduction reaction of the sorbent with hydrogen for the reduction duration of 8 min. Reduction reaction of the metal oxide sorbent with hydrogen may be dominant over initial absorption reaction of the metal oxide sorbent with hydrogen sulfide at higher absorption temperature.

- Moisture, ligher than H_2S, enhances mobility of H_2S through the porous matrix of the sorbent. Moisture, ligher than H_2S, may retard initial surface reaction of the metal oxide sorbent by oxygen dissolved into distilled water. Distilled water containing dissolved air is fed into the preheater to produce steam, where gaseous oxegen is released.

- Transfer rates of H_2S from the reactive gas mixture toward the outer surface in the macro porous matrix of the solid sorbent particles may not affect significantly initial dynamic absorption of H_2S into the sorbent at the space time of 0.072 - 0.12 seconds and 530^{o}C. Space times do not affect equilibrium absorption capacity of the sorbent in the presence of H_2S as an absorbed reactive gas.

PRESENTATION/PUBLICATION

“Reaction Kinetics on Removal of Hydrogen Sulfide with Metal Oxide Sorbents at High Temperatures and Pressures”, was presented at the Ninth Symposium on SEPARATION SCIENCE AND TECHNOLOGY FOR ENERGY APPLICATIONS, Park Vista Hotel & Convention Center, Gatlinburg, Tennessee, October 22-26, 1995.

“Removal of Hydrogen Sulfide from Simulated Coal Gases, Using Metal Oxide Sorbents at High Temperature and High Pressure “, presented at The Fourth Annual HBCU/Private Sector-Energy Research and Development Technology Transfer Symposium, Greensboro, North Carolina, April 2-4, 1996.

“Reaction Kinetics on Removal of Hydrogen Sulfide with Metal Oxide Sorbents at High Temperature and Pressure”, Separation Science and Technology, V. 32, No. 1-4, Pg. 775-792, 1997.

“Effects of moisture and hydrogen on removal kinetics of hot hydrogen sulfide with metal oxide sorbents”, presented at Tenth Symposium on Separation Science and Technology for Energy Applications, Park Vista Hotel & Convention Center, Gatlinburg, Tennessee, October 20-24, 1997.

“Reactivity of metal oxide sorbents with hot hydrogen sulfide in wet coal gases” ,presented at the 1998 Spring National Meeting, Sheraton New Orleans Hotel, New Orleans, LA, March 8-12, 1998.

“Reactivity of formulated metal oxide sorbents with hot hydrogen sulfide”, submitted for publication in Separation Science and Technology

“Reactivity of Metal Oxide Sorbents”, presented at the Advanced Coal-Fired Power Systems ‘96 Review Meeting, Morgantown Energy Technology Center, West Virginia, July 16-18, 1996.

“Reactivity of Promising Metal Oxide Sorbents for Removal of Hydrogen Sulfide from Hot Coal Gases”, presented for the Session 110-Reactive Separation Processes I at 3:35 PM, November 13, 1996, 1996 Annual AIChE Meeting, Chicago, November 10 -15, 1996.

“Formulation of Metal Oxide Sorbents for Removal of Wet Hydrogen Sulfide”, presented at the 1997 Spring National AIChE Meeting, Houston, March 9 - 13, 1997.

“Reactivity of Metal Oxide Sorbents for Removal of Wet Hydrogen Sulfide at High Temperatures”, presented at the Fifth Annual HBCU/Private Sector-Energy Research and Development Technology Transfer Symposium, Baton Rouge, Louisiana, March 4-5, 1997

“Reactivity of Metal Oxide Sorbents for Removal of Wet Hydrogen Sulfide at High Temperatures”, was published in the Proceedings of the Fifth Annual HBCU/Private Sector-Energy Research and Development Technology Transfer Symposium, Baton Rouge, Louisiana, March 4-5, 1997.

“Effects of Moisture and Hydrogen on Absorption of Hot Hydrogen Sulfide into Formulated Metal Oxoide Sorbents”, presented at the 1997 Annual AIChE Meeting, Los Angeles, November 1997.

Filename: FINAL-R.RTF
Directory: C:\REPORT\FINAL-R
Template: C:\MSOFFICE\WINWORD\TEMPLATE\NORMAL.DOT
Title: Investigation on Durability and Reactivity of Promising Metal
Subject:
Author: Word Development
Keywords:
Comments:
Creation Date: 09/01/98 5:03 PM
Revision Number: 1
Last Saved On: 09/01/98 5:13 PM
Last Saved By: Kyung C. Kwon
Total Editing Time: 14 Minutes
Last Printed On: 09/08/98 4:38 PM
As of Last Complete Printing
  Number of Pages: 46
  Number of Words: 8,026 (approx.)
  Number of Characters: 45,750 (approx.)

Investigation on Durability and Reactivity of Promising Metal Oxide Sorbents during Sulfidation and Regeneration

Technical Progress Report for the Period
April 1 to June 30, 1998

Final Report - Appendix (Formulation of Sorbents)

K. C. Kwon

August 1998

Work Performed Under Contract No.: DE-FG21-94MC31206

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ABSTRACT

Hot-gas desulfurization for the integrated gasification combined cycle (IGCC) process has been investigated by many researchers to remove effectively hydrogen sulfide with various metal oxide sorbents at high pressures and high temperatures. Metal oxides such as zinc titanate oxides, zinc ferrite oxide, copper oxide, manganese oxide and calcium oxide, were found to be promising sorbents in comparison with other removal methods such as membrane separations and reactive membrane separations. Some metal oxide sorbents exhibited the quite favorable performance in terms of attrition resistance and sulfur capacity. Removal reaction of H_2S from simulated coal gas mixtures with promising sorbents was performed in a batch reactor to formulate durable metal oxide sorbents with high-sulfur-absorbing capacity for the IGCC process.

The objectives of this research project are to formulate promising durable metal oxide sorbents for removal of sulfur compounds from simulated coal gas mixtures, to find initial reaction kinetics for a sorbent-hydrogen sulfide heterogeneous reaction system, to obtain effects of concentrations of coal gas components such as hydrogen and moisture on equilibrium absorption as well as dynamic absorption of hydrogen sulfide into formulated sorbents for the reaction system at various reaction temperatures, and to obtain effects of concentrations of coal gas components such as hydrogen and moisture on reaction rates of hydrogen sulfide with formulated sorbents at various reaction temperatures.

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SCHEDULE AND MILESTONES

	FY 1994-1995												FY 1995-1996											
	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Procurements of Materials and Equipment	━	━	━	━																				
Fabrication of a Micro Batch Reactor						━	━	━	━															
Development of Analytical Procedures for Concentrations of Sulfur compounds					━	━	━	━	━	━	━	━												
Development of Experimental Procedures for Sulfidation Reaction of Fresh Metal Oxide Sorbents						━	━	━	━	━	━	━												
Formulation of Durable Metal Oxide Sorbents with High-Sulfur Removal Capacity												━	━	━	━	━	━	━	━	━	━	━	━	━
Reaction Kinetics on Sulfidation of Metal Oxide Sorbents										━	━	━	━	━	━	━	━	━	━	━	━	━	━	━
Reaction Kinetics on Regeneration of Sulfur-loaded Metal Oxide Sorbents																		━	━	━	━	━	━	━
Development of an Intraparticle Diffusivity Model for Sulfidation of Metal Oxide Sorbents													━	━	━									
Delineation of Effects of Hydrogen Partial Pressures and Moisture Amounts on Sulfidation of Metal Oxide Sorbents										━	━	━	━	━	━	━	━	━						
Equilibrium Absorption of Hydrogen Sulfide into Metal Oxide Sorbents													━	━	━	━	━	━	━	━	━	━	━	━
Development of a Micro Differential Reactor													━	━	━	━	━	━	━	━	━	━	━	━

EXECUTIVE SUMMARY

This appendix of the final report includes formulating metal oxide sorbents using various ingredients as well as formulation conditions, and testing reactivity of formulated metal oxide sorbents with hydrogen sulfide for 120 seconds at 550^{o}C, and develop a formula of a sorbent suitable for removal of hydrogen sulfide from coal gases. Reactivity of formulated sorbents was tested in a batch reactor. Hardness of formulated sorbents was tested with a hardness tester.

INTRODUCTION

Metal oxide sorbents were formulated with zinc oxide as an active sorbent ingredient, and titanium oxide as a supporting metal oxide. Various metal oxide additives such as Cu, Co, Ni, Mn, Cr, Fe, Mo and Ca were utilized to enhance sulfur-removal capacity of formulated metal oxide sorbents. This mixture was extrudated 1-mm cylindrical rods. The formulated metal oxide sorbents were calcined for 2 hours at 850 - 920^{o}C. The fresh formulated metal oxide sorbents in the form of 1-mm cylindrical rod were crushed to obtain 100 - 200 mesh particles, and were reacted with simulated coal gases containing hydrogen sulfide in the 35 cm^3 316 stainless steel batch reactor for 120 seconds at 550^{o}C. Concentrations of hydrogen sulfide were analyzed with a gas chromatograph to evaluate reactivity of formulated metal oxide sorbents with H_2S. Hardness of formulated sorbents was tested with a pellet hardness tester.

RESULTS AND DISCUSSION

This appendix of the final report includes formulating various metal oxide sorbents with various additives under various formulation conditions, testing initial reactivity of formulated sorbents with hydrogen sulfide in a batch reactor, and testing hardness of formulated sorbents with a hardness tester.

Experiments on reactivity of formulated metal oxide sorbents with hydrogen sulfide from a simulated coal gas mixture were carried out for 120 seconds at 550°C (see Table 1) to evaluate reactivity of formulated sorbents with hydrogen sulfide. A typical simulated coal gas mixture consists of 9107-ppm hydrogen sulfide (0.005 g; 1 wt %), 0.085-g water (15.84 wt %), 0.0029-g hydrogen (0.58 wt %), and 0.4046-g nitrogen (81.34 wt%).

Table 1. Experimental conditions for the reaction of hydrogen sulfide with formulated metal oxide sorbents in the presence of moisture, nitrogen and hydrogen.

Reactor Volume, cm^3:	35
Temperature, °C:	550
Pressure, psia	479
Reaction Time, s:	120
Particle Size, mesh	100 - 200
Amount of Sorbent, g	0.05
Initial Partial Pressure of Hydrogen at 25°C, psia:	14.7
Initial Amount of Water, g:	0.085
Initial Concentration of H_2S, ppm	7400
Initial Partial Pressure of Nitrogen at 25°C, psia:	150
Initial Total Pressure of Reaction Mixture at 25°C, psia:	164.7

Sorbents TU-2 through TU-56B

Metal oxide sorbents were formulated with various additives to enhance their reactivity with hydrogen sulfide from simulated coal gas mixtures (see Tables 2 through 7). Reactivity of formulated metal oxide sorbents was compared by reacting sorbents with initial 7400-ppm hydrogen sulfide for 120 seconds at 550°C (see Figures 1 and 2).

The metal oxide sorbents shown in Tables 4 through 7 were formulated with the cuprous oxide additive and the chromous oxide additive at various calcination temperatures and H_2O_2 concentrations in water.

Table 2. Formulation of sorbents TU-2 through TU-14.

Sorbents	TU-2	TU-3	TU-4	TU-5	TU-6	TU-7	TU-8	TU-9	TU-10	TU-11	TU-12	TU-13	TU-14
Amounts of Ingredients (gram) and Formulation Conditions													
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch						0.1	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Flour	0.3	0.3	0.3	0.3	0.1								
Calcium Carbonate						0.055	0.102	0.05	0.05	0.05	0.05	0.05	0.05
Bentonite	0.3	0.3	0.4	0.5	0.1	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Cobalt Oxide								0.016	0.017				
Molybdenum Oxide										0.017			
Nickel Oxide											0.016		
Cuprous Oxide												0.016	
Ferrous Oxide													0.015
Manganese Oxide													
0.5 w% H_2O_2	2.5								1.50				
1 w% H_2O_2		2	3										
2 w% H_2O_2				2.26	2	2	2	1.51		1.50	1.50	1.50	1.50
Calcination Temperature, °C	800	800	800	800	900	900	900	900	900	900	900	900	900
Calcination Duration, hr	2	2	2	2	2	2	2	2	2	2	2	2	2
H_2S, ppm at 2 min Reaction Duration	4435 4580		5140 4605	4760 4654	5443 5706	4604 4950	5293 5146	5785 5494	5179 5432	6129 5435 4554	4659 4848	4648 5040 4770	4836 5231

Table 3. Formulation of sorbents TU-15 through TU-28.

Sorbents	TU-15	TU-16	TU-17	TU-18	TU-19	TU-20	TU-21	TU-22	TU-23	TU-25	TU-26	TU-27	TU-28
Amounts of Ingredients (gram) and Formulation Conditions													
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.8	1.8	0.5	0.5	0.5	1.7
TiO_2	2	2	2	2	2	2	2	1.2	1.2	2.5	2.5	2.5	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	
Flour													0.5
Calcium Carbonate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Bentonite	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.1
Cobalt Oxide				0.015		0.017			0.018			0.015	
Molybdenum Oxide							0.016					0.015	0.016
Nickel Oxide						0.016	0.016						
Cuprous Oxide			0.015	0.015				0.016	0.015		0.015	0.015	
Ferrous Oxide													
Manganese Oxide	0.016											0.015	
0.5 w% H_2O_2													
1 w% H_2O_2													
2 w% H_2O_2	1.50	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calcination Temperature, °C	900	900	900	900	850	850	850	850	850	900	900	900	870
Calcination Duration, hr hr	2	2	2	2	2	2	2	2	2	2	2	2	2
H_2S, ppm at 2 min Reaction Duration	4684 5030	4971 5010	4134 4009	4334 4688	4767 4892	4564 4851	4644 4440	2543 3628 4100	3690 3997	6074 6382 6675	5727 6012 6236	6445 6404 5573	5680 5952

Table 4. Formulation of sorbents TU-32 through TU-44C.

Sorbents	TU-32	TU-33	TU-34	TU-35	TU-36	TU-37	TU-38	TU-39	TU-40	TU-41	TU-42	TU-43	TU-44	TU-44C
Amounts of Ingredients (gram) and Formulation Conditions														
ZnO	2	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	1	2	2	2	2	2	2	1.8	2.2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.03	0.07	0.05	0.05	0.05
Calcium Carbonate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.07	0.03	0.03
Bentonite	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.10	0.15
Cuprous Oxide	0.03	0.015	0.015	0.015	0.015	0.015	0.030	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Chromous Oxide				0.015	0.015	0.030	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
0 w% H_2O_2														
0.5 w% H_2O_2														
1 w% H_2O_2														
2 w% H_2O_2		1.5		1.5		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
5 w% H_2O_2	1.5		1.5		1.5									
Calcination Temperature, °C	900	900	900	900	900	900	900	900	900	900	900	900	900	900
Calcination Duration, hr	2	2	2	2	2	2	2	2	2	2	2	2	2	2
H_2S, ppm at 2 min Reaction Duration	3755 3813 3486	4692 4647 4690	4409 4269 4396	3503 3673 3591	5159 5158 3768	4393 4217 4346	5387 5582 5498	3170 3490 3489	3106 3333	4213 4398	3536 3659 3533	5132 5009 5041	5503 5235 4710	4325 4229 4208

Table 5. Formulation of TU-45 through TU-51C.

Sorbents	TU-45	TU-46	TU-46C	TU-47	TU-47C	TU-48	TU-49	TU-50	TU-51A	TU-51B	TU-51C
Amounts of Ingredients (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Calcium Carbonate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Bentonite	0.10	0.020	0.20	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Cuprous Oxide	0.015	0.015	0.015	0.015	0.010	0.020	0.015	0.015	0.015	0.015	0.015
Chromous Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.010	0.020	0.015	0.015	0.015
0 w% H_2O_2											
0.5 w% H_2O_2											
1 w% H_2O_2									1.5		
2 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5		1.5	
5 w% H_2O_2											1.5
Calcination Temperature, °C	900	900	900	900	900	900	900	900	900	900	900
Calcination Duration, hr	2	2	2	2	2	2	2	2	2	2	2
H_2S, ppm at 2 min Reaction Duration	5688 5359 5077	4575 4591 4474	5107 4678	3976 4286 4117	4834 4617	5476 5493 5708	4811 4879 4918	5101 5253 5232	4024 4156 4107	4774 4879 4880	5212 5447 5317

Table 6. Formulation of TU-52A through TU-54D.

Sorbents	TU-52A	TU-52B	TU-52C	TU-52D	TU-53A	TU-53B	TU-53C	TU-53D	TU-54A	TU-54B	TU-54C	TU-54D
Amounts of Ingredients (gram) and Formulation Conditions												
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Calcium Carbonate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Bentonite	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Cuprous Oxide	0.015	0.015	0.015	0.015	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02
Chromous Oxide	0.015	0.015	0.015	0.015	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02
0 w% H_2O_2	1.5	1.5	1.5	1.5								
0.5 w% H_2O_2												
1 w% H_2O_2					1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
2 w% H_2O_2												
5 w% H_2O_2												
Calcination Tempera, °C	860	880	900	920	860	880	900	920	860	880	900	920
Calcination Duration, hr	2	2	2	2	2	2	2	2	2	2	2	2
H_2S, ppm at 2 min Reaction Duration	5151	6120	5890	5662	4874	4697	4884	5108	5073	5224	5204	5348
	5473	6023	6086	5839	4566	4827	4927	4761	5239	5081	5059	5238
	5463	5903	5965	5779	4623	4827	4612	4933	5284	5014	5224	5266

Table 7. Formulation of TU-55A through TU-56B.

Sorbents	TU-55A	TU-55B	TU-55C	TU-56A	TU-56B	ZT-4
Amounts of Ingredients (gram) and Formulation Conditions						
ZnO	1.7	1.7	1.7	1.7	1.7	
TiO_2	2	2	2	3	3	
Corn Starch	0.05	0.05	0.05	0.05	0.05	
Calcium Carbonate	0.05	0.05	0.05	0.05	0.05	
Bentonite	0.15	0.15	0.15	0.15	0.15	
Cuprous Oxide	0.015	0.015	0.015	0.015	0.015	
Chromous Oxide	0.015	0.015	0.015	0.015	0.015	
0 w% H_2O_2						
0.5 w% H_2O_2	1.5	1.5	1.5			
1 w% H_2O_2				1.5	1.5	
2 w% H_2O_2						
5 w% H_2O_2						
Calcination Temperature, °C	900	860	920	860	900	
Calcination Duration, hr	2	2	2	2	2	
H_2S, ppm at 2 min Reaction Duration	4342	5188	5808	4186	4600	4325
	4362	5065	6142	4131	4501	4362
	4340	5427	5718	4187	4450	4340

Figure 1. Reactivity of various sorbents reacted with initial 7400-ppm dry H_2S for 120 s at 550°C.

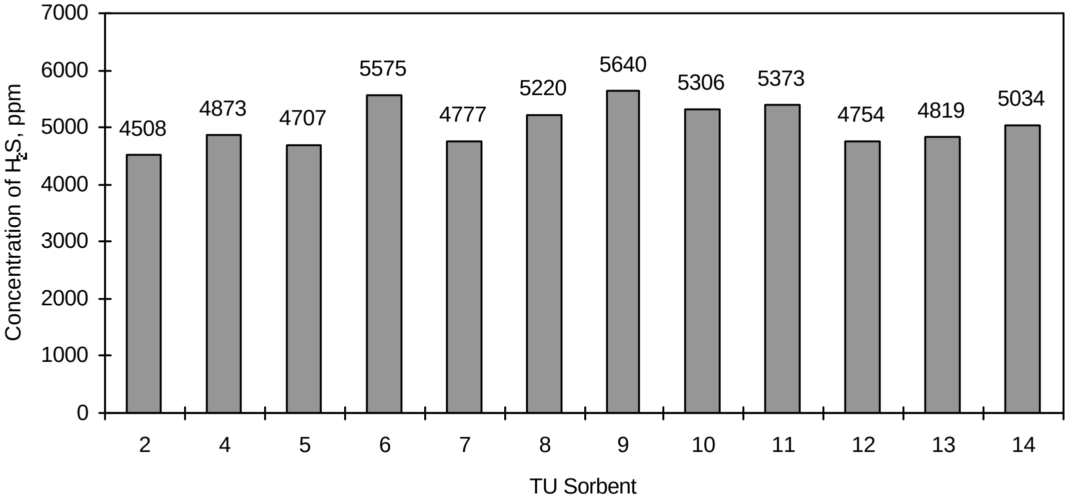
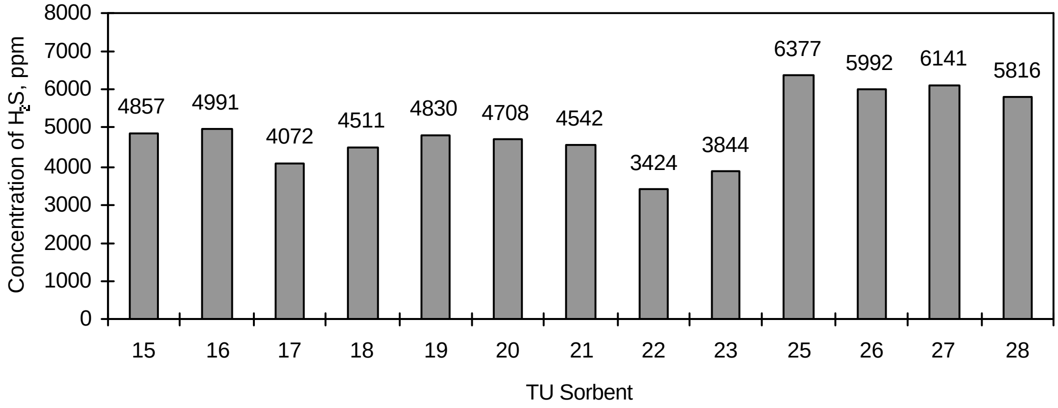
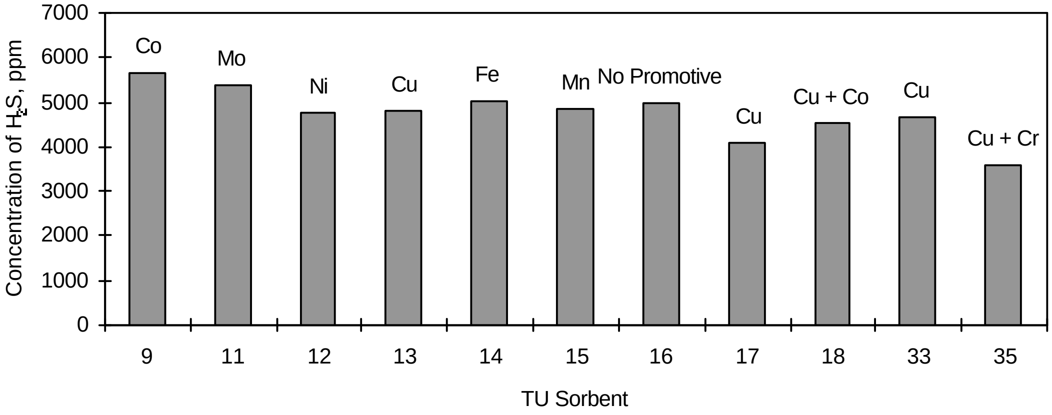


Figure 2. Reactivity of various 0.05-g sorbents with initial 7400-ppm dry H_2S for 120 s at 550°C.



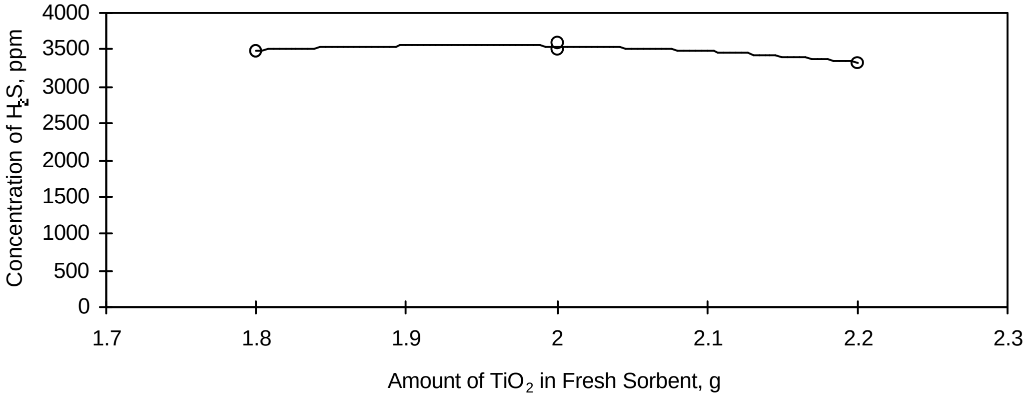
The metal oxide sorbents calcined for 2 hours at 900°C were formulated with various additives to identify their effects on reactivity of the sorbents (see Figure 3). The cuprous oxide additive, and the mixture consisting of the cuprous oxide additive and the chromous oxide additive appear to be most effective among other additives in enhancing reactivity of the sorbents.

Figure 3. Effects of additives on reactivity of sorbents with initial 7400 dry H_2S for 120 seconds at 550°C, calcined at 900°C.



A series of metal oxide sorbents such as TU-35, TU-39, and TU-40 (see Table 4) were formulated with various amounts of TiO_2, holding the amounts of the other ingredients and the formulation conditions constant. Reactivity of formulated sorbents appears to be independent of TiO_2 amounts (see Figure 4).

Figure 4. Effects of TiO_2 amount on reactivity of sorbents with initial 7400-ppm dry H_2S for 120 seconds at 550°C.



A series of metal oxide sorbents such as TU-35, TU-41, and TU-42 (see Table 4) were formulated with various amounts of corn starch, holding the amounts of the other ingredients and the formulation conditions constant. Reactivity of formulated sorbents increases with increased amount of corn starch (see Figure 5).

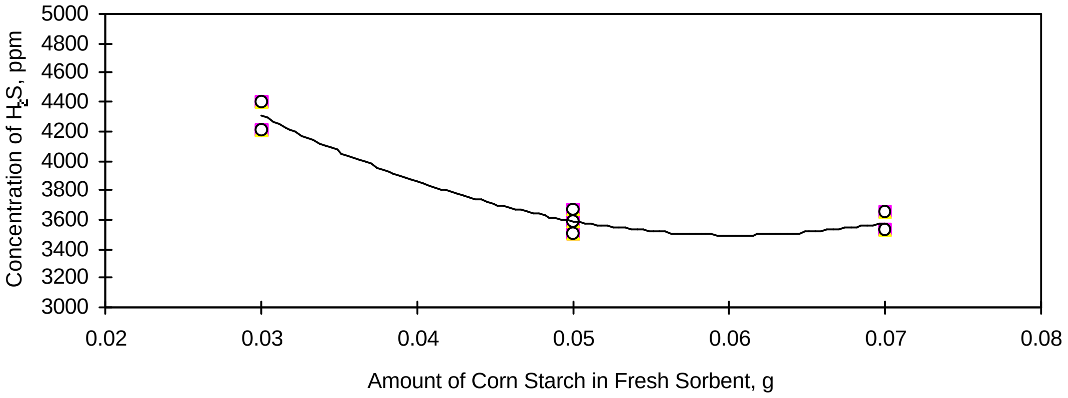


Figure 5. Effects of corn starch amount on reactivity of sorbents with initial 7400 ppm dry H_2S for 120 seconds at 550°C.

A series of metal oxide sorbents such as TU-43, TU-44C, and TU-47 (see Tables 4 and 5) were formulated with various amounts of calcium carbonate, holding the amounts of the other ingredients and the formulation conditions constant. Reactivity of formulated sorbents decreases with increased amount of calcium carbonate (see Figure 6).

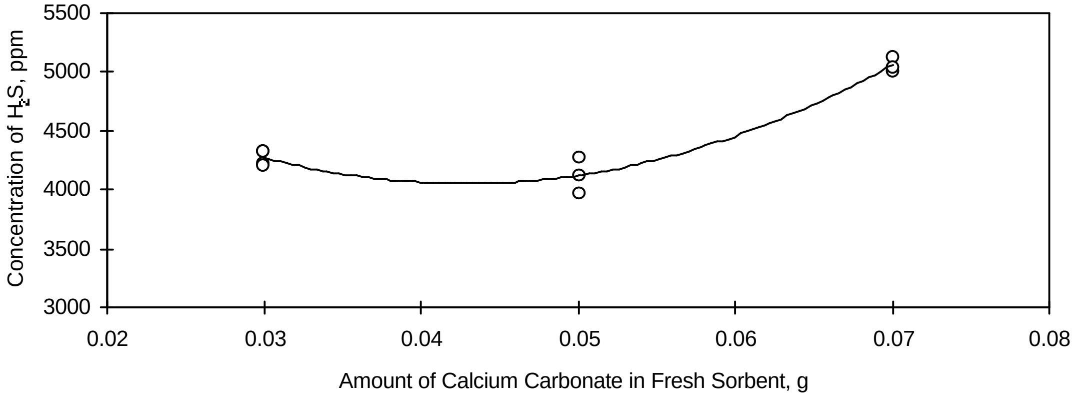


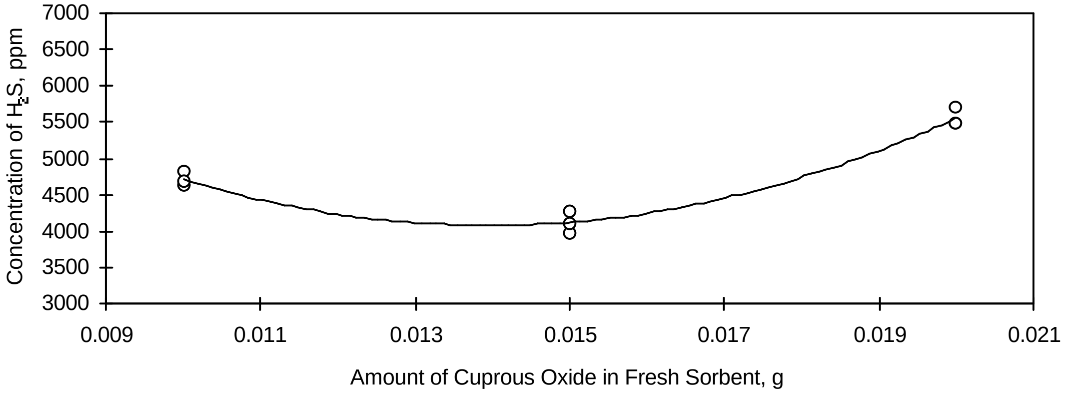
Figure 6. Effects of calcium carbonate amount on reactivity of sorbents with initial 7400-ppm-dry-H_2S for 120 seconds at 550°C.

A series of metal oxide sorbents such as TU-45, TU-46, TU-46C and TU-47 (see Table 5) were formulated with various amounts of bentonite, holding the amounts of the other ingredients and the formulation conditions constant. Reactivity of formulated sorbents appears not to be affected by the amount of bentonite (see Figure 7).

Figure 7. Effects of bentonite amount on reactivity of sorbents with initial 7400 ppm dry H_2S for 120 seconds at 550°C.

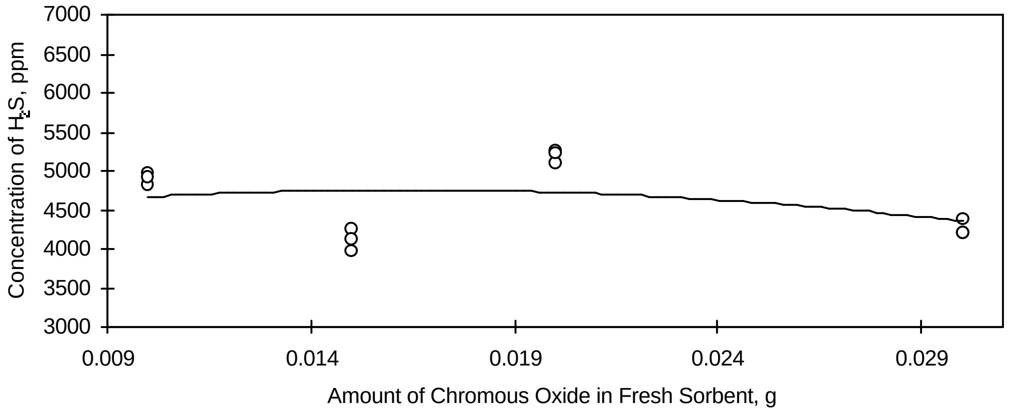
A series of metal oxide sorbents such as TU-47, TU-47C, and TU-48 (see Table 5) were formulated with various amounts of cuprous oxide, holding the amounts of the other ingredients and the formulation conditions constant. Reactivity of formulated sorbents decreases with increased amount of the cuprous oxide additive (see Figure 8).

Figure 8. Effects of cuprous-oxide amount on reactivity of sorbents with initial 7400-ppm-dry-H_2S for 120 seconds at 550°C.



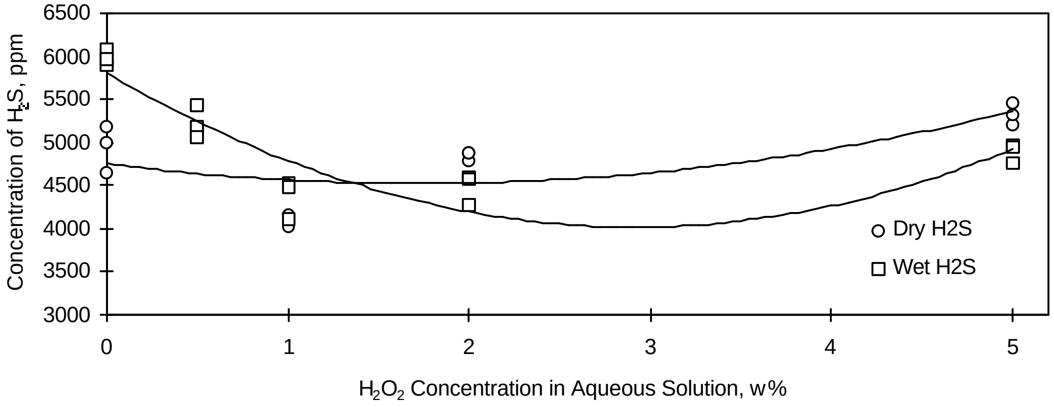
A series of metal oxide sorbents such as TU-37, TU-47, TU-49 and TU-50 (see Tables 4 and 5) were formulated with various amounts of chromous oxide, holding the amounts of the other ingredients and the formulation conditions constant. Reactivity of formulated sorbents appears not to be affected by the amount of the additive chromous oxide (see Figure 9).

Figure 9. Effects of chromous-oxide amount on reactivity of sorbents with initial 7400-ppm dry H_2S for 120 seconds at 550°C.



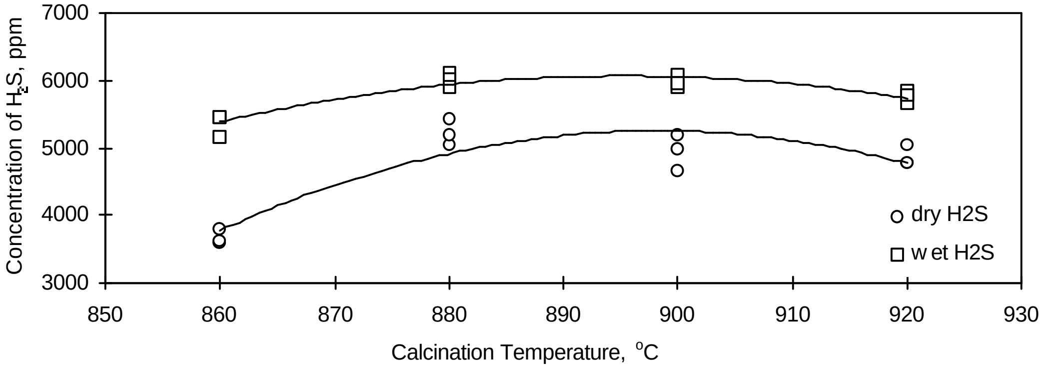
A series of metal oxide sorbents such as TU-51A, TU-51B, TU-51C, TU-52C and TU-55B (see Tables 5 through 7) were formulated with various amounts of H_2O_2, holding the amounts of the other ingredients and the formulation conditions constant. The reactivity of the sorbents in the presence of dry H_2S is higher than that of the sorbent in the presence of wet H_2S, when the sorbents were formulated with 0 - 1-w% H_2O_2 aqueous solution. The reactivity of the sorbents in the presence of dry H_2S is lower than that of the sorbents in the presence of wet H_2S, when the sorbents were formulated with 2 - 5-w% H_2O_2 aqueous solution (see Figure 10).

Figure 10. Effects of H_2O_2 concentration on reactivity of sorbents with initial 7400-ppm H_2S for 120 seconds at 550°C.



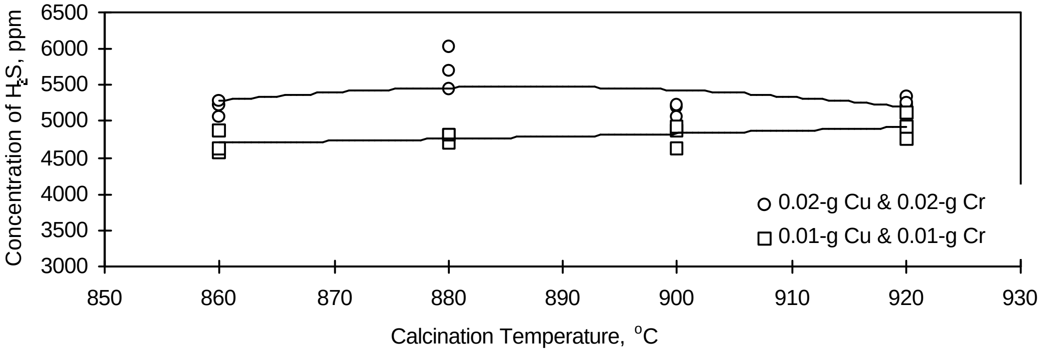
A series of metal oxide sorbents such as TU-52A, TU-52B, TU-52C and TU-52D (see Table 6) were formulated in the absence of H_2O_2, and calcined at various temperatures. The reactivity of the sorbents in the presence of dry H_2S is higher than that of the sorbents in the presence of wet H_2S. The reactivity of the sorbents with H_2S decreases with increased calcination temperature (see Figure 11).

Figure 11. Effects of calcination temperature on reactivity of sorbents with initial 7400-ppm -H_2S for 120 seconds at 550°C, fomulated with 0-% H_2O_2 aqueous solution.



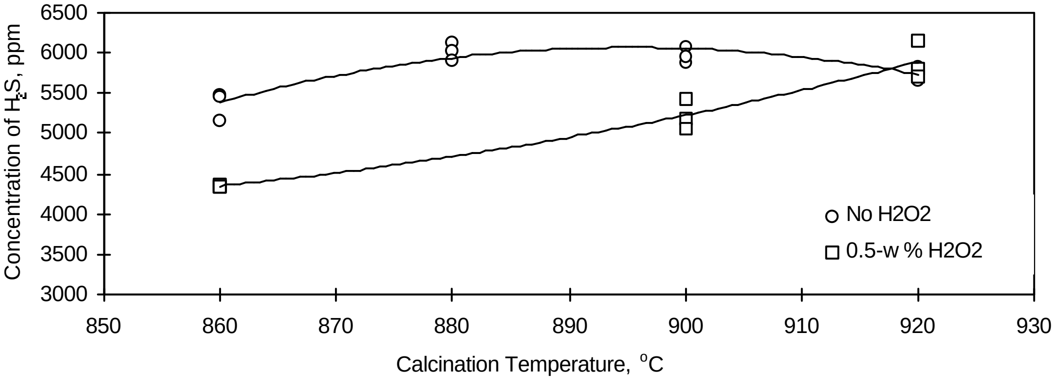
A series of metal oxide sorbents such as TU-53A, TU-53B, TU-53C and TU-53D (see Table 6) were formulated in the presence of 1-w% H_2O_2 with 0.01-g cuprous oxide and 0.01-g chromous oxide, and calcined at various temperatures. Another series of metal oxide sorbents such as TU-54A, TU-54B, TU-54C and TU-55D (see Table 6) were formulated in the presence of 1-w% H_2O_2 with 0.02-g cuprous oxide and 0.02-g chromous oxide, and calcined at various temperatures. The reactivity of the sorbents formulated with 0.01-g cuprous oxide and 0.01-g chromous oxide is higher than that of those formulated with 0.02-g cuprous oxide and 0.02-g chromous oxide. The reactivity of the sorbents with H_2S decreases with increased calcination temperature (see Figure 12).

Figure 12. Effects of calcination temperature on reactivity of sorbents with initial 7400-ppm -wet H_2S for 120 seconds at 550°C, fomulated with 1-% H_2O_2 aqueous solution.



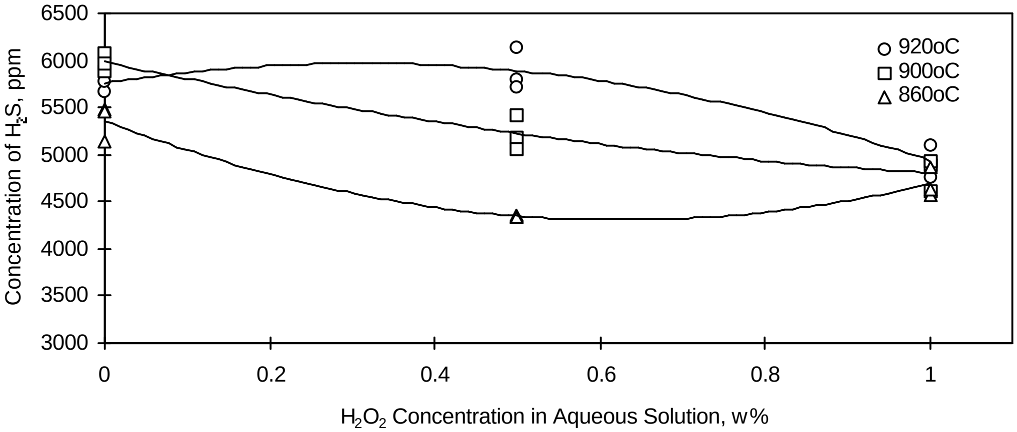
A series of metal oxide sorbents such as TU-52A, TU-52B, TU-52C and TU-52D (see Table 6) were formulated in the absence of H_2O_2, and calcined at various temperatures. Another series of metal oxide sorbents such as TU-55A, TU-55B, and TU-55C (see Table 7) were formulated in the presence of 0.5-w% H_2O_2, and calcined at various temperatures. The reactivity of the sorbents formulated in the presence of 0.5-w% H_2O_2 is higher than that of those formulated in the absence of H_2O_2. The reactivity of the sorbents with H_2S decreases with increased calcination temperature (see Figure 13).

Figure 13. Effects of calcination temperature on reactivity of sorbents with initial 7400-ppm -wet H_2S for 120 seconds at 550°C.



The metal oxide sorbents such as TU-52A, TU-53A, and TU-55A were calcined at 860°C. The metal oxide sorbents such as TU-52C, TU-53C, and TU-55B were calcined at 900°C. The metal oxide sorbents such as TU-52D, TU-53D, and TU-55C were calcined at 920°C. The reactivity of the metal oxide sorbents increases with increased concentration of H_2O_2 as a formulation additive. The reactivity of the metal oxide sorbents increases with decreased calcination temperature (see Figure 14).

Figure 14. Effects of H_2O_2 concentration on reactivity of sorbents with initial7400 ppm wet H_2S for 120 seconds at 550°C.



TU-57 through TU-96B

Metal oxide sorbents were formulated with various additives to enhance their reactivity with hydrogen sulfide from simulated coal gas mixtures (see Tables 8 through 13).

Reactivity of formulated metal oxide sorbents was compared by reacting sorbents with initial 7400-ppm hydrogen sulfide for 120 seconds at 550°C (see Figures 15 through 19).

The metal oxide sorbents TU-61 through TU-96B shown in Tables 8 through 13 were formulated with zirconium oxide and kaolin binders.

Table 8. Formulation of sorbents TU-57 through TU-68.

Sorbents	TU-57	TU-58	TU-59	TU-60	TU-61	TU-62	TU-63	TU-64	TU-65	TU-66	TU-67	TU-68
	Amounts of Ingredients (gram) and Formulation Conditions											
ZnO		1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Zinc Peroxide	2.6976											
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide			0.05		0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Aluminum Oxide												
Calcium Carbonate	0.05	0.05		0.05								
Bentonite	0.15	0.15	0.15									
Kaolin				0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Cobalt Oxide												
Molybdeum Oxide												
Nickel Oxide								0.015				
Cuprous Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015		0.015	0.015	
Ferrous Oxide						0.015					0.015	0.015
Ferrous Hydroxide		0.015					0.015					
Manganese Oxide									0.015	0.015	0.015	0.015
Chromous Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Cerium Oxide												
0.5 w% H_2O_2												
1 w% H_2O_2		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
2 w% H_2O_2												
5 w% H_2O_2	0.5											
Calcination Temperature, °C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	2	2	2	2	2	2	2	2	2	2	2	2
H_2S, ppm at 2-min reaction												
	2366	4590	4969	4362	5351	5272	4904	5206	5166	4546	5308	5294
	2337	4566	4913	4708	5358	5228	5192	4925	5243	4994	5425	5410
	2404	4627	5352	4484	5457	5133	4918	5165	4886	4617	6018	5027
	2363				5397	5392	5220	4840	5146		5968	5198
											5449	

Table 9. Formulation of sorbents TU-69 through TU-77.

Sorbents	TU-69	TU-70	TU-71A	TU-71B	TU-71C	TU-71D	TU-72	TU-73	TU-74	TU-75	TU-76	TU-77
	Amounts of Ingredients (gram) and Formulation Conditions											
ZnO	1.7	0.5	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Zinc Peroxide		1.35										
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Aluminum Oxide												
Calcium Carbonate												
Bentonite												
Kaolin	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Cobalt Oxide												
Molybdeum Oxide												
Nickel Oxide	0.015											
Cuprous Oxide		0.015	0.015	0.015	0.015	0.015		0.015				
Ferrous Oxide		0.015	0.015	0.015	0.015	0.015				0.015		
Ferrous Hydroxide												
Manganese Oxide	0.015										0.015	
Chromous Oxide	0.015	0.015	0.015	0.015	0.015	0.015			0.015			
Cerium Oxide												0.015
0.5 w% H_2O_2												
1 w% H_2O_2	1.5		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
2 w% H_2O_2												
5 w% H_2O_2		0.5										
Calcination Temperature, °C	860	860	860	880	900	920	860	860	860	860	860	860
Calcination Duration, hr	2	2	2	2	2	2	2	2	2	2	2	2
H_2S, ppm at 2-min reaction												
	5345	4672	5310	6157	5436	5824	4804	4819	5002	5347	5257	5085
	5403	4587	5190	6044	6449	5364	4827	4246	4663	5191	5051	4837
	5429		5086	6196	5735	5514	4438	4438	4687	5291	5161	4998
	5430		5260	6053	6187	5593	4787	4336	4609	5085	5077	4677
				6262		5437				5157	5214	4848

Table 10. Formulation of sorbents TU-78 through TU-86.

Sorbents	TU-78	TU-79	TU-80	TU-81	TU-82	TU-83	TU-84A	TU-84B	TU-84C	TU-84D	TU-85	TU-86
	Amounts of Ingredients (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Zinc Peroxide												
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Aluminum Oxide												
Calcium Carbonate												
Bentonite												
Kaolin	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Cobalt Oxide		0.015		0.015	0.015		0.015	0.015	0.015	0.015	0.015	0.015
Molybdeum Oxide			0.015									
Nickel Oxide	0.015					0.015						
Cuprous Oxide				0.015							0.015	
Ferrous Oxide												
Ferrous Hydroxide												
Manganese Oxide												
Chromous Oxide												0.015
Cerium Oxide												
0.5 w% H_2O_2												
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
2 w% H_2O_2												
5 w% H_2O_2												
Calcination Temperature, °C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	2	2	2	2	2	2	3	4	2	1	1	1
H_2S, ppm at 2-min reaction												
	4497	4082	6185	5384	4975	5157	5357	5577	4597	4334	4389	5817
	4672	4197	5876	5332	4830	5036	5436	5466	4280	4249	4280	5924
	4739	4299	5867	5360	4948	5121	5120	5179	4508	4189	4052	5830
	4333	4197	5640	5217	4838	4762	5118	5593	3975	4034	3964	5835
	4420	4239	5294	5291	5137	5279	5291	5247	4537	4351	4147	5736

Table 11. Formulation of sorbents TU-87 through TU-92.

	TU-87	TU-88	TU-89	TU-90	TU-91	TU-92	TU-93	TU-89	TU-85	TU-92	TU-89	TU-91
	Amounts of Ingredients (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Zinc Peroxide												
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.05	0.05	0.05	0.05	0.05	0.05		0.05	0.05	0.05	0.05	0.05
Aluminum Oxide							0.05					
Calcium Carbonate												
Bentonite												
Kaolin	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Cobalt Oxide	0.015	0.015	0.015	0.015	0.015			0.015	0.015		0.015	0.015
Molybdeum Oxide	0.015											
Nickel Oxide		0.015										
Cuprous Oxide					0.015	0.015			0.015	0.015		0.015
Ferrous Oxide												
Ferrous Hydroxide												
Manganese Oxide			0.015					0.015			0.015	
Chromous Oxide												
Cerium Oxide				0.015	0.015							0.015
0.5 w% H_2O_2												
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
2 w% H_2O_2												
5 w% H_2O_2												
Calcination Temperature, °C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1	1	1	1	1	1	1	1	1	1	1	1
H_2S, ppm at 2-min reaction	6337	5120	4267	4722	5354	5798	4974	5011	4337	5366	4983	4176
	6530	5159	3655	4368	5127	5652	4915	5092	4388	5195	4987	4222
	6211	5102	4151	4305	5062	5767	5135	4966	4299	5545	4956	4221
	6631	5253	3692	4835	5088	5769	5036	5079	4378	5446	4995	4083
	6158	5070	3725	4673	5215	5855	4937	4933	4404	5281		

Table 12. Formulation of various TU sorbents.

Sorbents	TU-81	TU-86	TU-93	TU-73	TU-84C	T-94A	T-95A	T-95B	T-95C	T-94B	T-94C	T-94D
	Amounts of Ingredients (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Zinc Peroxide												
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.05	0.05		0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Aluminum Oxide			0.05									
Calcium Carbonate												
Bentonite												
Kaolin	0.15	0.15	0.15	0.15	0.15							
Cobalt Oxide	0.015	0.015			0.015							
Molybdeum Oxide												
Nickel Oxide												
Cuprous Oxide	0.015			0.015		0.015				0.015	0.015	0.015
Ferrous Oxide												
Ferrous Hydroxide												
Manganese Oxide												
Chromous Oxide		0.015										
Cerium Oxide												
0.5 w% H_2O_2												
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
2 w% H_2O_2												
5 w% H_2O_2												
Calcination Temperature, °C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	2	1	1	2	2	0.5	0.5	1	2	1	2	3
H_2S, ppm at 2-min reaction												
	5145	4155	5158	4393	4967	4701	3979	4675	4928	5460	4993	4788
	5084	4046	5257	4359	4843	4635	3981	4754	4682	5304	5005	4724
	4932	3952	5198	4460	4941	4726	3920	4847	4784	5270	5031	4702
	5109	3961	5022	4458	5018	4661	3836	4692	4704	5228	4984	4685
	5092	4010	5161	4408	5036	4704	3912	4698	4477	5346	5072	4787

Table 13. Formulation of sorbents TU-95D through TU-96B.

Sorbents	TU-95D	TU-95A	TU-96A	TU-96B
	Amounts of Ingredients (gram) and Formulation Conditions			
ZnO	1.7	1.7	1.7	1.7
Zinc Peroxide				
TiO_2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05
Zirconium Oxide	0.05	0.05	0.05	0.05
Aluminum Oxide				
Calcium Carbonate				
Bentonite				
Kaolin	0.15	0.15	0.15	0.15
Cobalt Oxide			0.015	0.015
Molybdeum Oxide				
Nickel Oxide				
Cuprous Oxide				
Ferrous Oxide				
Ferrous Hydroxide				
Manganese Oxide				
Chromous Oxide				
Cerium Oxide				
0.5 w% H_2O_2				
1 w% H_2O_2	1.5	1.5	1.5	1.5
2 w% H_2O_2				
5 w% H_2O_2				
Calcination Temperature, ^oC	860	860	860	860
Calcination Duration, hr	3	0.5	1	0.5
H_2S, ppm at 2-min reaction	4702 4594 4685 4787	5235 5181 5260 5397 5287	5611 5624 5642 5649 5532	4053 4092 4036 4115 4175

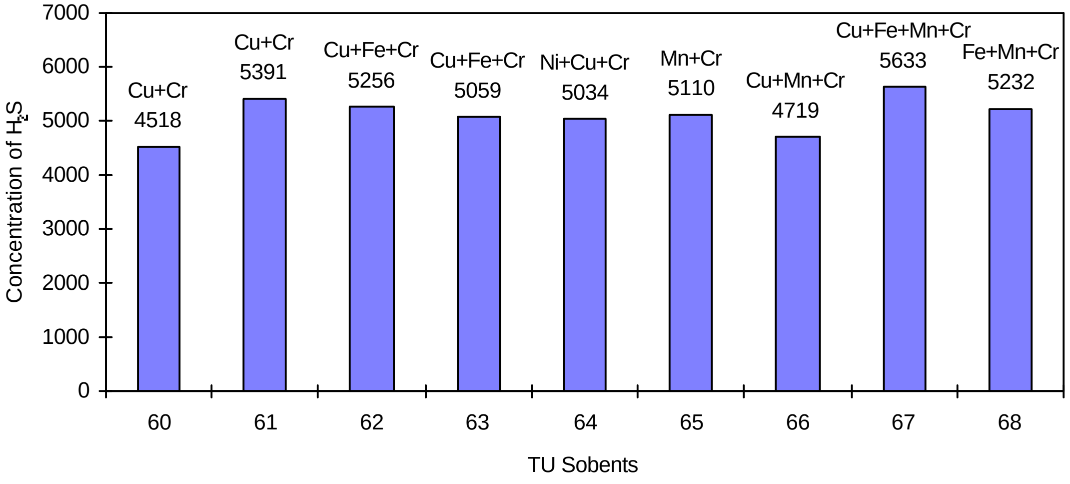
Table 14. Effects of Binders on durability of sorbents formulated with Cu and Cr additives.

		Additive, g		Binders, g			
Sorbent	Recovery, %	Cu	Cr	Calcium Carbonate	Bentonite	Zirconium Oxide	Kaolin
TU-54A	90.00	0.020	0.020	0.05	0.15		
TU-55B	85.27	0.015	0.015	0.05	0.15		
TU-54B	86.82	0.020	0.020	0.05	0.15		
TU-60	100.40	0.015	0.015	0.05			0.15
TU-61	100.20	0.015	0.015			0.05	0.15

Table 15. Effects of calcination durations on durability of sorbents calcined at 860°C.

Sorbent	Calcination Time,min	Recovery, %	Additive, 0.015 g	Sorbent	Calcination Time,min	Recovery, %	Additive, 0.015 g
95A	0.5	77	none	94B	1	97	Cu
95A	0.5	80	none	94B	1	97	Cu
95A	0.5	83	none	94C	2	98	Cu
95A	0.5	88	none	94C	2	100	Cu
95B	1	102	none	94D	3	98	Cu
95B	1	101	none	96B	0.5	97	Co
95B	1	104	none	96A	1	103	Co
95C	2	102	none	96A	1	103	Co
95D	3	101	none	84D	1	105	Co
94A	0.5	80	Cu	84C	2	101	Co
94B	1	96	Cu	84A	3	100	Co

Figure 15. Effects of additives on reactivity of sorbents with initial 7400-ppm wet H_2S for 120 s at 550°C.



The concentration of H_2S was reduced from initial 7400 ppm to 4518 ppm in the reaction with TU-60 sorbent (see Figure 15) formulated with Cu and Cr additives. The concentrations of H_2S was reduced from initial 7400 ppm to 4460 ppm in the reaction with TU-73 sorbent (see Figure 16) formulated with Cu additive. The concentrations of H_2S was reduced from initial 7400 ppm to 4167 ppm in the reaction with TU-85 sorbent (see Figure 17) formulated with Cu and Co additives.

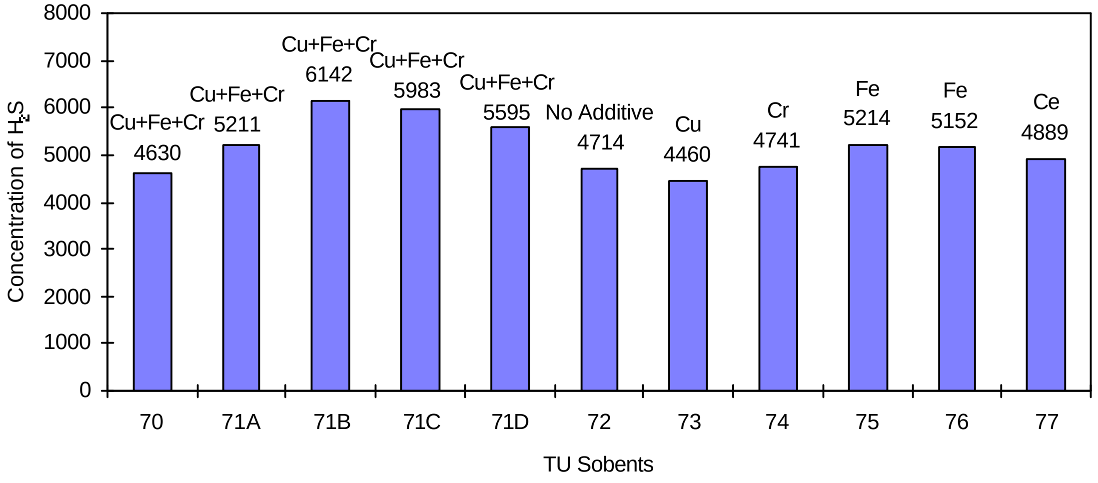


Figure 16. Effects of additives on reactivity of sorbents with initial 7400-ppm wet H_2S for 120 s at 550°C.

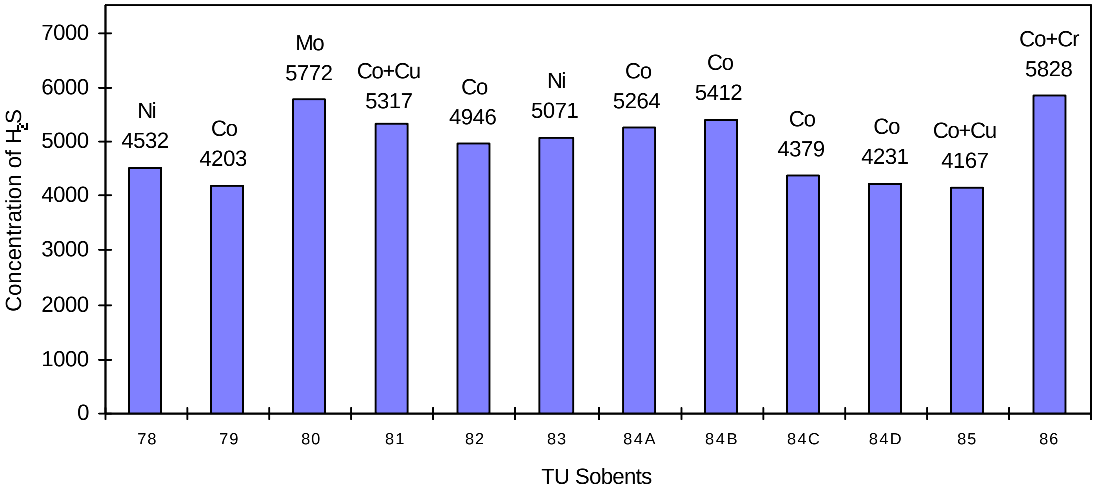
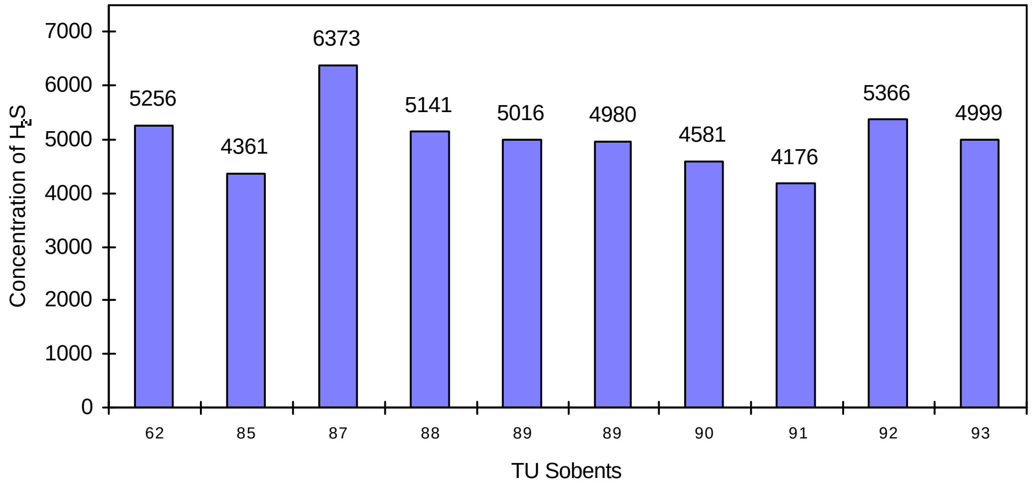


Figure 17. Effects of additives on reactivity of sorbents with initial 7400-ppm wet H_2S for 120 s at 550°C.

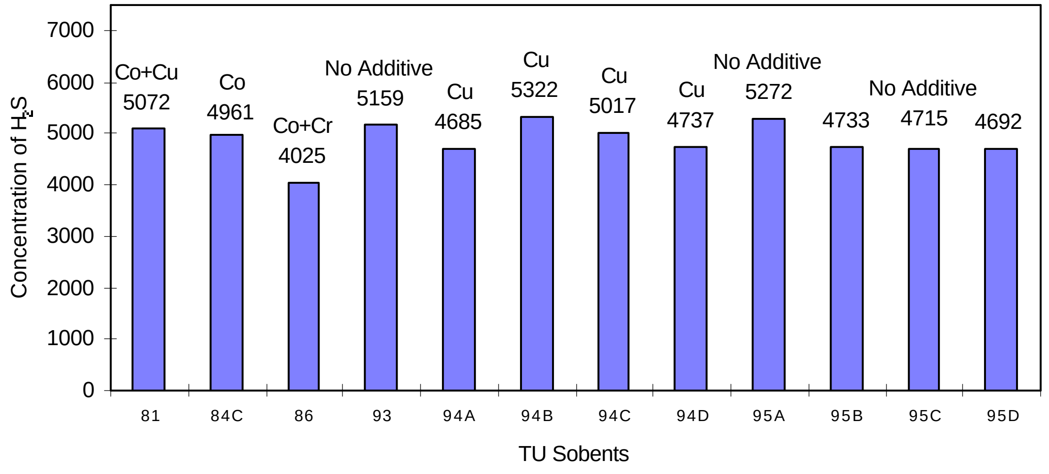
The concentration of H_2S was reduced from initial 7400 ppm to 4999 ppm in the reaction with TU-93 sorbent (see Figure 18) formulated without additive. The additive Cu appears to enhance reactivity of the above-mentioned formulated sorbents in comparison with TU-93 sorbent formulated without additive.

Figure 18. Reactivity of various sorbents reacted with initial 7400-ppm wet H_2S for 120 s at 550°C.



The concentration of H_2S was reduced from initial 7400 ppm to 4203 ppm in the reaction with TU-79 sorbent (see Figure 17) formulated with Co additive. The concentration of H_2S was reduced from initial 7400 ppm to 4231 ppm in the reaction with TU-84D sorbent (see Figure 17) formulated with Co additive.

Figure 19. Effects of additives on reactivity of sorbents with initial 7400-ppm wet H_2S for 120 s at 550°C.



The concentration of H_2S was reduced from initial 7400 ppm to 4581 ppm in the reaction with TU-90 sorbent (see Figure 18) formulated with Co and Ce additives. The concentration of H_2S was reduced from initial 7400 ppm to 4025 ppm in the reaction with TU-86 sorbent (see Figure 19) formulated with Co and Cr additives. The concentration of H_2S

was reduced from initial 7400 ppm to 5159 ppm in the reaction with TU-93 sorbent (see Figure 19) formulated without additive. The additive Co appears to enhance reactivity of the above-mentioned formulated sorbents in comparison with the TU-93 sorbent formulated without an additive.

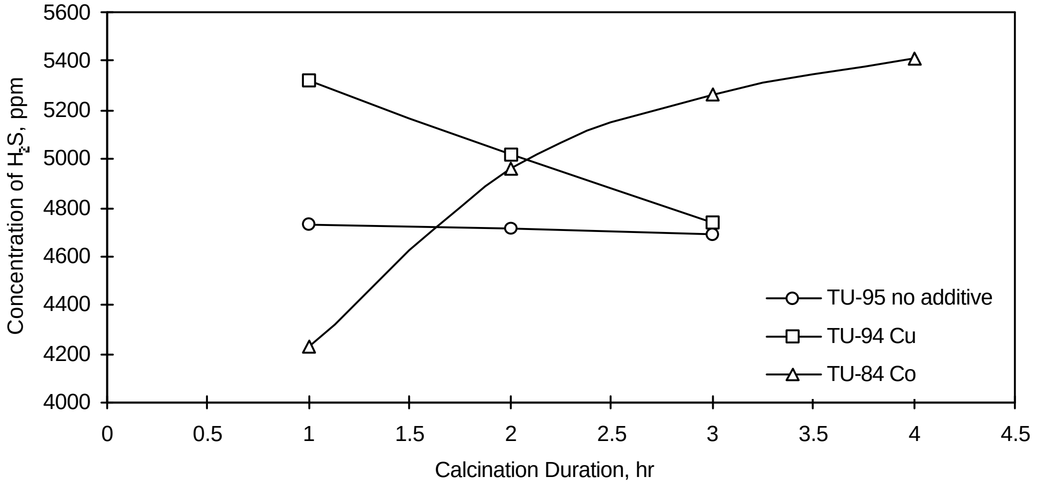
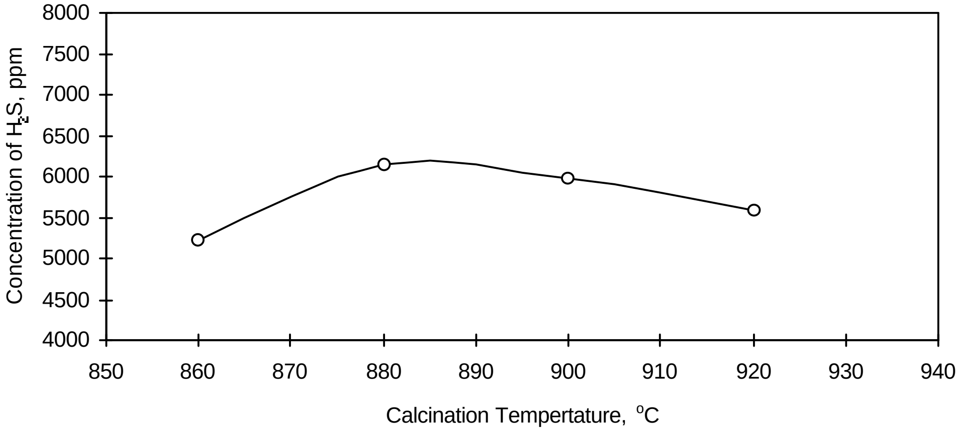


Figure 20. Effects of calcination duration on reactivity of TU sorbents, calcined at 860°C.

A series of metal oxide sorbents such as TU-84A, TU-84B, TU-84C and TU-84D (see Table 10) were formulated with 0.015-g cobalt additive, and calcined for various calcination durations at 860°C. The reactivity of the sorbents formulated with Co additive in the reaction with H_2S decreases with increased calcination durations (see Figure 20).



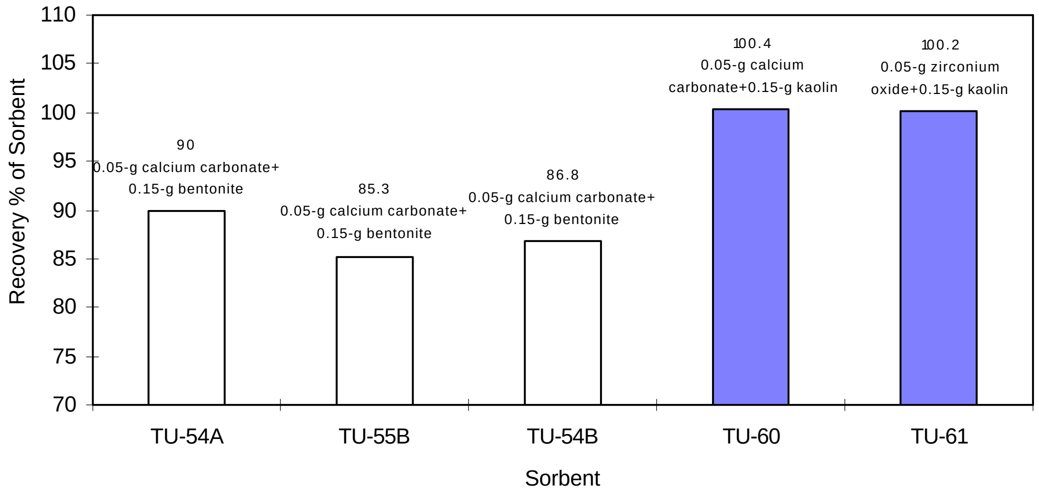
Figur 21. Effects of calcination temperature on reactivity of sorbents containing Cu, Fe and Cr additives.

A series of metal oxide sorbents such as TU-95B, TU-95C and TU-95D (see Table 12) were formulated without additive, and calcined for various calcination durations at 860°C. The reactivity of the sorbents formulated without additive in the reaction with H_2S appears to be independent of calcination durations (see Figure 20).

A series of metal oxide sorbents such as TU-94B, TU-94C and TU-94D (see Table 12) were formulated with copper additive, and calcined for various calcination durations at 860°C. The reactivity of the sorbents formulated with Cu additive in the reaction with H_2S appears to increase with calcination durations (see Figure 20). These data may suggest effects of calcination durations on reactivity of sorbents with wet hot hydrogen sulfide are dependent on chosen additives.

A series of metal oxide sorbents such as TU-71A, TU-71B, TU-71C and TU-71D (see Table 9) were formulated with 0.015-g Cu, 0.015-g Fe, and 0.015-g Cr additives, and calcined for 2 hours at various temperatures. The reactivity of the sorbents appears to decrease with increased calcination temperatures for the calcination temperature range of 860°C - 880°C, while the reactivity of the sorbents appears to increase with increased calcination temperatures for the calcination temperature range of 880°C - 920°C (see Figure 21).

Figure 22. Effects of Binders on durability of sorbent formulated with Cu and Cr additives.



The sorbents such as TU-54A, TU-55B, and TU-54B were formulated with Cu and Cr additives, and calcium carbonate and bentonite binders (see Table 14). The sorbent TU-60 was fomulated with Cu and Cr additives, and calcium carbonate and kaolin binders. The sorbent TU-61 was fomulated with Cu and Cr additives, and zirconium oxide and kaolin binders (see Table 14). These sorbents were calcined for 2 hours at 860 - 880°C. These 0.05-g fresh sorbents were reacted with the initial 7400-ppm H_2S and the initial 14.7-psia hydrogen in the presence of 0.085-g moisture for 120 min at 550°C.

During the runs, the batch reactor containing 0.05-g fresh sorbent was stirred horizontally 50 times per min. After the run, a gas sample was drawn for the analysis of H_2S concentrations, the reactor were purged with 150-psig nitrogen, the sorbent reacted with H_2S was recovered and weighed, and then the recovery percentage was obtained (see Table 14).

The recovery percentages of the sorbents such as TU-54A, TU-55B, and TU-54B were 90, 85, and 87, respectively, whereas the recovery percentages of the sorbents such as TU-60, and TU-61 were 100.4 and 100.2, respectively (see Figure 22). These data may suggest that durability of formulated sorbents appears to improve with kaolin binder in comparison with bentonite binder.

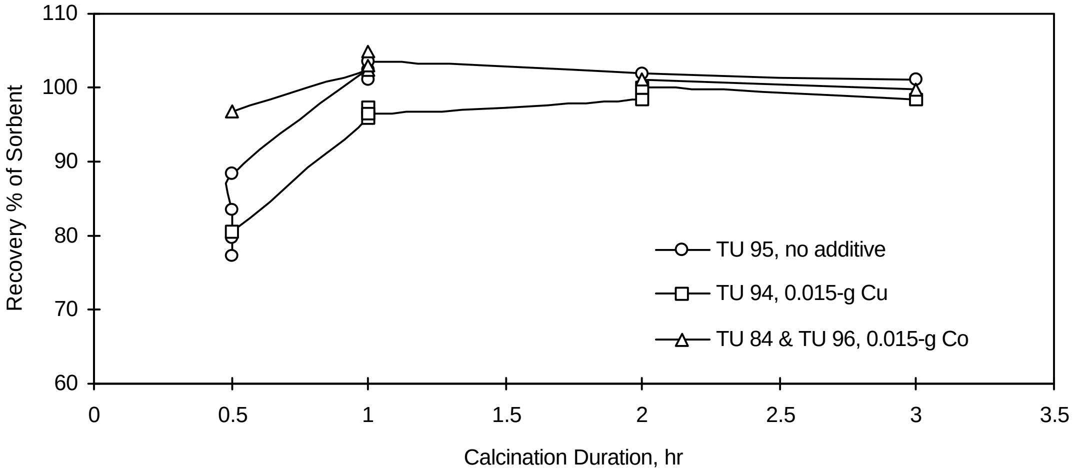


Figure 23. Effects of calcination durations on durability of sorbents calcined at 860°C.

The TU-95 sorbents (see Table 15 and Figure 23) were formulated without additive, and calcined for 0.5 - 3 hours at 860°C. The recovery percentages of the TU-95A sorbent calcined for 0.5 hour are 77 - 88, whereas the recovery percentages of the sorbents such as TU-95B, TU-95C and TU-95D, calcined for 1 - 3 hours, are 101- 104. The TU-94 sorbents (see Table 15 and Figure 23) were formulated with Cu additive, and calcined for 0.5 - 3 hours at 860°C. The recovery percentage of the TU-94A sorbent calcined for 0.5 hour is 80, whereas the recovery percentages of the sorbents such as TU-94B, TU-94C and TU-94D, calcined for 1 - 3 hours, are 96 - 100.

The TU-96 sorbents and TU-84 sorbents (see Table 15 and Figure 23) were formulated with Co additive, and calcined for 0.5 - 3 hours at 860°C. The recovery percentage of the TU-96B sorbent calcined for 0.5 hour is 97, whereas the recovery percentages of the sorbents such as TU-96A, TU-84A, TU-84C and TU-84D, calcined for 1 - 3 hours, are 100 - 105. These observations may indicate that durability of formulated sorbents appears to improve with increased calcination durations.

Sorbents TU-97 through TU-144

Metal oxide sorbents were formulated with various additives to enhance their reactivity with hydrogen sulfide contained in simulated coal gas mixtures (see Tables 16 through 19). Reactivity of formulated metal oxide sorbents was compared by reacting sorbents with initial 7400-ppm hydrogen sulfide for 120 seconds at 550°C (see Figures 24 through 31). Hardness of formulated metal oxide sorbents was compared by testing their hardness with a hardness tester (see Figures 24 through 31). Hardness of a fresh formulated sorbent is tested 7 times. The average value of seven hardness data is reported in the Tables. The hardness range of fresh formulated sorbents at room temperature is 3 -16 kg/pellet.

The metal oxide sorbents TU-97 through TU-105, as shown in Tables 16, were formulated without zirconium oxide, whereas the metal oxide sorbents TU-106 through TU-144, as shown in Tables 16 through 19, were formulated with zirconium oxide. Hardness of fresh formulated sorbents inceases significantly in the presence of zirconium oxide.

Table 16. Formulation of sorbents TU-97 through TU-108.

Sorbents	TU-97	TU-98	TU-99	TU-100	TU-101	TU-102	TU-103	TU-104	TU-105	TU-106	TU-107	TU-108
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide (Zr)										0.05	0.05	0.05
Gypsum	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Cobalt Oxide (Co)	0.005	.01	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.005	0.010	0.015
Cuprous Oxide (Cu)	0.015	0.015	0.005	0.010	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.005
Cerium Oxide (Ce)	0.015	0.015	0.015	0.015	0.015	0.015	0.005	0.010	0.015	0.015	0.015	0.015
Chromous Oxide (Cr)	0.015	0.015	0.015	0.015	0.005	0.010	0.015	0.015	0.015	0.015	0.015	0.015
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calculation Temperature, ^{o}C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1	1	1	1	1	1	1	1	1	1	1	1
H_2S, ppm at 2-min reaction	3998 3934 4112 3801	4092 4208 3998 4471 4540	4475 4421 4405	4728 4652 3217 3908 4679	4163 4048 5216 4616	4730 4372 4288 4340 4413	4536 4648 4519 4501 4319	5016 5050 4868 4758 4982	4410 4503 4338 4311 4435	4739 4676 4418 4855 4775	4314 4417 4401 4254 4514	4946 5109 5194 5123 4827
Hardness, kg/pellet	4.87	4.03	4.85	5.70	4.67	7.93	6.90	3.27	3.75	5.47	4	5.67

Table 17. Formulation of sorbents TU-109 through TU-120.

Sorbents	TU-109	TU-110	TU-111	TU-112	TU-113	TU-114	TU-115	TU-116	TU-117	TU-118	TU-119	TU-120
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide (Zr)	0.05	0.10	0.15	0.150	0.150	0.150	0.200	0.200	0.200	0.200	0.200	0.200
Gypsum	0.15	0.150	0.150	0.050	0. 10	0.0	0.0	0.050	0.100	0.15	0.200	0.250
Cobalt Oxide (Co)	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Cuprous Oxide (Cu)	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Cerium Oxide (Ce)	0.015	0.015	0.015	0.015	0.015	0.010	0.015	0.015	0.015	0.015	0.015	0.015
Chromous Oxide (Cr)	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calcination Temperature, ^{o}C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1	1	1	1	1	1	1	1	1	1	1	1
H_2S, ppm at 2-min reaction	4210 4257 4172 4141 4276	3488 5224 3613 5003 3565 5167 3543 4753 3600 4830	5423 5431 5515 5388 5432	4548 5075 4771 4661	4427 4694 4466 4469 4285 4724 4122 4699 4705	5232 5064 5051 4890 5093	4820 4485 4843 4757 4570	4623 4767 4940 4159 4996	437 4210 426 8 4231 451 7 4094 429 0 4162 1 4307	4930 4948 4752 4631 4578	4249 5028 4272 5151 4041 4836 4229 4567 4035 4692	5943 5207 5950 5451 5838 5320 5761 5239 5827 5257
Hardness, kg/pellet	3.5	4.67	10.75	11.2	11.83	9.83	5.75	9.50	11.5	10.88	8.75	8.88

Table 18. Formulation of sorbents TU-121 through TU-132.

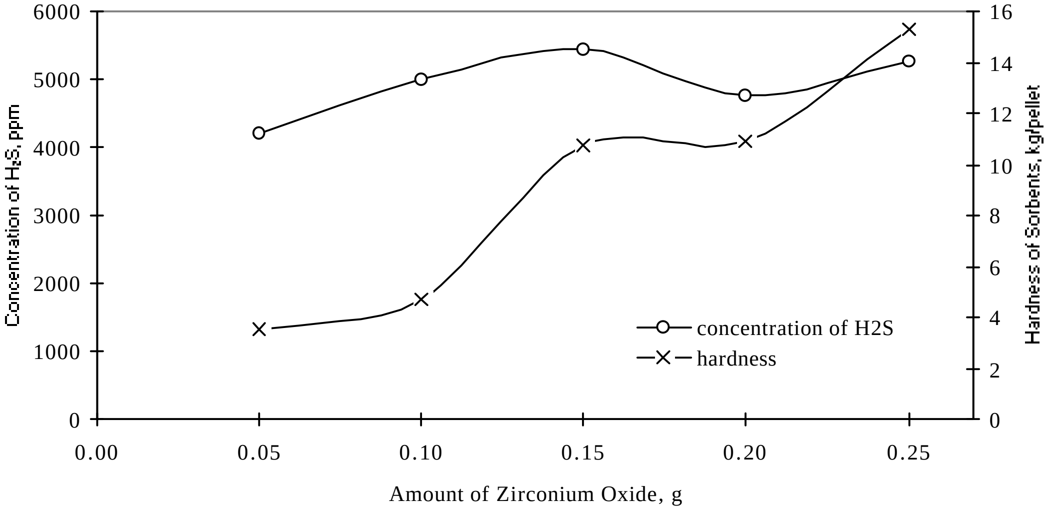
Sorbents	TU-121	TU-122	TU-123	TU-124	TU-125	TU-126	TU-127	TU-128	TU-129	TU-130	TU-131	TU-132
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	2
TiO2	2	2	2	2	2	2	2	2	2	2	2	1.7
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide (Zr)	0.250	0.250	0.250	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200	0.200
Gypsum	0.05	0.100	0.150	0.10	0.10	0.10	0.10	0.10	0.100	0.100	0.100	0.100
Cobalt Oxide (Co)	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.005	0.01	0.015	0.015	0.015
Cuprous Oxide (Cu)	0.015	0.015	0.015	0.015	0.015	0.005	0.01	0.015	0.015	0.005	0.01	0.015
Cerium Oxide (Ce)	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Chromous Oxide (Cr)	0.015	0.015	0.015	0.005	0.01	0.015	0.015	0.015	0.015	0.015	0.015	0.005
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calculation Temperature, ^{o}C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1	1	1	1	1	1	1	1	1	1	1	1
H_2S, ppm at 2-min reaction												
	4864	5144	5101	4334	4741	4905	5649	4783	4615	5318	5035	5064
	4866	4942	5083	4446	5042	4834	5927	4800	5032	5183	4775	4834
	4816	4991	5325	4604	4949	4733	5906	4916	4926	5177	4759	4601
	4753	5024	5417	4440	4556	5011	5607	4830	5030	5090	4953	5181
	4830	6143	5419	4513	4882	4859	5274	4712	4748	5164	4770	4953
Hardness, kg/pellet	11.7 10.83	11.13 13.57	10.38 15.31	11.82	12.36	12.04	11.30	12.38	11.70	11.67	10.38	11.17

Table 19. Formulation of sorbents TU-133 through TU-144.

Sorbents	TU-133	TU-134	TU-135	TU-136	TU-137	TU-138	TU-139	TU-140	TU-141	TU-142	TU-143	TU-144
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	2	2	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO2	1.7	1.7	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide (Zr)	0.200	0.200	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.25
Gypsum	0.100	0.100	0.100	0.100	0.10	0.10	0. 10	0.10	0.10	0.10	0.10	0.20
Cobalt Oxide (Co)	0.015	0.015	0.015	0.015	0.020	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Cuprous Oxide (Cu)	0.015	0.015	0.015	0.015	0.015	0.020	0.015	0.015	0.025	0.030	0.035	0.015
Cerium Oxide (Ce)	0.015	0.005	0.01	0.02	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Chromous Oxide (Cr)	0.01	0.015	0.015	0.015	0.015	0.015	0.020	0.015	0.015	0.015	0.015	0.015
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calculation Temperature, ^{o}C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1	1	1	1	1	1	1	1	1	1	1	1
H_2S, ppm at 2-min reaction												
	5035	4860	4926	4912	4597	4209	4966	4322	5087	4920	4933	5152
	5068	5355	4976	5021	4776	4333	5008	3458	4802	4936	4874	5143
	5278	4581	4768	4993	5054	3972	4767	4443	5065	4996	4805	4848
	4986	5241	4806	4606	5034	4216	4848	4105	4850	4790	4713	5038
	4856	4294	4747	4851	4561	4045	4560	4032	5020	4979	4951	4881
Hardness, kg/pellet	11.00	13.14	11.92	12.29	11.42	12.25	10.25	12.20	10.57	11.00	12.07	10.36

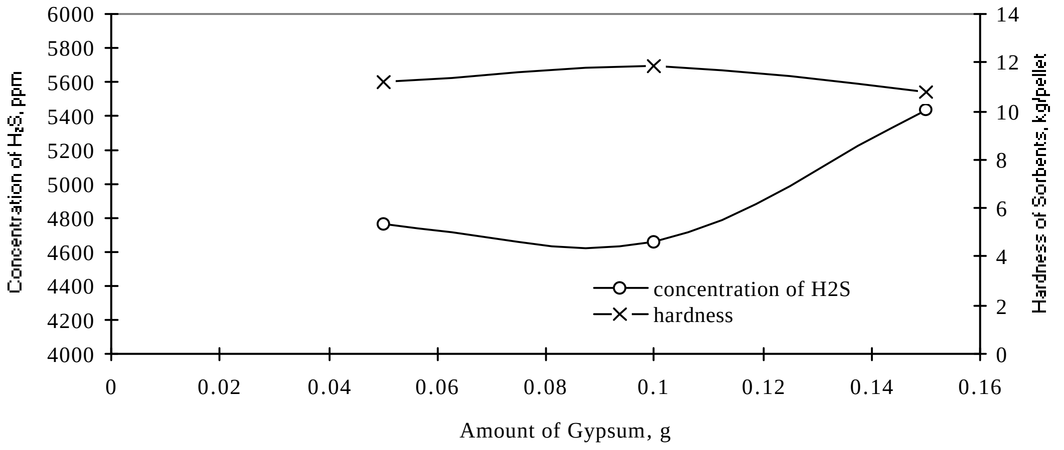
The sorbents TU-109, TU-110, TU-111, TU-118 and TU-123 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.15-g gypsum, and 0.015 g of cuprous oxide , cobalt oxide, cerium oxide, and chromous oxide , respectively, varying amounts of zirconium oxide. The sorbents TU-109, TU-110, TU-111, TU-118 and TU-123 were formulated with zirconium oxide of 0.05 g, 0.1 g, 0.15 g, 0.2 g and 0.25 g, respectively. The TU-109, TU-110, TU-111, TU-118 and TU-123 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbents with H_2S decreases with increased amounts of zirconium oxide, while hardness of the sorbents increases with amounts of zirconium oxide (see Figure 24). Hardness of the sorbents increases from 3.5 kg to 15.31 kg /pellet by varying the amounts of zirconium oxide in the formulation of the sorbents from 0.05 g to 0.25 g. These observations indicate that zirconium oxide in the formulation of the sorbents affect significantly their hardness.

Figure 24. Effects of zirconium oxide on absorption of H_2S into sorbents and their hardness containing 0.15-g gypsum, and 0.015-g of Cu, Co, Ce and Cr, respectively.



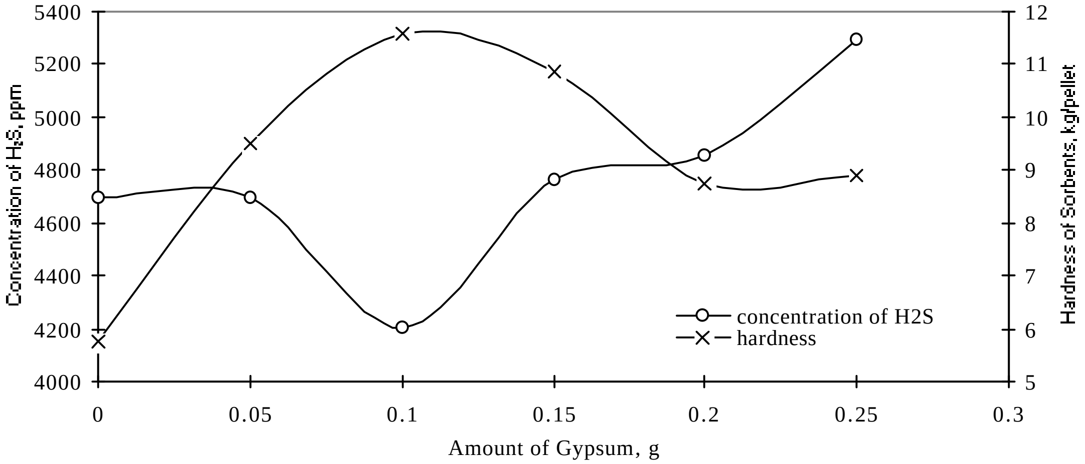
The sorbents TU-112, TU-113, and TU-111 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.15-g zirconium oxide, and 0.015 g of cuprous oxide, cobalt oxide, cerium oxide, and chromous oxide , respectively, varying amounts of gypsum. The sorbents TU-112, TU-113, and TU-111 were formulated with gypsum of 0.05 g, 0.1 g, and 0.15 g, respectively. The sorbents TU-112, TU-113, and TU-111 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbents with H_2S decreases with increased amounts of gypsum, while hardness of the sorbents is independent of amounts of gypsum (see Figure 25). These data show that amounts of gypsum do not affect hardness of the formulated sorbents in the presence of 0.15-g zirconium oxide, but affect their reactivity with hydrogen sulfide.

Figure 25. Effects of gypsum on absorption of H_2S into sorbents and their hardness, containing 0.15-g zirconium oxide, and 0.015-g of Cu, Co, Ce and Cr, respectively.



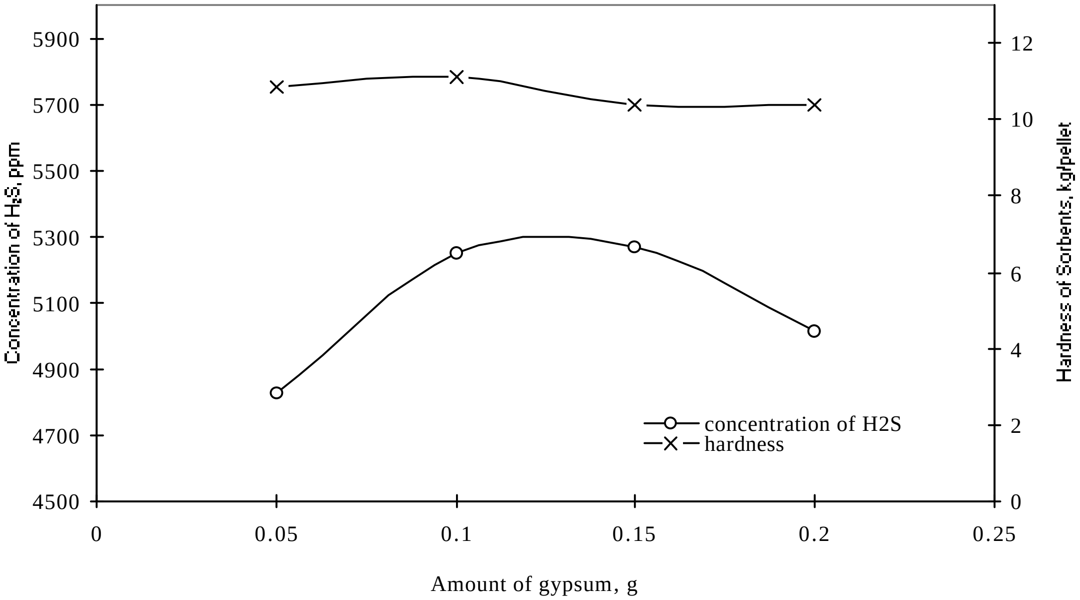
The sorbents TU-115, TU-116, TU-117, TU-118, TU-119 and TU-120 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, and 0.015 g of cuprous oxide , cobalt oxide, cerium oxide, and chromous oxide, respectively, varying amounts of gypsum. The sorbents TU-115, TU-116, TU-117, TU-118, TU-119 and TU-120 were formulated with gypsum of 0.05 g, 0.1 g, 0.15 g, 0.2 g, and 0.25 g, respectively. The sorbents TU-115, TU-116, TU-117, TU-118, TU-119 and TU-120 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent, containing 0.1-g gypsum, with H_2S is highest among others, while hardness of the sorbent, containing 0.1-g gypsum, is highest among others (see Figure 26). These data show that amounts of gypsum affect both hardness of the formulated sorbents and their reactivity with hydrogen sulfide in the presence of 0.2-g zirconium oxide.

Figure 26. Effects of gypsum on absorption of H_2S into sorbents and their hardness, containing 0.2-g zirconium oxide, and 0.015-g of Cu, Co, Ce and Cr, respectively.



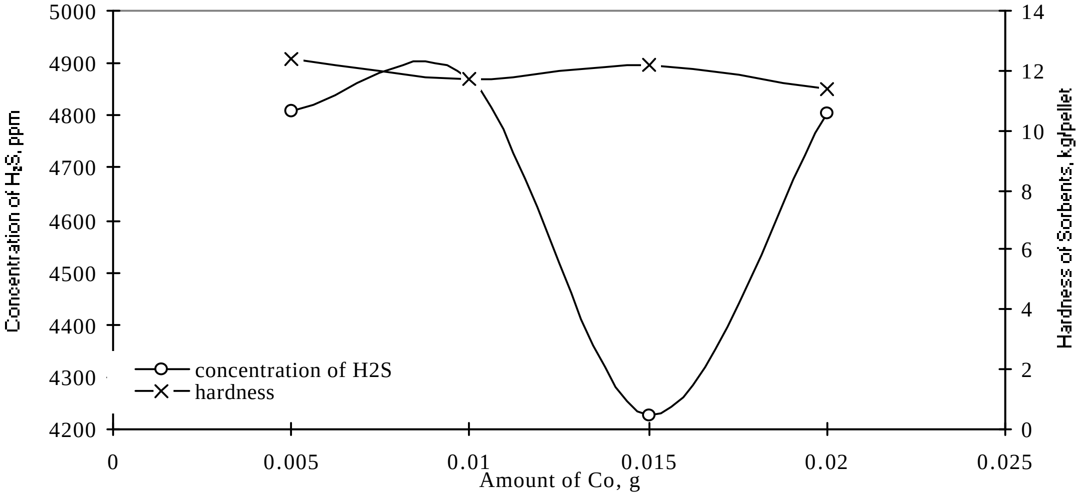
The sorbents TU-121, TU-122, TU-123, and TU-144 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.25-g zirconium oxide, and 0.015 g of cuprous oxide, cobalt oxide, cerium oxide, and chromous oxide, respectively, varying amounts of gypsum. The sorbents TU-121, TU-122, TU-123, and TU-144 were formulated with gypsum of 0.05 g, 0.1 g, 0.15 g, and 0.2 g, respectively. The sorbents TU-121, TU-122, TU-123, and TU-144 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent, containing 0.1-g gypsum, with H_2S is lowest among others, while hardness of the sorbents decreases slightly with amounts of gypsum (see Figure 27). These data show that amounts of gypsum do not affect significantly hardness of the formulated sorbents in the presence of 0.25-g zirconium oxide, but affect their reactivity with hydrogen sulfide.

Figure 27. Effects of gypsum on absorption of H_2S into sorbents and their hardness, containing 0.25-g zirconium oxide, and 0.015-g of Cu, Co, Ce and Cr, respectively.



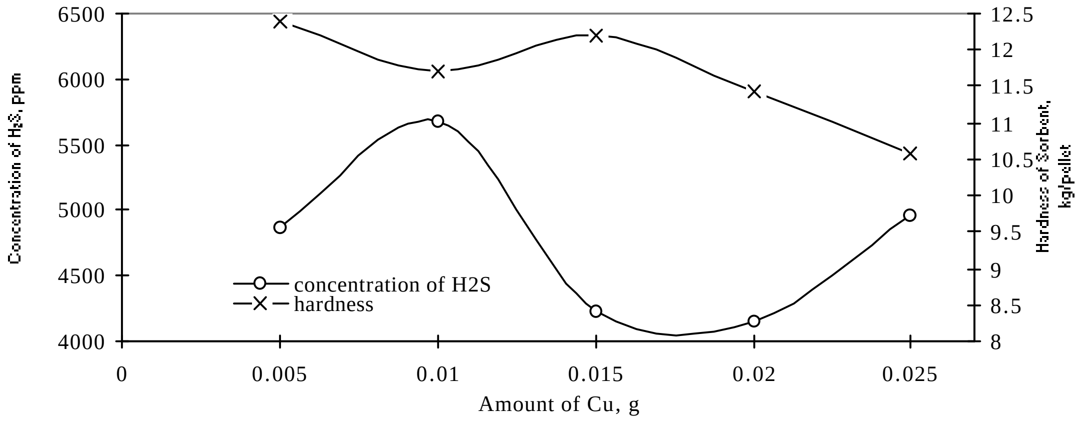
The sorbents TU-128, TU-129, TU-140, and TU-137 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g gypsum, and 0.015 g of cuprous oxide, cerium oxide, and chromous oxide, respectively, varying amounts of cobalt oxide. The sorbents TU-128, TU-129, TU-140, and TU-137 were formulated with cobalt oxide of 0.05 g, 0.1 g, 0.15 g, and 0.2 g, respectively. The sorbents TU-128, TU-129, TU-140, and TU-137 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent, containing 0.015-g cobalt oxide, with H_2S is highest among others, while hardness of the sorbents decreases slightly with amounts of cobalt oxide (see Figure 28). These data show that amounts of cobalt oxide do not affect significantly hardness of the formulated sorbents, but affect their reactivity with hydrogen sulfide.

Figure 28. Effects of Co on absorption of H_2S into sorbents and their hardness, containing 0.2-g zirconium oxide, 0.1-g gypsum, nd 0.015-g of Cu, Ce and Cr, respectively.



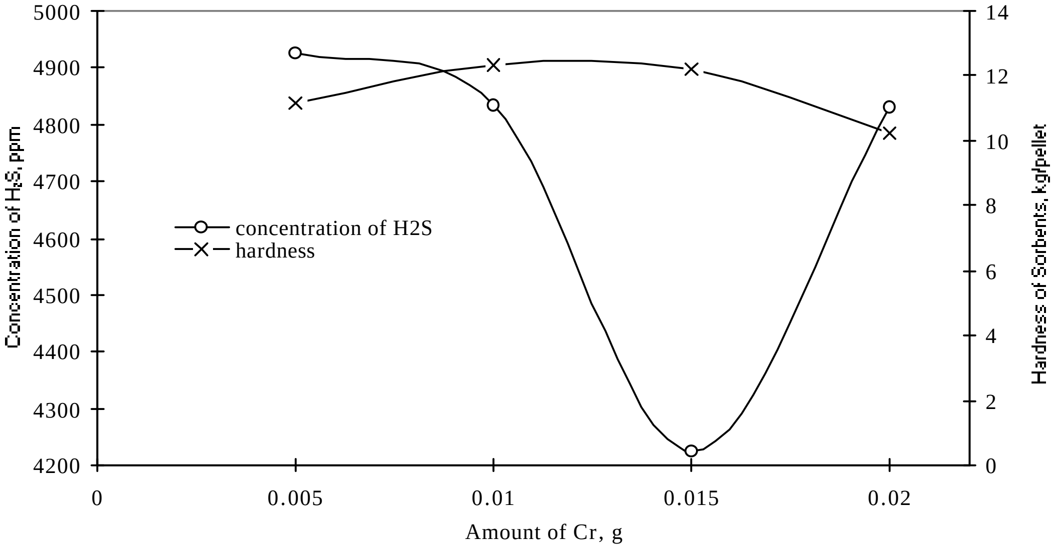
The sorbents TU-126, TU-127, TU-140, TU-139 and TU-141 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g gypsum, and 0.015 g of cobalt oxide, cerium oxide, and chromous oxide, respectively, varying amounts of cuprous oxide . The sorbents TU-126, TU-127, TU-140, TU-139 and TU-141 were formulated with cuprous oxide of 0.005 g, 0.01 g, 0.015 g, 0.02 g and 0.25 g, respectively. The sorbents TU-126, TU-127, TU-140, TU-139 and TU-141 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent, containing 0.02-g cuprous oxide, with H_2S is highest among others, while hardness of the sorbents decreases with amounts of cuprous oxide (see Figure 29). These data show that amounts of cuprous oxide affect significantly both hardness of the formulated sorbents and their reactivity with hydrogen sulfide.

Figure 29. Effects of Cu on absorption of H_2S into sorbents and their hardness, containing 0.2-g zirconium oxide, 0.1-g gypsum, and 0.015-g of Co, Ce and Cr, respectively.



The sorbents TU-132, TU-125, TU-140, and TU-139 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g gypsum, and 0.015 g of cobalt oxide, cerium oxide, and cuprous oxide , respectively, varying amounts of chromous oxide . The sorbents TU-132, TU-125, TU-140, and TU-139 were formulated with chromous oxide of 0.005 g, 0.01 g, 0.015 g, and 0. 02 g, respectively. The sorbents TU-132, TU-125, TU-140, and TU-139 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent, containing 0.015-g chromous oxide , with H_2S is highest among others, while hardness of the sorbents is independent of amounts of chromous oxide (see Figure 30). These data show that amounts of chromous oxide do not affect significantly hardness of the formulated sorbents, but affect their reactivity with hydrogen sulfide.

Figure 30. Effects of Cr on absorption of H_2S into sorbents and their hardness, containing 0.2-g zirconium oxide, 0.1-g gypsum, and 0.015-g of Co, Ce and Cu, respectively.



The sorbents TU-134, TU-135, TU-140, and TU-136 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g gypsum, and 0.015 g of cobalt oxide, cuprous oxide, and chromous oxide, respectively, varying amounts of cerium oxide. The sorbents TU-134, TU-135, TU-140, and TU-136 were formulated with cerium oxide of 0.005 g, 0.01 g, 0.015 g, and 0.02 g, respectively. The sorbents TU-134, TU-135, TU-140, and TU-136 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent, containing 0.015-g cerium oxide, with H_2S is highest among others, while hardness of the sorbents is independent of amounts of cerium oxide (see Figure 31). These data show that amounts of cerium oxide do not affect significantly hardness of the formulated sorbents, but affect their reactivity with hydrogen sulfide.

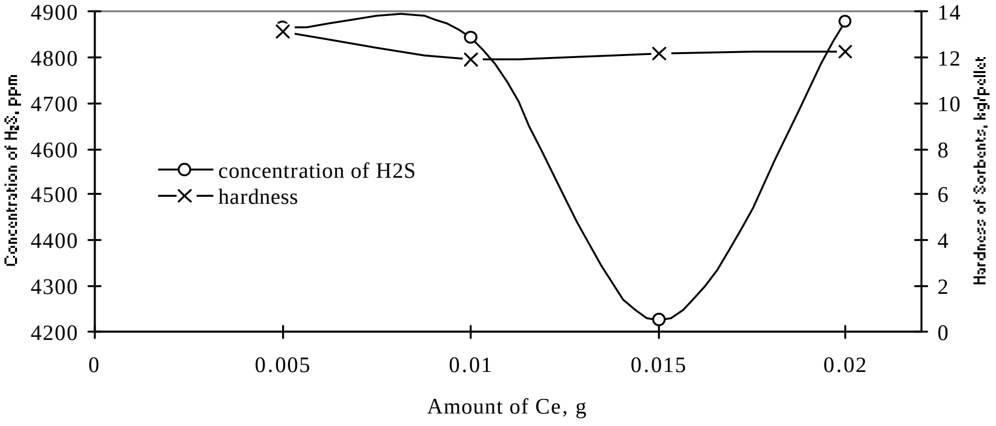


Figure 31. Effects of Ce on absorption of H_2S into sorbents and their hardness, containing 0.2-g zirconium oxide, 0.1-g gypsum, and 0.015-g of Co, Cu and Cr, respectively.

Sorbents TU-145 through TU-185

Metal oxide sorbents were formulated with various additives to enhance their reactivity with hydrogen sulfide contained in simulated coal gas mixtures (see Tables 20 through 28). Reactivity of formulated metal oxide sorbents was compared by reacting sorbents with initial 7400-ppm hydrogen sulfide for 120 seconds at 550°C (see Figures 32 through 42). Hardness of formulated metal oxide sorbents was compared by testing their hardness with a hardness tester (see Figures 32 through 42). Hardness of a fresh formulated sorbent is tested 7 times. The average value of seven hardness data is reported in the Tables. The hardness range of fresh formulated sorbents at room temperature is 8 - 32 kg/pellet. Concentrations of hydrogen sulfide at the reaction duraion of 2 minutes were analyzed 5 times for each run, and averaged, as shown in Tables 20 through 28.

Table 20. Formulation of sorbents TU-145 through TU-151B.

Sorbents	TU-145	TU-146	TU-147	TU-148	TU-149A	TU-149B	TU-149C	TU-149D	TU-150A	TU-150B	TU-151A	TU-151B
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05			0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Flour			0.05									
Heptanol				0.05								
Zirconium Oxide	0.25	0.3	0.2	0.2	0.20	0.20	0.20	0.20			0.10	0.10
Aluminum Oxide									0.20	0.20	0.10	0.10
Kaolin	0.25	0.05	0.1	0.1	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cobalt Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Cuprous Oxide	0.015	0.015	0.015	0.015	0.020	0.020	0.020	0.020	0.015	0.015	0.015	0.015
Cerium Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Chromous Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CalcinationTemperature, °C	860	860	860	860	870	880	860	860	860	880	860	880
Calcination Duration, hr	1	1	1	1	1	1	1.5	1.25	1	1	1	1
H_2S, ppm at 2-min reaction	5208	4597	5257	4826	4650	4311	4748	4435	4509	4742	4713	4641	4905	4920
Hardness, kg/pellet	8.64	10.00	8.86	9.00	14.50	16.57	31.14	16.29	4.5	5.71	4.43	10.00

21.00

Table 21. Formulation of sorbents TU-152 through TU-157E.

Sorbents	TU-152	TU-153	ZT-4	TU-138	TU-154	TU-155	TU-156	TU-157A	TU-157B	TU-157C	TU-157D	TU-157E
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7		1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2		2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05			0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Heptanol				0.05								
Zirconium Oxide	0.20	0.2		0.2	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Bentonite		0.10										
Kaolin	0.10			0.1	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cobalt Oxide	0.015	0.015		0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Cuprous Oxide	0.015	0.020		0.020	0.025	0.030	0.020	0.020	0.020	0.020	0.020	0.020
Cerium Oxide	0.015	0.015		0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Chromous Oxide	0.015	0.015		0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
1 w% H_2O_2	1.5	1.5		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CalcinationTemperature, ^oC	860	860		860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1	1		1	1.5	1.5	1.5	1	1	1.5	1.5	1.5
H_2S, ppm at 2-min reaction	4611	4199	4352	3796	4256	3935	4472	4213	4218	4339	4310	3761
Hardness, kg/pellet	22.00 12.79 14.64	11.36	-----	12.25	11.93	11.57	9.43	12	12.21	15.0	13.5	15.07

Table 22. Formulation of sorbents TU-157F through TU-163.

Sorbents	TU-157F	TU-157G	TU-157H	TU-157I	TU-158A	TU-158A1	TU-158B	TU-159	TU-160	TU-161	TU-162	TU-163
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Kaolin	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cobalt Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	------
Cuprous Oxide	0.020	0.020	0.020	0.020	0.015	0.015	0.015	0.020	0.015	0.020	0.015	0.015
Cerium Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	-------	0.015
Chromous Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	----	0.02	0.020	0.015	0.015
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calcination Temperature, ^oC	860	860	870	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1.5	1.5	1	2	1.5	1.5	1	1.5	1.5	1.5	1.5	1.5
H_2S, ppm at 2-min reaction	4503	4207	3793	4306	4352	4377	4372	3992	3699	4069	4504	4420
Hardness, kg/pellet	13.63	14.64	11.21	15.79	21.50 17.04	21.50 17.04	11.21	11	23.14 16.50	12.70	12.29	13.29

Table 23. Formulation of sorbents TU-164 through TU-167.

Sorbents	TU-164	TU-165	TU-166	TU-167	TU-168	TU-169	TU-170	TU-171	TU-172	TU-173	TU-160	TU-167
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Kaolin	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cobalt Oxide	0.02	0.015	0.02	0.015	0.02	0.015	0.015	0.015	0.015	------	0.015	0.015
Nickel Oxide				0.015			0.015					0.015
Cuprous Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Cerium Oxide	0.015	0.02	0.02	0.015	0.015	0.02	0.015	0.015	-------	0.015	0.015	0.015
Manganese Oxide								0.015				
Chromous Oxide	0.015	0.015	0.02	0.015	0.02	0.02	0.02	0.02	0.02	0.020	0.02	0.015
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calcination Temperature, °C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
H_2S, ppm at 2-min reaction	5095	4492	4179	3750	4022	4308	4977	4656	3961	4731	4268	4415
Hardness, kg/pellet	12.21	11.86	12.93	12.93	13.5	15..36	14.14	14.43	13.86	14.75	23.14 16.50	12..93

Table 24. Formulation of sorbents TU-174 through TU-179.

Sorbents	TU-174	TU-175	TU-174R	TU-175R	TU-174R1	TU-175R1	TU-176	TU-177	TU-178	TU-179	TU-179	TU-175R1
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Kaolin	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cobalt Oxide	0.015	0.015	0.015	0.015	0.02	0.015	0.015	0.015	0.015	0.02	0.02	0.015
Cuprous Oxide	0.015	0.015	0.015	0.015	0.015	0.015	--------	---------	0.02	0.02	0.02	0.015
Cerium Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Chromous Oxide	0.015	0.02	0.015	0.02	0.015	0.02	0.015	0.02	0.015	0.015	0.02	0.02
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calcination Temperature, °C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
H_2S, ppm at 2-min reaction	4489	4465	4732	4782	4657	4509	4638	5060	4822	4691	4470	4055
Hardness, kg/pellet	12.79 15.19 16.21	13.14 12.21 13.00	15.86	13.29 16.64	15.86	13.29 16.64	12.46	15.86	13.43	11.79	11.79 new H2S	13.29 16.04

Table 25. Formulation of various TU sorbents.

Sorbents	TU-174R1	TU-174R	TU-178	TU-177	TU-176	TU-175	TU-174	TU-173	TU-172	TU-171	TU-170	TU-169
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Kaolin	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cobalt Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	-------	0.015	0.02	0.015	0.015
Nickel Oxide											0.015	
Cuprous Oxide	0.015	0.015	0.02	---------	--------	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Cerium Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	--------	0.015	0.015	0.020
Manganese Oxide										.015		
Chromous Oxide	0.015	0.015	0.015	0.02	0.015	0.02	0.015	0.02	0.020	0.02	0.02	0.02
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calcination Temperature, °C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
H_2S, ppm at 2-min reaction	4967	5149	4956	4978	5423	5048	5052	5248	5161	5157	5091	5117
Hardness, kg/pellet	15.86	15.86	13.43	15.86	12.46	13.14 12.21 13.00	12.79 15.19 16.21	14.75	13.86	14.43	14.14	15.36

Table 26. Formulation of various TU sorbents.

Sorbents	TU-168	TU-167	TU-166	TU-165	TU-164	TU-163	TU-162	TU-161	TU-160	TU-159	TU-158A	157C
	Ingredient Amounts (gram) and Formulation Conditions											
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Kaolin	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cobalt Oxide	0.02	0.015	0.02	0.015	0.02	------	0.015	0.015	0.015	0.02	0.015	0.015
Cuprous Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.02	0.015	0.02	0.015	0.02
Cerium Oxide	0.015	0.015	0.02	0.02	0.015	0.02	--------	0.015	0.015	0.015	0.015	0.015
Chromous Oxide	0.02	0.015	0.02	0.02	0.015	0.02	0.015	0.02	0.020	------	0.015	0.015
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calcination Temperature, °C	860	860	860	860	860	860	860	860	860	860	860	860
Calcination Duration, hr	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
H_2S, ppm at 2-min reaction	5450	4458	4879	4791	5060	4751	5001	4838	4752	4836	4154	4423
Hardness, kg/pellet	13.50	12.93	12.93	11.86	12.21	13.29	12.29	12.70	23.14 16.50	11	21.50 17.04	15.00

Table 27. Formulation of various TU sorbents.

Sorbents	TU-157E	TU-157G	ZT-4	TU-158A	TU-175R	TU-157E	TU-157C	TU-157G	TU-180	TU-181	TU-182
	Ingredient Amounts (gram) and Formulation Conditions										
ZnO	1.7	1.7		1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2		2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05		0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.20	0.20		0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Kaolin	0.10	0.10		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cobalt Oxide	0.015	0.015		0.015	0.02	0.015	0.015	0.015	0.015	0.015	0.015
Cuprous Oxide	0.02	0.02		0.015	0.015	0.02	0.02	0.02	0.02	0.015	0.015
Cerium Oxide	0.015	0.015		0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Chromous Oxide	0.015	0.015		0.015	0.02	0.015	0.015	0.015	0.015	0.015	0.02
1 w% H_2O_2	1.5	1.5		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calcination Temperature, °C	860	860		860	860	860	860	860	860	860	860
Calcination Duration, hr	1.5	1.5		1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
H_2S, ppm at 2-min reaction	2987	4565	4588	4549	4509	4583	4372	4038	4163	4576	4491
Hardness, kg/pellet	15.07	16.64	----	21.50 17.04	13.29 16.64	15.07	15.0	14..64	16.96	13.50	16.21

Table 28. Formulation of sorbents TU-180C through TU-185.

Sorbents	TU-180C	TU-183	TU-184	TU-185	TU-186	TU-183	TU-185
	Ingredient Amounts (gram) and Formulation Conditions						
ZnO	1.7	1.7	1.7	1.7	1.7	1.7	1.7
TiO_2	2	2	2	2	2	2	2
Corn Starch	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Zirconium Oxide	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Kaolin	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Cobalt Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Cuprous Oxide	0.015	0.025	0.030	0.025	0.025	0.025	0.020
Cerium Oxide	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Chromous Oxide	0.015	0.02	0.02	0.025	0.030	0.02	0.025
1 w% H_2O_2	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Calcination Temperature, °C	860	860	860	860	860	860	860
Calcination Duration, hr	2.0	1.5	1.5	1.5	1.5	1.5	1.5
H_2S, ppm at 2-min reaction	4748	3579	4490	4239	4679	4428	4340
Hardness, kg/pellet	16.89	15.96	14.29	15.64	14.21	15.96	15.64

Sorbents TU-180B, TU-149B, TU-149D, TU-157G, and TU-180C were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.1-g kaolin, 0.2-g zirconium oxide, 0.02-g cuprous oxide, and 0.015 g of cobalt oxide, cerium oxide, and chromous oxide, respectively, varying calcination durations from 0.5 hour to 2 hour. The sorbents were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbents with H_2S decreases generally with increased calcination durations, while hardness of the sorbents increases with calcination durations (see Figure 32). Hardness of the sorbents increases from 10 kg/pellet to 17 kg/pellet by varying the durations of calcining the formulated sorbents from 0.5 hr to 2 hr. These observations indicate that calcination duration in the formulation of the sorbents affects significantly their hardness as well as reactivity with hydrogen sulfide.

Figure 32. Effects of calcination duration on absorption of H_2S into sorbents and their hardness, containing 0.2-g zirconium oxide, 0.05-g corn starch, 0.1-g kaolin, 0.02-g Cu and 0.015-g of Co, Ce and Cr, respectively.

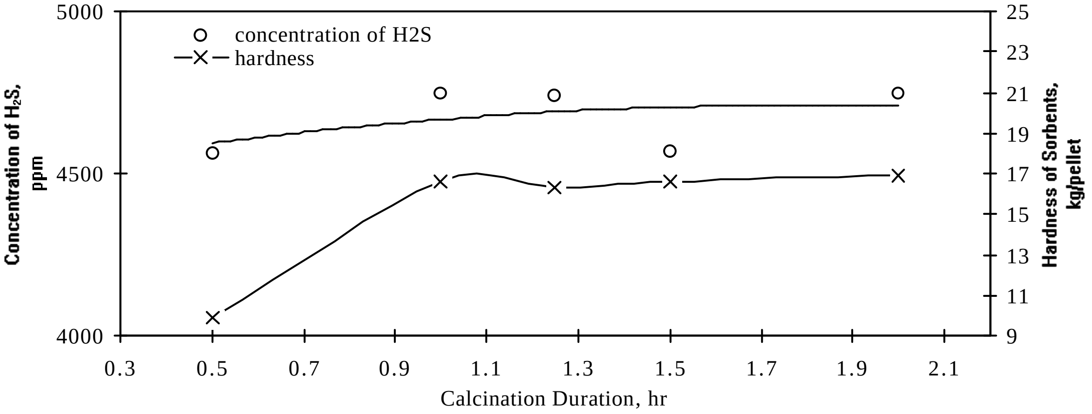
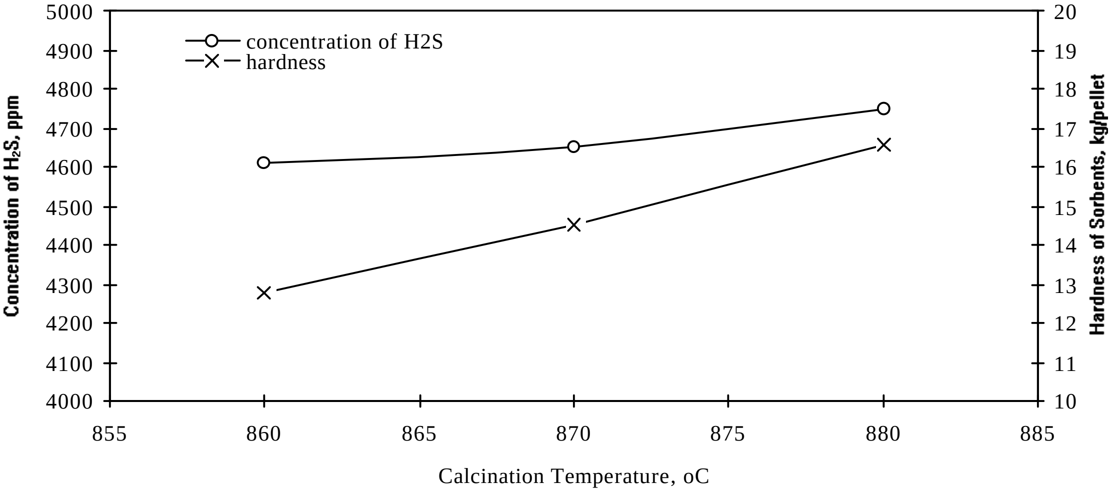
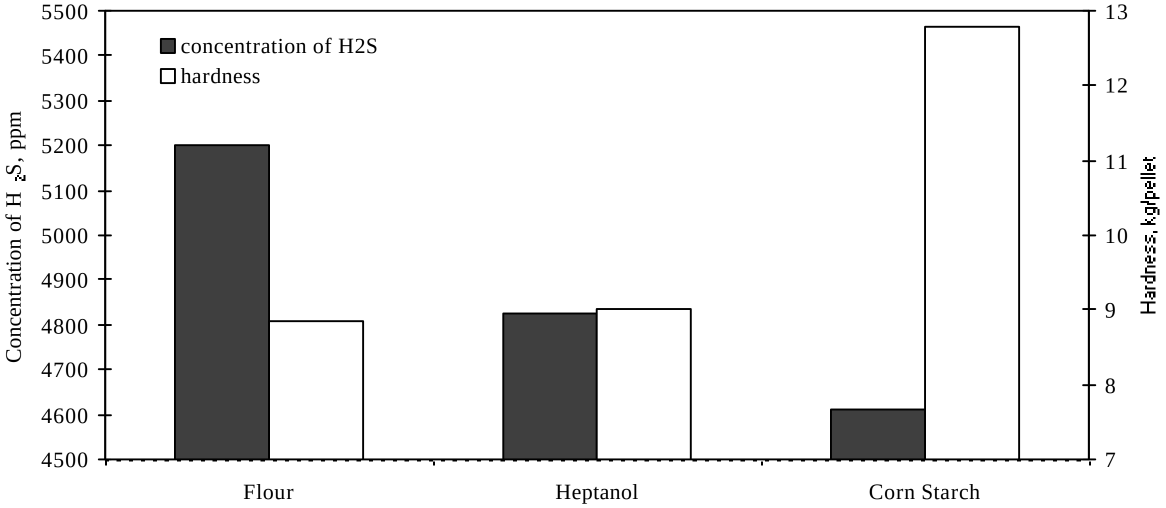


Figure 33. Effects of calcination temperature on absorption of H_2S into sorbents and their hardness, containing 0.2-g zirconium oxide, 0.05-g corn starch, 0.1-g kaolin, 0.02-g Cu and 0.015-g of Co, Ce and Cr, respectively.



The sorbents TU-152, TU-149A, and TU-149B were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.1-g kaolin, 0.2-g zirconium oxide, 0.02-g cuprous oxide, and 0.015 g of cobalt oxide, cerium oxide, and chromous oxide, respectively, varying calcination temperatures. The sorbents TU-152, TU-149A, and TU-149B were reacted with the initial 7400-ppm H_2S for 120 seconds at 550^{o}C. Reactivity of the sorbents with H_2S decreases with increased calcination temperatures, while hardness of the sorbents increases with calcination temperature (see Figure 33). These data show that calcination temperatures affect significantly hardness of the formulated sorbents, but affect slightly their reactivity with hydrogen sulfide.

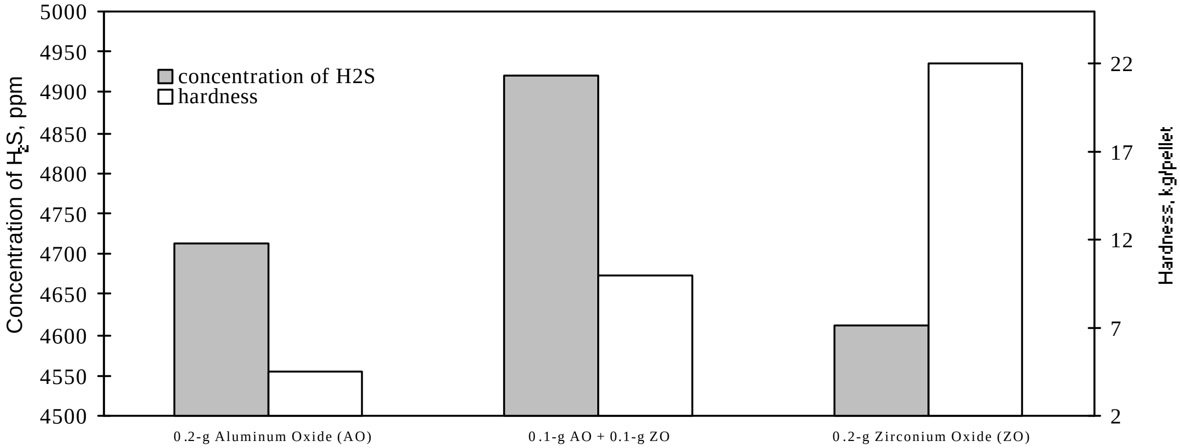
Figure 34. Effects of 0.05-g burnout matter on absorption of H_2S into sorbents and their hardness, containing 0.2-g zirconium oxide, 0.1-g kaolin, and 0.015-g of Co, Ce, Cu and Cr, respectively.



The sorbents TU-147, TU-148, and TU-152 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, and 0.015 g of cuprous oxide, cobalt oxide, cerium oxide, and chromous oxide, respectively, using various burnout matter. The sorbents TU-147, TU-148, and TU-152 were formulated with 0.05-g flour, 0.05-g heptanol, and 0.05-g corn starch, respectively. The sorbents were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent, containing 0.05-g corn starch, with H_2S is highest among others, while hardness of the sorbent, containing 0.05-g corn starch, is highest among others (see Figure 34). These data show that types of burnout matter affect both hardness of the formulated sorbents and their reactivity with hydrogen sulfide in the presence of 0.2-g zirconium oxide.

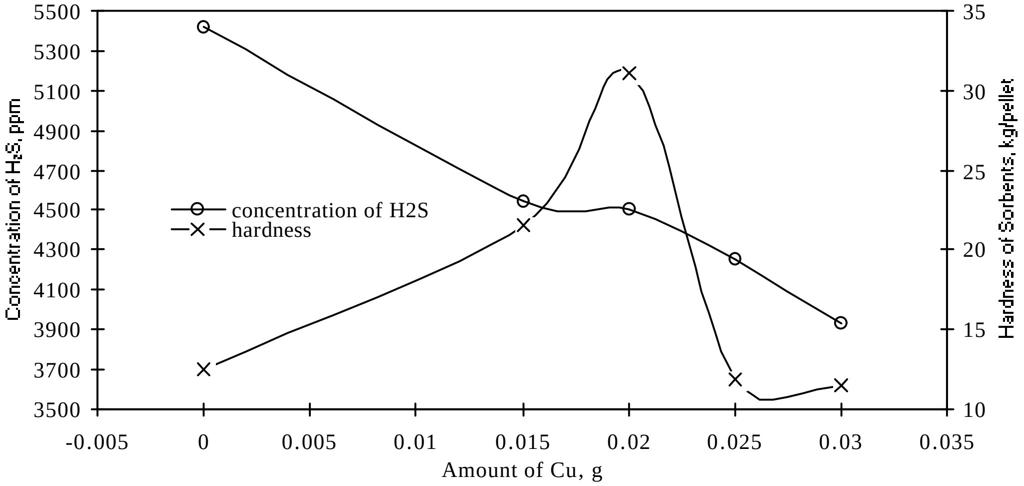
The sorbents TU-150A, TU-151A, and TU-152 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.1-g kaolin, and 0.015 g of cuprous oxide, cobalt oxide, cerium oxide, and chromous oxide, respectively, using zirconium oxide and aluminum oxide as hardening agent. The sorbents TU-150A, TU-151A, and TU-152 were formulated with 0.2 g aluminum oxide, 0.1 g aluminum oxide and 0.1-g zirconium oxide, and 0.2 g zirconium oxide, respectively. The sorbents TU-150A, TU-151A, and TU-152 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent, containing 0.2-g zirconium oxide, with H_2S is highest among them. Zirconium oxide seems to enhance hardness of the sorbents (see Figure 35). These data show that zirconium oxide promotes reactivity with hydrogen sulfide, and increases hardness of the formulated sorbents.

Figure 35. Effects of 0.2-g hardening agent on absorption of H_2S into sorbents and their hardness, containing 0.05-g corn starch, 0.1-g kaolin, and 0.015-g of Co, Ce, Cu and Cr, respectively.



The sorbents TU-176, TU-158A, TU-149C, TU-154, and TU-155 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, and 0.015 g of cerium oxide, and chromous oxide, respectively, varying amounts of cobalt oxide. The sorbents TU-176, TU-158A, TU-149C, TU-154, and TU-155 were formulated with cuprous oxide of 0 g, 0.015 g, 0.02 g, 0.025 g, and 0.03 g, respectively. The sorbents TU-176, TU-158A, TU-149C, TU-154, and TU-155 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Hardness of the sorbent, containing 0.02-g cuprous oxide, with H_2S is highest among others, while reactivity of the sorbents increases with amounts of cuprous oxide (see Figure 36). These data show that amounts of cuprous oxide affect significantly hardness of the formulated sorbents as well as their reactivity with hydrogen sulfide.

Figure 36. Effects of Cu on absorption of H_2S into sorbents and their hardness, containing 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, and 0.015-g of Co, Cr and Ce, respectively.



The sorbents TU-177, TU-175R, TU-161, TU-183 and TU-184 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, 0.02-g chromous oxide, and 0.015 g of cobalt oxide and cerium oxide, respectively, varying amounts of cuprous oxide. The TU-177, TU-175R, TU-161, TU-183 and TU-184 were formulated with cuprous oxide of 0.0 g, 0.015 g, 0.02 g, 0.025 g and 0.03 g, respectively. The sorbents TU-177, TU-175R, TU-161, TU-183 and TU-184 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent with H_2S increases with amounts of cuprous oxide, while hardness of the sorbents decreases with increased amounts of cuprous oxide (see Figure 37). These data show that amounts of cuprous oxide affect reactivity of the formulated sorbents with hydrogen sulfide as well as their hardness.

The sorbents TU-159, TU-157G, TU-182, TU-185 and TU-186 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, 0.02-g cuprous oxide, and 0.015 g of cobalt oxide, and cerium oxide, respectively, varying amounts of chromous oxide. The sorbents TU-159, TU-157G, TU-182, TU-185 and TU-186 were formulated with chromous oxide of 0.0 g, 0.015 g, 0.02 g, 0.025 g and 0.03 g, respectively. The sorbents TU-159, TU-157G, TU-182, TU-185 and TU-186 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbent, containing 0.025-g chromous oxide, with H_2S is highest among others, while hardness of the sorbents increases with amounts of chromous oxide (see Figure 38). These data show that amounts of chromous oxide affect significantly hardness of the formulated sorbents as well as their reactivity with hydrogen sulfide.

Figure 37. Effects of Cu on absorption of H_2S into sorbents and their hardness, containing 0.2-g zircinium oxide, 0.05-g corn starch, 0.1-g kaolin, 0.02-g Cr, and 0.015-g of Co and Ce, respectively.

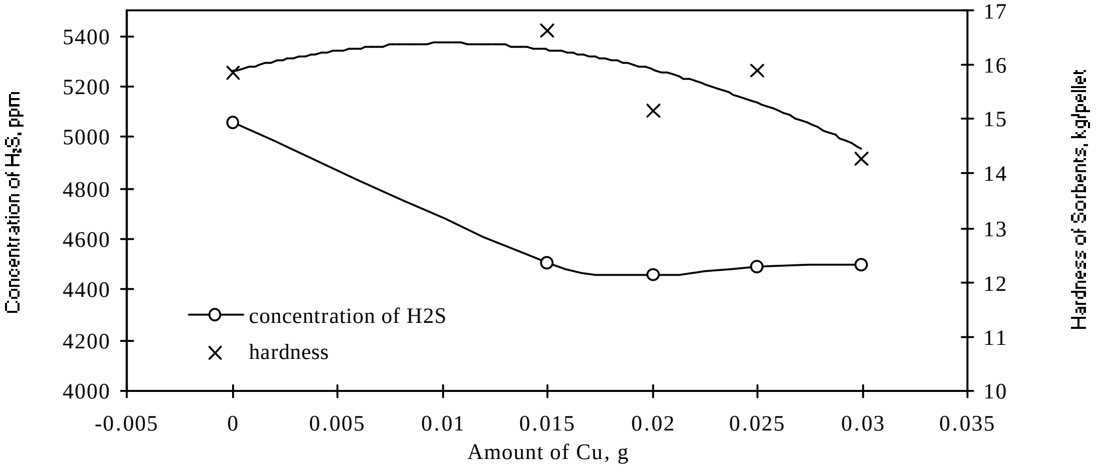
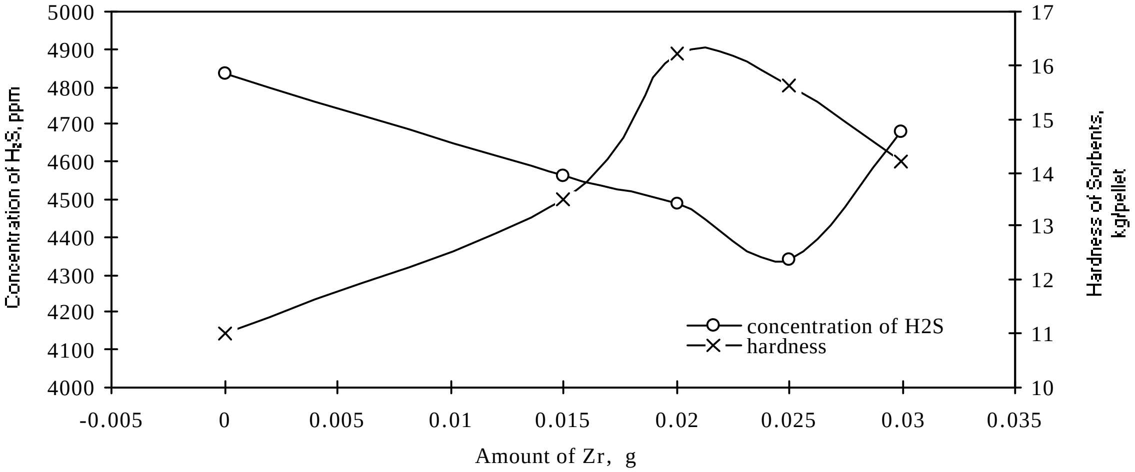
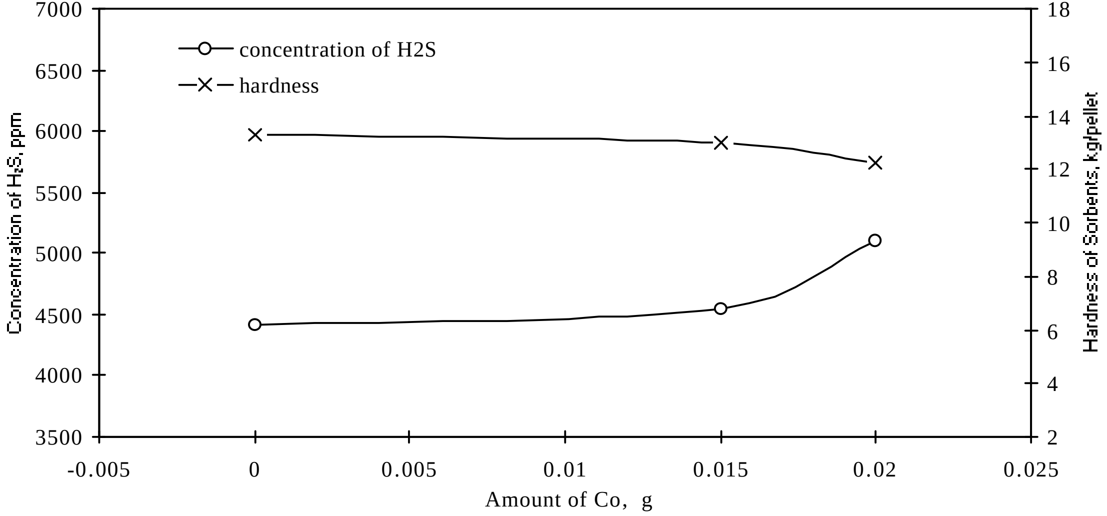


Figure 38. Effects of Cr on absorption of H_2S into sorbents and their hardness, containing 0.05-g corn starch, 0.1-g kaolin, 0.02-g zirconium oxide, 0.02-g Cu, and 0.015-g of Co, and Ce, respectively.



The sorbents TU-163, TU-181, and TU-164 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, and 0.015 g of cerium oxide, cuprous oxide, and chromous oxide, respectively, varying amounts of cobalt oxide. The sorbents TU-163, TU-181, and TU-164 were formulated with cobalt oxide of 0.0 g, 0.015 g, and 0.02 g, respectively. The sorbents TU-163, TU-181, and TU-164 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbents decreases slightly with increased amounts of cobalt oxide, while hardness of the sorbents decreases slightly with increased amounts of cobalt oxide (see Figure 39).

Figure 39. Effects of Co on absorption of H_2S into sorbents and their hardness, containing 0.05-g corn starch, 0.1-g kaolin, 0.02-g zirconium oxide, and 0.015-g of Cu, Ce, and Cr, respectively.



The sorbents TU-173, TU-175R, and TU-168 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, 0.02-g chromous oxide, and 0.015 g of cerium oxide, and cuprous oxide, respectively, varying amounts of cobalt oxide. The sorbents TU-173, TU-175R, and TU-168 were formulated with cobalt oxide of 0.0 g, 0.015 g, and 0.02 g, respectively. The sorbents TU-173, TU-175R, and TU-168 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550°C. Reactivity of the sorbents decrease with increased amounts of cobalt oxide, while hardness of the sorbents appears to decrease slightly with increased amounts of cobalt oxide (see Figure 40).

Figure 40. Effects of Co on absorption of H_2S into sorbents and their hardness, containing 0.05-g corn starch, 0.1-g kaolin, 0.02-g zirconium oxide, 0.02-g Cr and 0.015-g of Cu, and Ce, respectively.

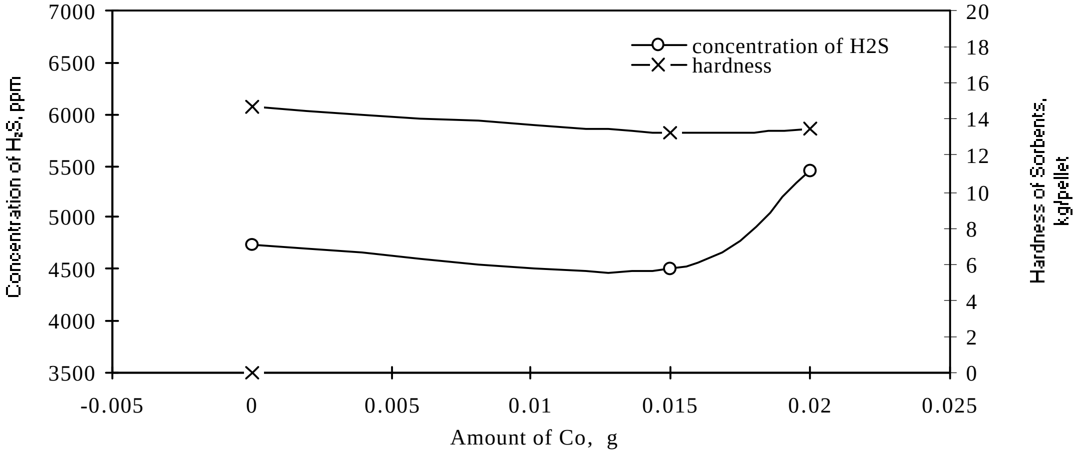
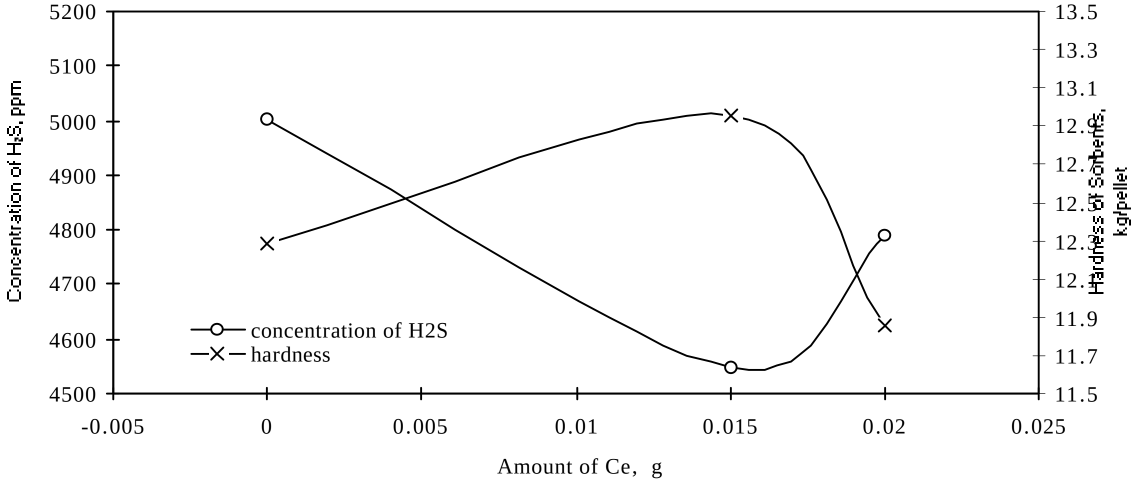


Figure 41. Effects of Ce on absorption of H_2S into sorbents and their hardness, containing 0.05-g corn starch, 0.1-g kaolin, 0.02-g zirconium oxide, and 0.015-g of Co, Cu and Cr, respectively.



The sorbents TU-162, TU-181, and TU-165 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, and 0.015 g of cobalt oxide, cuprous oxide, and chromous oxide, respectively, varying amounts of cerium oxide. The sorbents TU-162, TU-181, and TU-165 were formulated with cerium oxide of 0.0 g, 0.015 g, and 0.02 g, respectively. The sorbents TU-162, TU-181, and TU-165 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550^{o}C. Reactivity of the sorbent, containing 0.015-g of cerium oxide, is highest among them, while hardness of the sorbent, containing 0.015-g of cerium oxide, is also highest among them (see Figure 41).

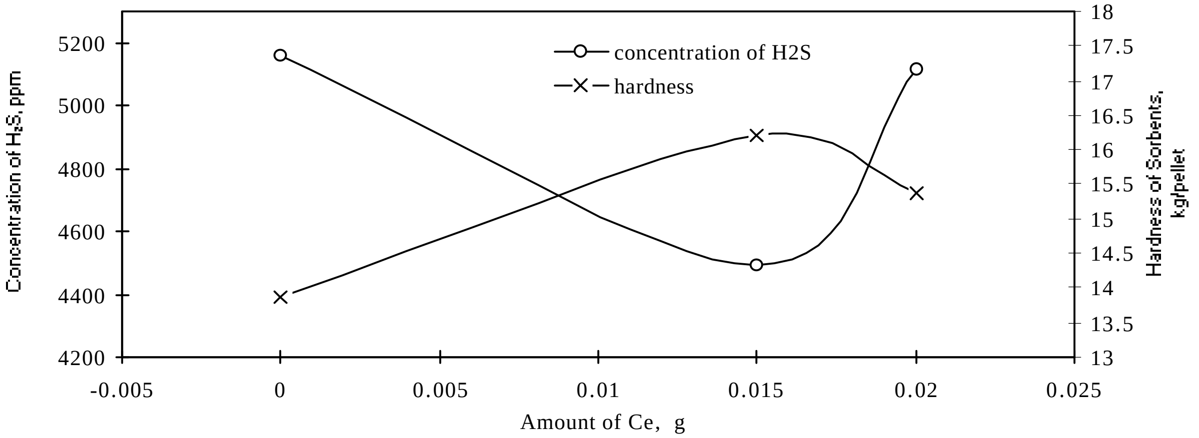


Figure 42. Effects of Ce on absorption of H $_2$S into sorbents and their hardness, containing 0.05-g corn starch, 0.1-g kaolin, 0.02-g zirconium oxide, 0.02-g Cr, and 0.015-g of Co, and Cu, respectively.

The sorbents TU-172, TU-182, and TU-169 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, 0.02-g chromous oxide, and 0.015 g of cobalt oxide, and cuprous oxide, respectively, varying amounts of cerium oxide. The sorbents TU-172, TU-182, and TU-169 were formulated with cerium oxide of 0.0 g, 0.015 g, and 0.02 g, respectively. The TU-172, TU-182, and TU-169 were reacted with the initial 7400-ppm H_2S for 120 seconds at 550^{o}C. Reactivity of the sorbent, containing 0.015-g cerium oxide, is highest among them, while hardness of the sorbent, containing 0.015-g cerium oxide, is highest among them (see Figure 42).

CONCLUSION

The following conclusions are drawn, based on experimental data on reactivity of formulated sorbents with hydrogen sulfide from simulated coal gas mixtures, and their interpretations.

- The additives Cu and Co appear to enhance reactivity of sorbents in the reaction with wet hot hydrogen sulfide at 550^{o}C. Durability of formulated sorbents appears to improve with kaolin binder in comparison with bentonite binder. Durability of formulated sorbents appears to improve with increased calcination durations. Reactivity of sorbents formulated with Co additive appears to decrease with increased calcination durations at the calcination temperature of 860°C. Reactivity of sorbents formulated with Cu additive appears to increase with calcination durations. Reactivity of sorbents formulated without additive appears to be independent of calcination durations.

- The sorbent TU-138 and the sorbent TU-140 appear to be most promising sorbents among others, considering their reactivity as well as hardness. The sorbent TU-138 was formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, zirconium oxide, 0.1-g gypsum, 0.02-g cuprous oxide , and 0.015 g of cobalt oxide, cerium oxide and chromous oxide , respectively. The sorbent TU-140 was formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g gypsum, and 0.015 g of cobalt oxide, cuprous oxide , cerium oxide, and chromous oxide, respectively.

- The sorbents TU-157G, TU-180, TU-175R, and TU-182 appear to be most promising sorbents among others, considering their reactivity as well as hardness. The sorbents TU-157G and TU-180 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, 0.02-g cuprous oxide, and 0.015 g of cobalt oxide, cerium oxide and chromous oxide, respectively. The sorbents were calcined at 860°C for 1.5 hr. The sorbent TU-175R and TU-182 were formulated with 1.7-g zinc oxide, 2-g titanium dioxide, 0.05-g corn starch, 0.2-g zirconium oxide, 0.1-g kaolin, 0.02-g chromous oxide, and 0.015 g of cobalt oxide, cuprous oxide and cerium oxide, respectively. The sorbents were calcined at 860°C for 1.5 hr.

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Title:
Subject:
Author: K. C. KWON
Keywords:
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Creation Date: 09/08/98 11:27 AM
Revision Number: 8
Last Saved On: 09/08/98 2:43 PM
Last Saved By: K. C. KWON
Total Editing Time: 163 Minutes
Last Printed On: 09/08/98 3:07 PM
As of Last Complete Printing
- Number of Pages: 55
- Number of Words: 12,201 (approx.)
- Number of Characters: 69,546 (approx.)