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## Characterization and Fixed-Bed Testing of a Nickel-Based Hot Gas Desulfurization Sorbent

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### OBJECTIVES

The objective of this project was to (1) extend a preliminary investigation completed earlier on dispersed nickel sorbents<sup>1</sup> by developing new processing methods, characterizing sorbent materials more extensively, and evaluating the materials in fixed bed reactor tests, and (2) to determine the feasibility of using dispersed nickel sorbents with reductive regeneration for hot gas desulfurization.

### BACKGROUND

There has been interest and active research on desulfurization of coal-derived gases since they were first produced by coal carbonization more than a century ago. A comprehensive review of the literature on metal and binary oxide sorbents was published by Swisher and Schwerdtfeger<sup>2</sup>. A later paper by the same authors<sup>3</sup> reviewed literature on mixed oxide sorbents and discussed the importance of thermodynamics in research on sulfur sorbents.

During the past 10 years, research in this field has focused on desulfurization at high temperatures because of the need for application of the technology to Integrated Gasification Combined Cycle (IGCC) systems. In the

1980's, the sorbent material receiving the most attention was zinc ferrite<sup>4</sup>. While it was very effective in reducing hydrogen sulfide ( $H_2S$ ) concentrations in the product gas to the low ppmv level, it suffered from zinc loss due to vaporization and poor resistance to decrepitation and attrition.

More recently, zinc titanate sorbents have been shown to have comparable desulfurizing ability to zinc ferrite and to be better in durability<sup>5-10</sup>. There is now more research being done on zinc titanate than any other class of sorbents. However, there are still unanswered questions about its durability and reactivity over many sulfidation/regeneration cycles and its ability to serve applications in which the temperature of the gas to be desulfurized is 750°C or higher. Therefore, continuing research is justified on alternate sorbent materials.

There has been some, but not an extensive amount, of prior work on sorption of sulfur (S) by nickel (Ni) for hot gas desulfurization applications. One of the properties of nickel that is somewhat unique is that it forms a liquid sulfide at sufficiently high temperatures with high sulfur potentials or  $H_2S$  levels<sup>11,12</sup>. A eutectic exists in the Ni-S phase diagram at 637°C and a composition of 33.4 wt % or 21.5 wt % S<sup>13</sup>. Under controlled conditions, the formation of a liquid

phase can be used to advantage in hot gas desulfurization. The approach used by Steiner and Gutterman<sup>14</sup> was to use pellets of Ni and NiO in a fixed-bed reactor. When simulated coal gas was passed through the beds at 740°C, liquid sulfide formed and flowed away from the pellets. Thus, there was no solid sulfide present to serve as a diffusion barrier and curtail the reaction. Their concept included a provision for collecting the sulfide formed and regenerating it in a separate reactor.

Thermodynamic calculations show that the solid Ni-liquid Ni sulfide equilibrium will not reduce H<sub>2</sub>S levels in coal gasification product gas to the low ppmv level. Fortunately, however, another mechanism can be used for sorption of S by Ni in the low concentration range. Patel, Rich, and Maru<sup>15</sup> showed that chemisorption of S on Ni occurs readily in the 500 to 700°C temperature range. They evaluated ten commercial catalysts containing dispersed Ni in a fixed-bed reactor, and success was achieved in reducing S species concentrations from 10 ppmv to 20 ppbv. The sulfur capacity varied from 2,000 to 10,000 ppmw or 0.2 to 1.0% by weight, depending on reactor conditions.

Initial work on sorbents containing dispersed Ni in an alumina (Al<sub>2</sub>O<sub>3</sub>) matrix was carried out by Swisher and Schwerdtfeger<sup>16</sup>. Two compositions were studied. One contained 26 wt % Ni in Al<sub>2</sub>O<sub>3</sub>, and the other contained 24 wt % Ni plus 7 wt % copper (Cu) in Al<sub>2</sub>O<sub>3</sub>. Copper was added because it is known to decrease the melting temperature and broaden the composition range of the liquid sulfide formed during sulfur sorption. There is a ternary eutectic reaction in the Ni-Cu-S system at 575°C. The eutectic composition in wt % is 69.8% Ni, 5.7% Cu, and 24.5% S<sup>17,18</sup>. The reactivity of individual pellets was studied in a Cahn thermogravimetric analyzer (TGA). Sulfidation was carried out in a mixture of 1 volume % H<sub>2</sub>S in H<sub>2</sub>, and regeneration was carried out in H<sub>2</sub>.

Results of the TGA experiments showed that the sorbents could be subjected to four sulfidation/regeneration cycles with no loss of reactivity. The temperature range for the experiments was 500° to 1000°C. It was found through visual observation and scanning electron microscopy that the liquid sulfide was retained in the Al<sub>2</sub>O<sub>3</sub> structure during these TGA experiments.

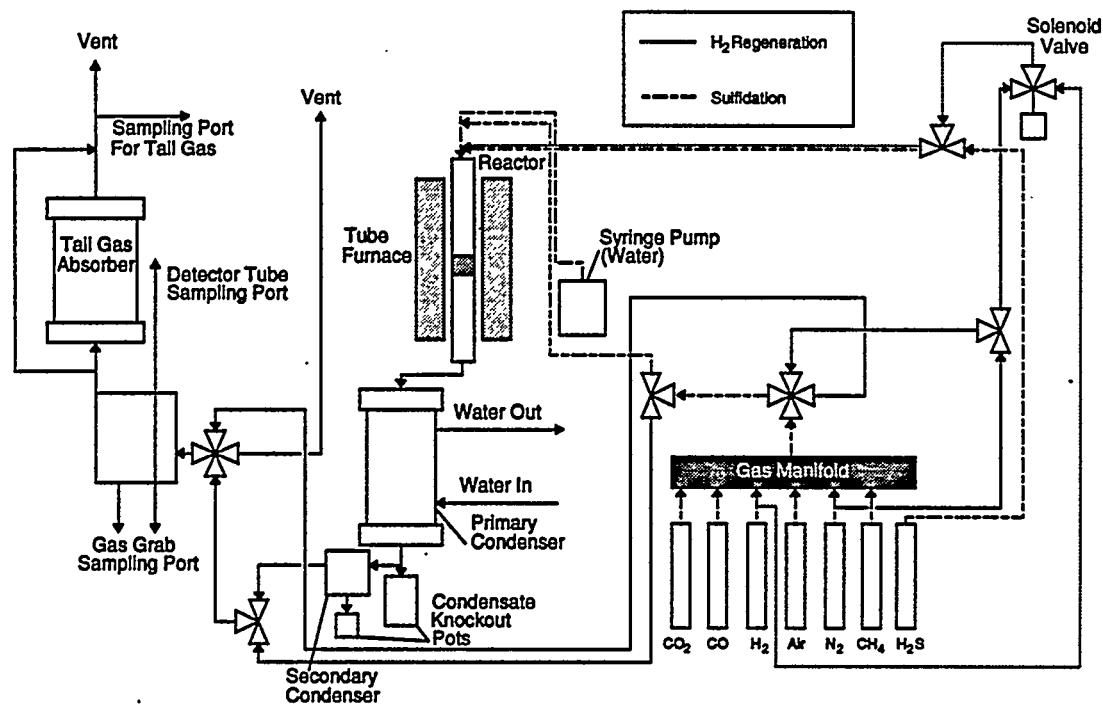
## PROJECT DESCRIPTION

### Sorbent Preparation

The sorbent was prepared for evaluation using traditional powder processing methods. Reagent-grade NiO, CuO, and Al<sub>2</sub>O<sub>3</sub> powders (all -325 mesh size) were blended in a 1 wt % solution of starch in water. Excess water was decanted, and the resulting paste was extruded through a metal tube to produce cylindrical pellets 9.3 mm in diameter and 10 to 12 mm long. The extrudates were dried in an oven at 120°C for 24 h. The dried extrudates were then placed in an electrically heated kiln; the temperature of the kiln was ramped up over a period of several hours, with a holding time of 2 h at the final sintering temperature of 1520°C. The extrudates were crushed and sieved to obtain samples in the -6, +16 mesh size range for fixed bed testing. The sorbent designation was 24Ni-7Cu-Al<sub>2</sub>O<sub>3</sub>, indicating a nominal composition of 24 wt % nickel and 7 wt % copper.

### Description of Experimental Unit

The experimental studies were carried out in a bench-scale fixed bed reactor. A simplified schematic of the reactor system is shown in Figure 1. The reactor tube was alonized 316 stainless steel with an inside diameter of 2.21 cm (0.87 in) and a 0.165-cm (0.065-in) wall thickness. The sorbent bed was located in approximately the center of the 114.3-cm (45-in) long reactor tube, and the bed height was 5.08 cm



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Figure 1. One-Inch Sorbent Screening Unit

(2 in). Gases were supplied from gas cylinders, and the flow rates were controlled through MKS mass flow controllers. All of the gases except hydrogen sulfide were first mixed together in a manifold prior to being fed into the reactor. Hydrogen sulfide gas was added to the other gases separately just upstream of the reactor inlet. Steam was provided by adding a predetermined amount of water into the preheated gas stream via an Isco model 100DM syringe pump. Both sulfidation and regeneration were conducted in the downflow mode. A heavy metal shield and a hydrogen flame detector with automatic reactive gas shutoff were installed for the protection of the operators from possible flames or explosions due to hydrogen leaks. The reactor temperature was maintained with a single-zone tubular electric furnace. The temperatures of the gases flowing into the bed and

at the core of the bed (3.8 cm [1.5 in] from the bottom of the bed) were measured using type K thermocouples. The maximum allowable temperature of the reactor was 927°C (1700°F), which precluded doing the regeneration at higher and possibly kinetically more favorable temperatures. A preheat coil consisting of a 0.635-cm (0.25-in) outside diameter, 0.089-cm (0.035-in) wall thickness 316 stainless steel tube placed between the reactor and the furnace was used to preheat all inlet components, except for hydrogen sulfide and water, during the first two and a half cycles of sulfidation/regeneration. (A cycle is defined as one complete sulfidation followed by a complete regeneration of the sorbent.) This preheat coil was removed, and gases were heated to the required temperatures while passing through the top portion of the reactor tube during all subsequent experiments.

## Experimental Procedure

Before the first sulfidation could be performed, the sorbent was pretreated to reduce the NiO to Ni metal. A 3-hour pretreatment with pure hydrogen was conducted at 871°C (1600°F) at the beginning of each series of cycles. A simulated Shell oxygen-blown entrained gasifier mixture was used as the sulfidation gas, and pure hydrogen was used as the regeneration gas. The Shell gas was chosen because it is the most likely to be applicable to this sorbent; clean fuel gas of this type could potentially be used instead of hydrogen for regeneration. The inlet gas compositions and other reaction conditions for sulfidation and regeneration are given in Table 1. Each sulfidation of the sorbent was stopped when the outlet concentration of H<sub>2</sub>S reached 1000 ppmv. The regenerations were stopped when the outlet concentration of H<sub>2</sub>S was less than or equal to 200 ppmv. The outlet stream was tested for hydrogen sulfide by the use of Sensidyne gas detector tubes of various ranges and gas grab samples, which were analyzed using gas chromatography.

A first series of six and a half cycles (designated JS1 experiments) were performed on the sorbent; afterward, the sorbent was removed from the reactor and sent for analysis. Blank runs on the empty reactor were conducted before and after the six and a half cycles of JS1 were performed; the blank runs consisted of two complete cycles of sulfidation/regeneration in each case. The reactor tube was replaced, and a second series of cycles were performed. The second series consisted of three and a half cycles (designated JS2 experiments). Two complete cycles of blank runs were conducted on the empty reactor just prior to performing the JS2 experiments.

The main difference between the JS1 and the JS2 series was that a preheat coil was located upstream of the reactor for the first two

and a half cycles of the JS1 series. However, the preheat coil was removed after two and a half cycles and not replaced during the remaining experiments. The reason for removing it was that extensive carbon deposition in it caused a significant increase in pressure drop. It was thought that the carbon deposition occurred because, although the unalozined preheat coil had been passivated with nitric acid, it catalyzed the reaction in which carbon monoxide disproportionated to form carbon dioxide and carbon solids.

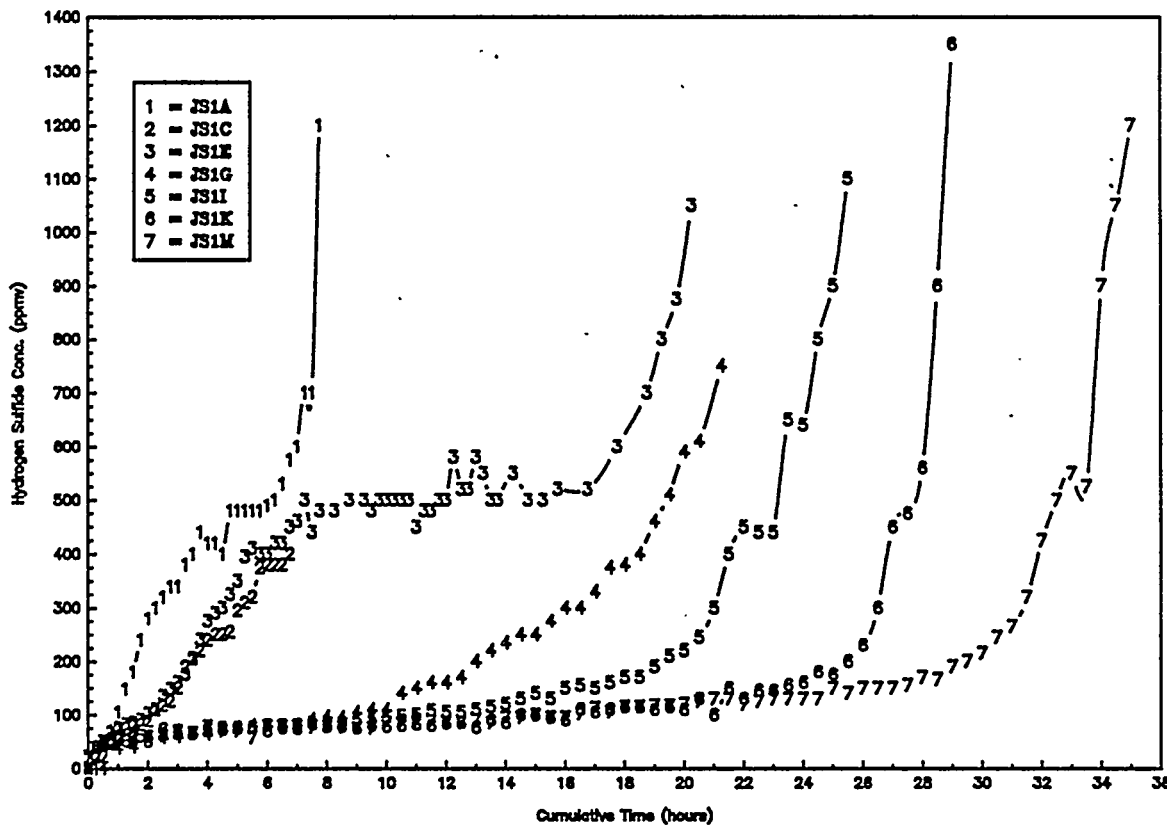
## RESULTS

The H<sub>2</sub>S breakthrough curves for the JS1 and JS2 series experiments are shown in Figures 2 and 3, respectively. It appears that the sorbent increased in capacity with each successive cycle, as evidenced by the longer times required for breakthrough. (Breakthrough is defined here as the point at which the concentration of H<sub>2</sub>S in the outlet gas reaches 200 ppmv.) After the first three cycles of series JS1, and the first two cycles of JS2, the prebreakthrough concentration of H<sub>2</sub>S in the outlet gas plateaued between 50 and 100 ppmv, with a gradual drift above these values as the sorbent approached breakthrough.

Since pure hydrogen was used as the regeneration gas, H<sub>2</sub>S was released during regeneration. The regeneration curves showing H<sub>2</sub>S outlet concentration as a function of time on-stream are shown in Figures 4 and 5 for the JS1 and JS2 series experiments, respectively. Note that the time required for regeneration increased during the first three cycles and then tended to stabilize. Regeneration took significantly more time than the corresponding sulfidation of the same cycle. Typically, the duration of each regeneration was more than six times that of the previous sulfidation.

Table 1. Reaction Conditions

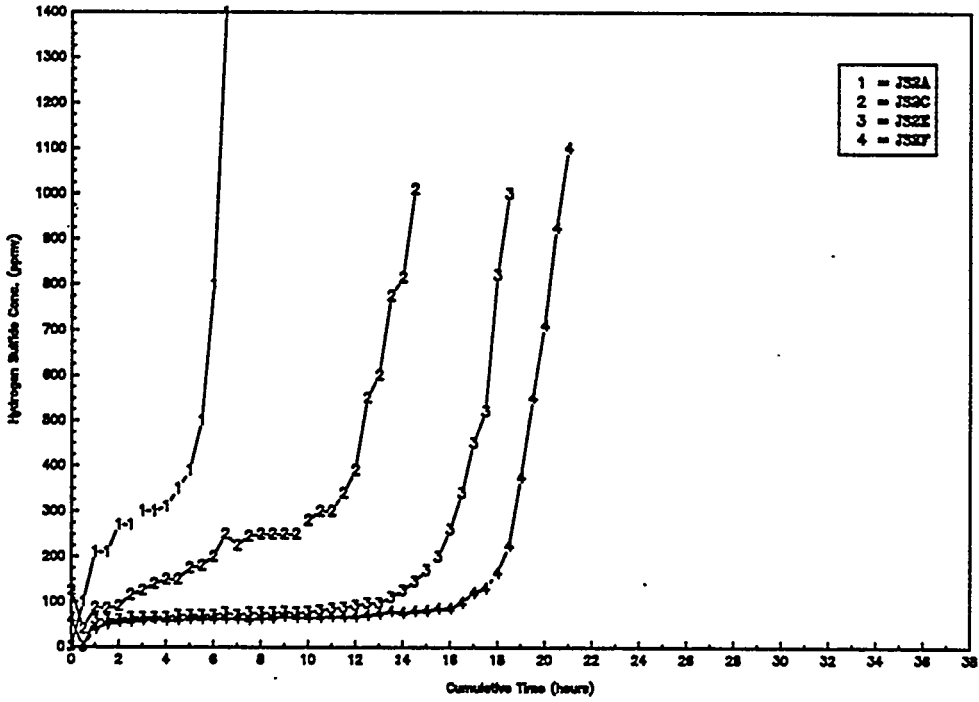
Regeneration		Sulfidation	
871°C (1600°F)		704°C (1300°F)	
205 kPa (15 psig)		205 kPa (15 psig)	
320 cc/min or 1000 l/hr		639 cc/min or 2000 l/hr	
Regeneration Gas		Gas Mixture (Volume %)	
Hydrogen	100.0%	Carbon Monoxide	64.1
End at 200 ppmv H <sub>2</sub> S in Outlet		Hydrogen Sulfide	0.3
		Nitrogen	4.3
		Hydrogen	27.3
		Water	2.0
		Carbon Dioxide	2.0
		End at 1000 ppmv H <sub>2</sub> S in Outlet	



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Figure 2. JS1 Sulfidation of 24Ni - 7Cu - Al<sub>2</sub>O<sub>3</sub> at 704°C (1300°F)

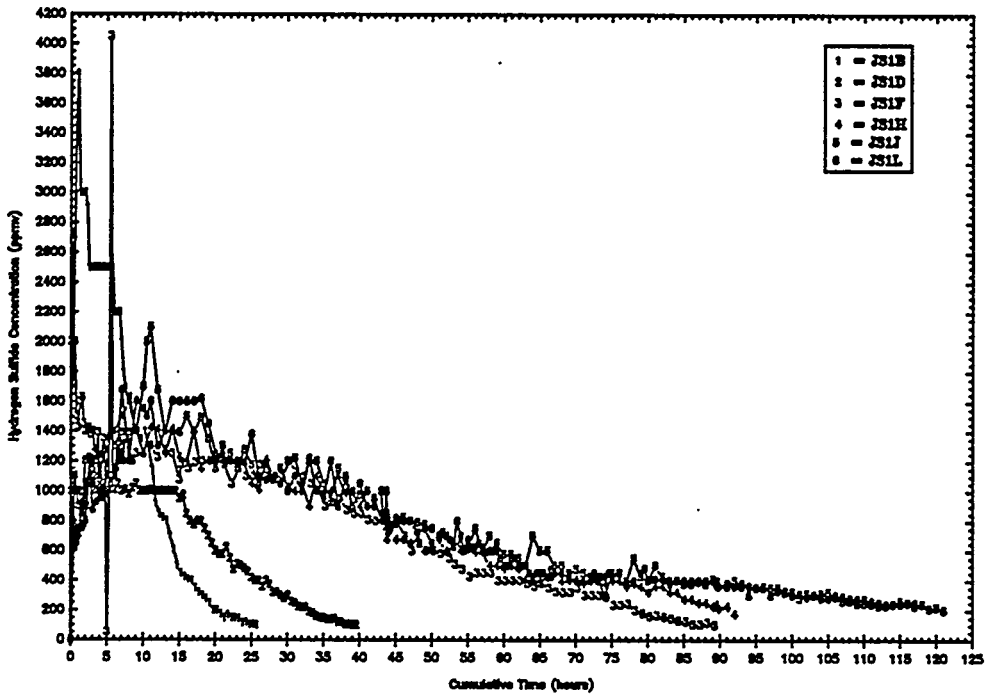




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Figure 3. JS2 Sulfidation of 24Ni - 7Cu - Al<sub>2</sub>O<sub>3</sub> at 704°C (1300°F)

Fig. 4 JS1 Regeneration of 24Ni - 7Cu - Al<sub>2</sub>O<sub>3</sub> at 871°C (1600°F)



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Figure 4. JS1 Regeneration of 24Ni - 7Cu - Al<sub>2</sub>O<sub>3</sub> at 871°C (1600°F)

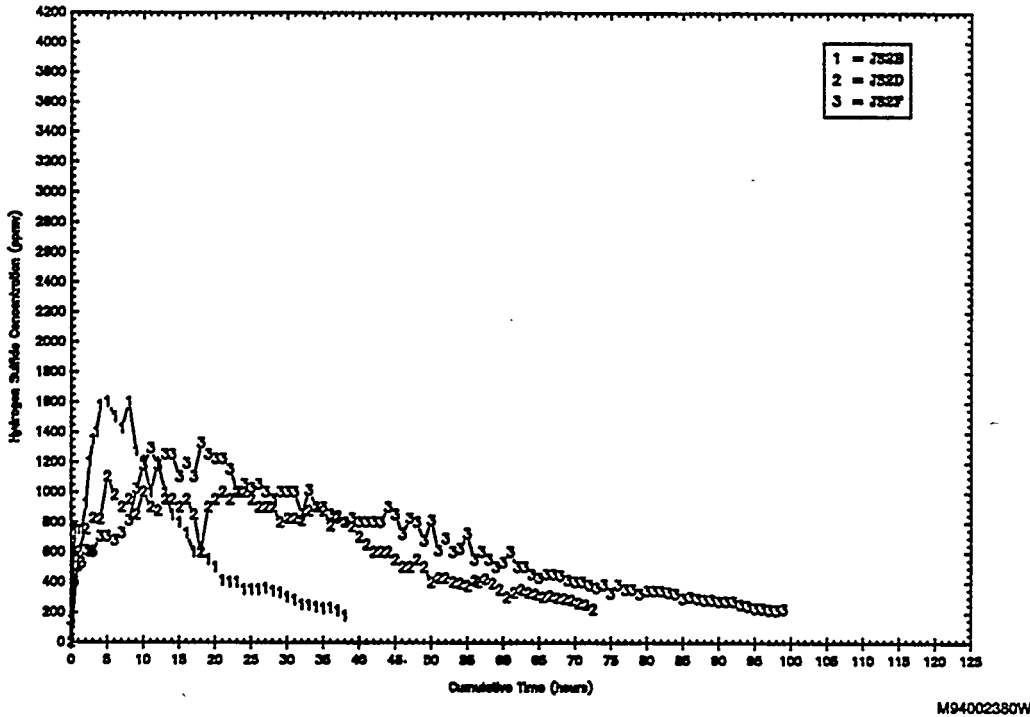


Figure 5. JS2 Regeneration of 24Ni - 7Cu - Al<sub>2</sub>O<sub>3</sub> at 871°C (1600°F)

Figure 6 shows the H<sub>2</sub>S breakthrough curves for the blank runs (empty reactor tests), which were conducted before and after the JS1 experiments and on the new reactor before the JS2 experiments. Breakthrough time on the empty reactor was significantly longer for runs conducted at the end of the test than those conducted at the beginning. However, the blank runs conducted at the end of the JS1 series had a much shorter breakthrough time than the 7th sulfidation, which was performed just prior to these, indicating that the sorbent had indeed increased remarkably in capacity.

Both the H<sub>2</sub>S breakthrough curves and the regeneration curves shown in Figures 2 through 6 were determined using Sensidyne detector tubes. Gas chromatographic analysis of the reactor outlet gas, collected downstream from the condenser units during sulfidations,

showed the dry basis volume concentrations of all the major gaseous components, in addition to H<sub>2</sub>S, SO<sub>2</sub>, and COS. Small amounts of methane (CH<sub>4</sub>) were formed, resulting in a concentration that was always less than 0.8%. The SO<sub>2</sub> concentration usually stayed below 5 ppmv, with a few excursions to higher values during some of the sulfidations, after several hours on-stream. The concentrations of CO, CO<sub>2</sub>, and H<sub>2</sub> indicated that little, if any, water-gas shift occurred. The COS concentration usually remained below 100 ppmv, and tended to increase during each experiment, as H<sub>2</sub>S increased toward breakthrough.

The chemical compositions of the fresh sorbent and the sorbent reacted for six and a half cycles (JS1 series) are shown in Table 2. The atomic absorption analysis was run twice on both the fresh and spent sorbents to recheck the

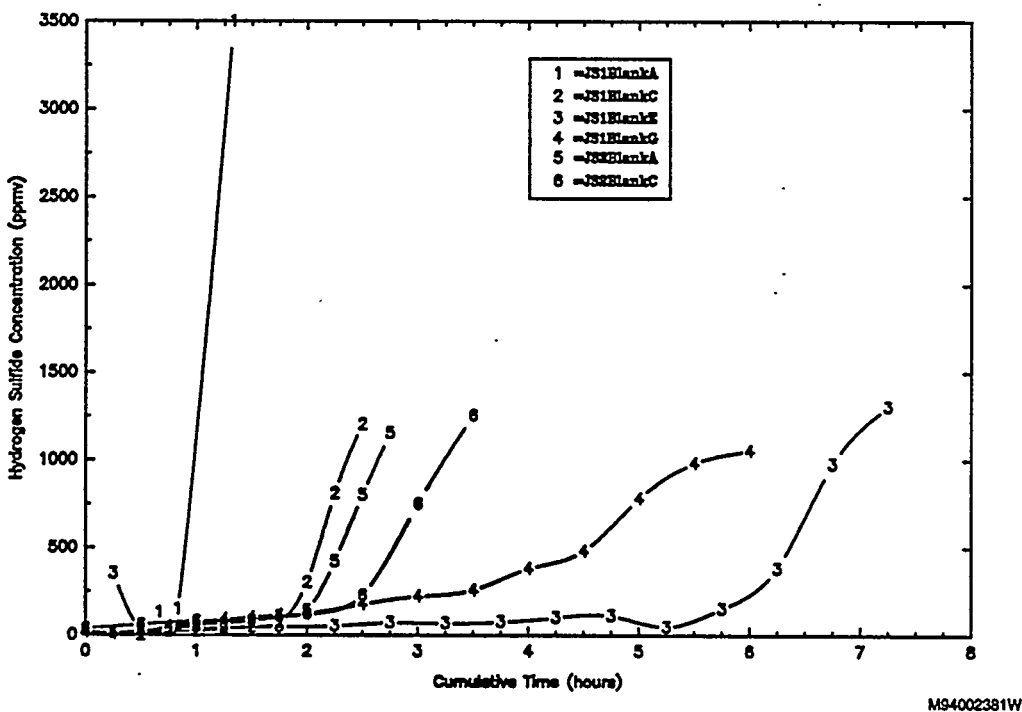


Figure 6. Blank Runs of 24Ni - 7Cu - Al<sub>2</sub>O<sub>3</sub> at 704°C (1300°F)

Table 2. Chemical Compositions of Fresh and Reacted Sorbent

Element	Fresh (wt %)	Reacted (wt %)
Aluminum	28.10	28.60
Nickel	23.60	15.80
Copper	3.75	3.90
Total Sulfur	0.08	6.63

Ni content, resulting in exactly the same results for each. The analysis of Ni in the fresh sorbent also agreed quite well with the amount of Ni that was put into the sorbent during preparation (i.e., 24.0 wt % Ni was added during preparation, and the analysis showed 23.6 wt % Ni).

Calculations from the atomic absorption analysis of Al, Ni, and Cu were made assuming that the total amount of Al in the sorbent remained constant during the six and a half cycles. The calculations showed a 32% loss of Ni after the six and a half cycles; however,

there was no loss of Cu. The sulfided sorbent contained 6.63 wt % sulfur. If it is assumed that each three Ni atoms can react with two S atoms to form Ni<sub>3</sub>S<sub>2</sub> (although there are many different stoichiometric forms of Ni<sub>x</sub>S<sub>y</sub> possible<sup>1</sup>), and two Cu atoms react with one S atom to form Cu<sub>2</sub>S, then the theoretical capacity of the sorbent is 9.54 g S/100 g fresh sorbent. Assuming the Al content of the sorbent to be constant, the actual sulfur content of the sorbent was 6.75 g S/100 g fresh sorbent, or 70.7% of theoretical capacity.

It should be noted that there is some question as to how the breakthrough time increased with each cycle, while there was simultaneously a loss of Ni from the sorbent. For example, fairly extensive redistribution of the remaining Ni would have to take place during hydrogen regeneration to compensate for this apparent volatilization loss of Ni.

Table 3 shows the physical characteristics of the fresh sorbent and the sorbent reacted for six and a half cycles (JS1 series). The mercury skeletal density, particle density, and cumulative pore volume remained essentially constant. However, the nitrogen pore volume increased seven-fold, and the BET nitrogen surface area increased 33-fold. The average pore diameter decreased to 28 percent of its original value. Porosity increased very little, if at all.

Electron micrographs of cross sections of the fresh and JS1 reacted sorbents are shown in Figure 7(a) and Figure 7(b), respectively. The sorbent appeared to be more uniform and more dispersed after reaction for six and a half cycles.

There was a concern about the possibility that some hydrogen embrittlement of the stainless steel reactor may have occurred, particularly during regeneration. Hydrogen embrittlement occurs when  $H_2$  diffuses into the metal lattice and reacts with C in the metal to form  $CH_4$ . Cracks are formed as the  $CH_4$  escapes. To determine whether this may have occurred, the reactor used during the JS1 series experiments was cut open length-wise, and electron micrographs were taken of the inner reactor wall. Microcracks and pitting were indeed observed on this inner surface of the reactor wall.

## DISCUSSION

The 24Ni-7Cu- $Al_2O_3$  sorbent was unusual, compared to zinc-based and other sorbents, in that it increased in capacity with each successive cycle. The breakthrough curve performance of most sorbents tend to either stabilize after about three cycles, or gradually deteriorate with successive cycles. The physical characteristics of the fresh and reacted sorbent indicate that there was a large increase in surface area and in the number of small pores. This may have occurred through redistribution of the Ni and Cu to finer dispersions during each hydrogen regeneration.

The blank runs conducted on the empty reactor before and after the JS1 series experiments showed that there was increased sulfur sorption by the apparatus. Two possible explanations follow. Since there was an apparent large loss of Ni through volatilization from the sorbent, Ni may have been deposited on the walls of the reactor or downstream tubing, where it might have reacted with  $H_2S$ , resulting in a longer breakthrough time for the empty reactor. Electron micrographs suggested that hydrogen embrittlement of the reactor walls may also have occurred, resulting in microcracks which could penetrate the alonized surface, creating additional surface area for S sorption. However, it should be noted that the increase in breakthrough time on the empty reactor was small compared to the increase in breakthrough time between the first and seventh sulfidations. Therefore, the largest part of the increase in apparent sorbent capacity was due to changes in the sorbent itself. Corrective actions for the problem of hydrogen embrittlement could include the use of a reactor made of ceramic material, quartz, or an alloy with a very low C content.

**Table 3. Physical Characteristics of Fresh and Reacted Sorbent**

Item	Fresh	Reacted
N <sub>2</sub> Pore Volume (cc/g)	0.006354	0.04684
Hg Skeletal Density (g/ml)	4.16	4.20
Hg Bulk Density (g/ml)	2.38	2.37
Cum. Hg Pore Vol. (ml/g)	0.18	0.19
Surface Area (m <sup>2</sup> /g)	0.0963	3.21
Avg. Pore Diameter (μm)	0.5858	0.1622
Porosity (%)	42.79	43.76



**7a. Fresh**



**7b. After Six and a Half Cycles**

**Figure 7. 24 Ni - 7Cu - Al<sub>2</sub>O<sub>3</sub> Sorbent  
Magnified 3,000 Times**

The prebreakthrough concentration of  $H_2S$  in the outlet gas was higher than expected. Patel, Rich, and Maru<sup>15</sup> had observed a reduction in S species concentration from 10 ppmv to 20 ppbv; in that case, a typical commercial Ni catalyst, 20 wt % Ni on  $Al_2O_3$ , was used for  $H_2S$  removal from a simulated coal gas. However, in the present study, the higher levels of inlet  $H_2S$  concentration apparently caused the reactive surface sites to become rapidly occupied by sulfur, after which bulk sulfidation took place.

Sulfides that form in commonly studied sorbents, such as zinc ferrite and zinc titanate, are solids at their hot gas desulfurization reaction temperatures. However, nickel sulfide became a liquid at the reaction conditions studied here. Since liquids tend to have higher vapor pressures than solids, it might be expected that the liquid nickel sulfide could give rise to vapors which could then be swept away by the simulated coal gas.

Long regeneration times were required by the sorbent (usually at least six times as long as the respective sulfidation breakthrough time, and as much as 22 times longer). If it is assumed that the species to be regenerated were  $Ni_3S_2$  and  $Cu_2S$ , 70.7% of theoretical capacity of the sorbent had been reached (9.54 g sulfur/100 g fresh sorbent), and the shortest regeneration time observed is considered (i.e., from the first cycle of the JS1 series), then 310 gmole of  $H_2$  were required to remove each gmole of S from the sorbent. This makes the sorbent impractical for commercial use in a fixed-bed mode under these conditions, since at least as many reactors as the greatest number of times the length of regeneration was greater than its respective sulfidation would be required. Also, large volumes of reducing gas would be required for regeneration.

However, it should be noted that Jhunjunwala<sup>1</sup> showed in TGA experiments that when sulfidation was carried out at 700°C and regeneration at 950°C on the same type of sorbent, the regeneration time was slightly less than the time required for sulfidation. Unfortunately, the fixed-bed unit used in the present studies could not be operated at temperatures greater than 871°C.

## FUTURE WORK

Since the presence of copper tends to reduce the temperature at which liquid nickel sulfides form, a  $Ni/Al_2O_3$  without copper will be studied. Also, a lower reaction temperature will be used (593°C [1100°F] instead of 704°C [1300°F]); hopefully, this will help avoid nickel loss through volatilization. Since the time required for hydrogen regeneration was unacceptably long, oxidative regeneration will be attempted and directly compared with hydrogen regeneration.

## ACKNOWLEDGMENTS

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