

# Properties of Sulfur Sorbents Containing Dispersed Nickel in an $\text{Al}_2\text{O}_3$ Matrix

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For advanced coal gasification systems, regenerable sorbents are being developed to remove sulfur (S) from the hot product gas prior to its use in gas turbines and high-temperature fuel cells. Whereas zinc (Zn) base sorbents are attractive for these applications, they have limitations in high-temperature capability and in durability. Materials containing dispersed nickel (Ni) in an  $\text{Al}_2\text{O}_3$  matrix have the potential to be better in both respects. Their main limitation is that they do not reduce  $\text{H}_2\text{S}$  concentrations to the low parts per million (ppm) level. Results are reported here on the second phase of a program on dispersed Ni sorbents. Included are the results of crush strength, thermogravimetric analysis, and fixed-bed reactor experiments. An important conclusion drawn from the results is that chemisorption of  $\text{H}_2\text{S}$  plays a major role in reducing its concentration in gas exiting the bed below the levels expected from the Ni-Ni sulfide equilibrium.

## Keywords

coal gasification, desulfurization, nickel

## 1. Introduction and Literature Review

DESULFURIZATION of coal-derived gases has been a subject of interest and active research 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 (Ref 1). Later, the same authors (Ref 2) reviewed literature on mixed oxide sorbents and discussed the importance of thermodynamics in research on S sorbents.

During the past ten years, research in this field has focused on desulfurization at high temperatures because of the need for application of the technology to fluidized-bed coal combustion and to integrated gasification combined cycle (IGCC) systems. The IGCC systems provided the impetus for the project described here. In the 1980s, the sorbent material receiving the most attention was zinc ferrite (Ref 3). While it very effectively reduced  $\text{H}_2\text{S}$  concentrations in the product gas to the low ppm level, it suffered from Zn loss due to vaporization and poor resistance to decrepitation and attrition.

More recently, zinc titanate sorbents were shown to have comparable desulfurizing ability to zinc ferrite and to be less susceptible to vaporization losses of Zn (Ref 4-9). Now, more research is being done on zinc titanate than on any other class of sorbents. However, there are still unanswered questions about its durability over many sulfidation-regeneration cycles (Ref 4, 8) and its ability to serve applications in which the temperature of the gas to be desulfurized is above 700 °C. Therefore, continuing research is justified on alternate sorbent materials.

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There has been some research on sorption of S from coal gases by Ni. One somewhat unique property of Ni is that it forms a liquid sulfide at sufficiently high temperatures and S potentials or  $\text{H}_2\text{S}$  levels (Ref 10, 11). A eutectic exists in the Ni-S phase diagram at 637 °C and 33.4 at.% or 21.5 wt% S (Ref 12). Under controlled conditions, the formation of a liquid phase can be used to advantage in hot gas desulfurization. Steiner and Guterman (Ref 13) used 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, no solid sulfide was present to serve as a diffusion barrier and curtail the reaction. The concept included a provision for collecting the sulfide formed and regenerating it in a separate reactor.

Nogita et al. (Ref 14) briefly studied the adsorption of S on dispersed cobalt (Co), Ni, molybdenum (Mo), and copper (Cu) on  $\text{TiO}_2$  at 300 °C. The criterion they used for ranking materials was S capacity, which is defined as the mass of S absorbed as a fraction of the initial total mass of the sorbent. The capacity of the Ni-containing material was 9 g S/100 g sorbent, which was second only to Co among the four studied. Since the source of S was a 1%  $\text{H}_2\text{S}$  mixture in  $\text{N}_2$ , NiS was the reaction product.

The solid Ni-liquid Ni sulfide equilibrium will not in theory reduce  $\text{H}_2\text{S}$  levels in coal gasification product gas to as low as 10 ppmv (parts per million volume) (Ref 1). Fortunately, however, another mechanism can be used for sorption of S by Ni in the low concentration range. Patel et al. (Ref 15) showed that chemisorption of S on Ni occurs readily in the 500 to 700 °C temperature range. Ten commercial catalysts containing dispersed Ni were evaluated in a fixed-bed reactor, and success was achieved in reducing S species concentrations from 10 ppmv to 20 ppbv (parts per billion volume). The S capacity varied from 2,000 to 10,000 ppm or 0.2 to 1.0 wt%, depending on reactor conditions.

Initial work on sorbents containing dispersed Ni in an  $\text{Al}_2\text{O}_3$  matrix was carried out by Swisher and Schwerdtfeger (Ref 16). Two compositions were studied. One contained 26 wt% Ni in  $\text{Al}_2\text{O}_3$ , and the other contained 24 wt% Ni plus 7 wt% Cu in  $\text{Al}_2\text{O}_3$ . Copper was added because it decreases the melting temperature and broadens the composition range of the liquid sulfide formed during S sorption. A ternary eutectic reaction

occurs in the Ni-Cu-S system at 575 °C. The eutectic composition is 69.8 wt% Ni, 5.7 wt% Cu, and 24.5 wt% S (Ref 17, 18). The reactivity of individual pellets was studied in a Cahn thermogravimetric analyzer (TGA). Sulfidation was carried out in a mixture of 1% H<sub>2</sub>S in H<sub>2</sub>, and regeneration was carried out in H<sub>2</sub>. Oxidative regeneration was not attempted because little or no weight change would occur on converting NiO to a composition near Ni<sub>3</sub>S<sub>2</sub>. Also, the apparatus did not contain a provision for analyzing the gas to determine the amount of SO<sub>2</sub> evolution. Results of the TGA experiments showed that the sorbents could be subjected to four sulfidation-regeneration cycles with no change in reactivity. The temperature range for the experiments was 500 to 1000 °C. Visual observation and scanning

electron microscopy (SEM) showed that the liquid sulfide formed was retained in the Al<sub>2</sub>O<sub>3</sub> pore structure.

Since the results described above appeared promising, the research was extended in the present investigation to include the following tasks:

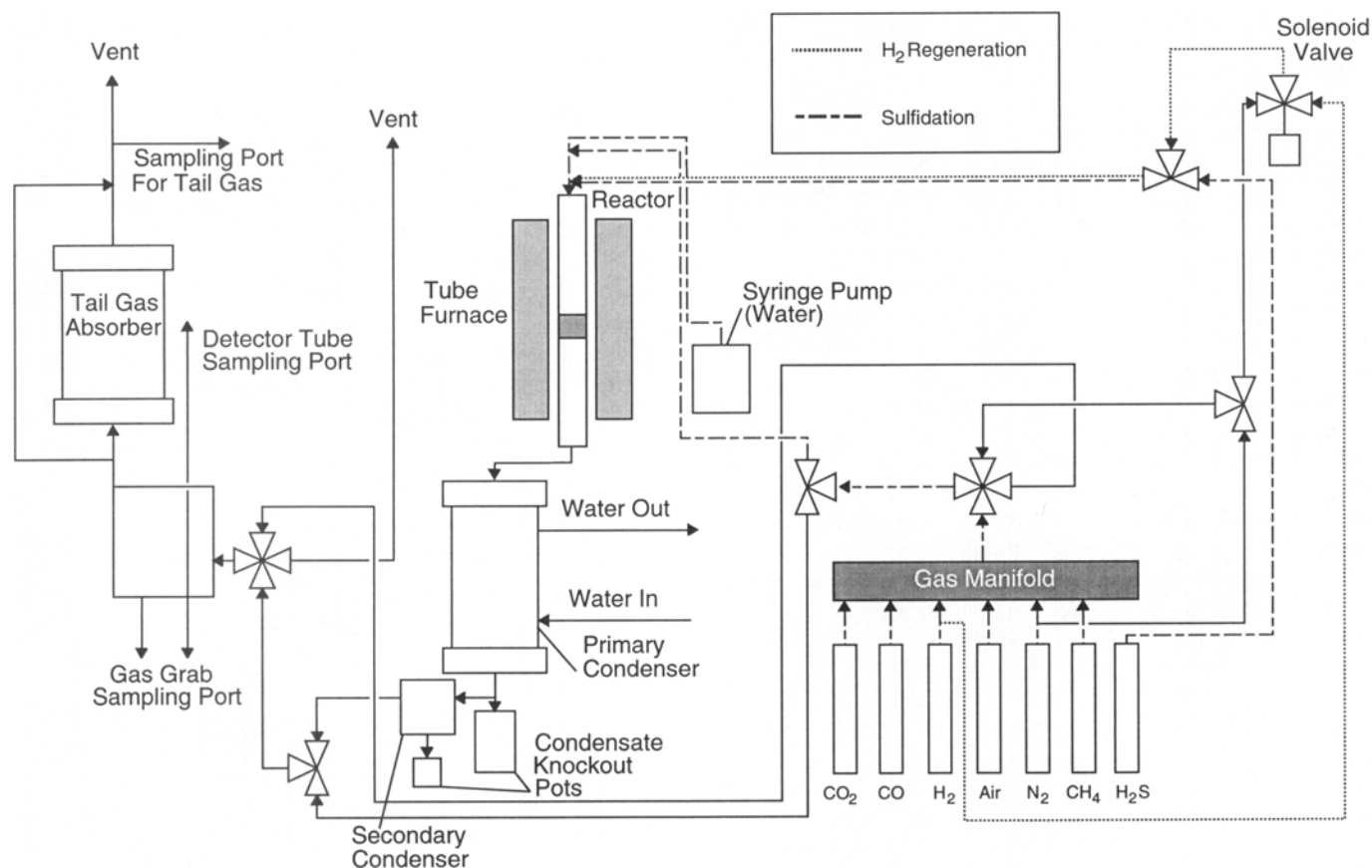
- Preparation of larger quantities of material
- TGA reactivity measurements in simulated coal gas
- Measurement of compressive strengths
- Additional characterization studies, which included x-ray diffraction (XRD), electron microscopy, chemical analysis, Brunauer-Emmett-Teller (BET) surface area measurements, and mercury porosimetry
- Testing of materials in a fixed-bed reactor

**Table 1 Gas composition for sulfidation (simulated Shell gasifier composition)**

Component	Concentration, %
H <sub>2</sub>	27.3
CO	64.1
CO <sub>2</sub>	2.0
N <sub>2</sub>	4.3
H <sub>2</sub> O	2.0
H <sub>2</sub> S	0.3
<b>Total</b>	<b>100.0</b>

## 2. Experimental Procedures

Materials were prepared for evaluation using traditional powder processing methods. Reagent-grade NiO, CuO, and Al<sub>2</sub>O<sub>3</sub> powders were blended in a 1% solution of starch in water. The powders were all -325 mesh size. Excess water was decanted; then the resulting paste was extruded through a metal tube to produce cylindrical pellets 9.3 mm diameter and 10 to 12 mm long. Pellets were dried with 24 h treatments in a controlled oven at 120 °C. For sintering, the pellets were heated overnight to about 700 °C. The next day, they were heated to



**Fig. 1** Fixed-bed sorbent screening unit

the sintering temperature of 1450 or 1520 °C over a period of 5 h. The holding time at the sintering temperature was 2 h.

Most of the pellets were crushed to obtain samples in the -6, +16 mesh size range. This material was used for both TGA and fixed-bed reactor tests. Several pellets from each formulation were used for density and crush strength measurements. After the end surfaces were ground flat, the bulk density was calculated from the dimensions and weights of the pellets. Crush strength measurements were made using a model MTS-810 apparatus (Materials Testing Systems Corp., Eden Prairie, MN). For each formulation, six pellets were tested, and the results were averaged.

Most of the TGA experiments were carried out in a DuPont model 950 (TA Instruments, Inc., New Castle, DE) instrument. These were supplemented with a few weight gain and weight loss experiments carried out in a controlled-atmosphere tube furnace. The gas mixtures used for sulfidation and regeneration were prepared by controlling the flow rates of gases taken from cylinders.

SEM was used to characterize pore structures and the appearance of the dispersed metal and metal sulfide particles. A Hitachi model instrument S-570 (Hitachi Instruments, Inc., Santa Clara, CA) was used. It was necessary to vapor deposit Au-Pd films on the specimen surfaces to obtain satisfactory resolution of their structures.

Several specimens were subjected to XRD analysis. Measurements were made with a Rigaku x-ray diffractometer, model DMAX-B (Rigaku International Corp., Tokyo, Japan), using Cu-K $\alpha$  radiation. Prior to testing, the samples were ground to -200 mesh size.

The fixed-bed tests were carried out in the apparatus shown in Fig. 1, which has a reactor tube made from alonized 316 stainless steel. Tests were carried out with approximately 14 g of sorbent in a bed that was 2.2 cm diameter and 5.1 cm high. For sulfidation, simulated coal gasification product gas was used. More specifically, gases from cylinders were mixed to match a typical composition obtained in the oxygen-blown gasifier developed by the Shell Oil Company. H<sub>2</sub>S was added in the amount of 3000 ppmv to yield the gas composition given in Table 1. The gas was passed downward through the bed at a

space velocity of 2000/h. The corresponding flow rate was 639 standard cm<sup>3</sup>/min. Regeneration was carried out with H<sub>2</sub> flowing downward at a space velocity of 1000/h. The apparatus was limited in temperature capability to 927 °C (1700 °F), which was lower than the temperature desired for efficient regeneration. The reactor pressure was 205 kPa (15 psig). Gas exiting the bed during the tests was analyzed primarily with Sensidyne detector tubes (Sensidyne, Inc., Largo, FL) for H<sub>2</sub>S, but checks were made hourly with gas chromatograph samples.

### 3. Results and Discussion

Table 2 summarizes the compositions and sintering temperatures of the four formulations studied. In the left column, the compositions are expressed as the percentages by weight of Ni, Cu, and Al<sub>2</sub>O<sub>3</sub> after reduction of NiO and CuO in H<sub>2</sub>. The compositions are expressed this way in the text and illustrations. The second column gives the equivalent compositions for the oxides in the initial mixtures. The last column lists porosities in the as-sintered material. These values were calculated from measured bulk densities and handbook values for the phases present after sintering. These phases and their theoretical densities are as follows: Al<sub>2</sub>O<sub>3</sub>,  $\rho = 3.99 \text{ g/cm}^3$ ; NiAl<sub>2</sub>O<sub>4</sub>,  $\rho = 4.51 \text{ g/cm}^3$ ; and CuAl<sub>2</sub>O<sub>4</sub>,  $\rho = 4.60 \text{ g/cm}^3$ . The presence of these phases after sintering was consistent with XRD measurements. However, a detailed analysis to obtain percentages of each phase from the x-ray spectra was not possible because of overlapping x-ray peaks.

Table 3 lists crush strength data for the as-sintered materials. The data are given both in stress units (MPa) and in force divided by contact length, in this case, diameter (N/mm). Stress units are used traditionally for specifying properties of materials, but force divided by contact length is used more frequently for catalysts and sulfur sorbents. As expected, the crush strengths in Table 3 increase with decreasing porosity. (See Table 2.)

The crush strengths reported here are very high compared to those of zinc titanate and zinc ferrite; see Table 4. Since other investigators frequently report data in units of N/mm, the com-

**Table 2 Composition and porosity data**

Composition, wt %	Starting material, wt %	Sintering temperature, °C	Porosity (as-sintered), %
26Ni-Al <sub>2</sub> O <sub>3</sub>	33.3%NiO, 66.7%Al <sub>2</sub> O <sub>3</sub>	1450	61
26Ni-Al <sub>2</sub> O <sub>3</sub>	33.3%NiO, 66.7%Al <sub>2</sub> O <sub>3</sub>	1520	49
24Ni-7Cu-Al <sub>2</sub> O <sub>3</sub>	30.5%NiO, 8.9%CuO, 60.6%Al <sub>2</sub> O <sub>3</sub>	1450	47
24Ni-7Cu-Al <sub>2</sub> O <sub>3</sub>	30.5%NiO, 8.9%CuO, 60.6%Al <sub>2</sub> O <sub>3</sub>	1520	40

**Table 3 Crush strength data for dispersed Ni sorbent materials**

Composition, wt %	Sintering temperature, °C	Crush strength, MPa	Crush strength, N/mm	Standard deviation, N/mm
26Ni-Al <sub>2</sub> O <sub>3</sub>	1450	26	186	29
26Ni-Al <sub>2</sub> O <sub>3</sub>	1520	38	278	41
24Ni-7Cu-Al <sub>2</sub> O <sub>3</sub>	1450	58	430	90
24Ni-7Cu-Al <sub>2</sub> O <sub>3</sub>	1520	130	866	84

parisons are made in these units. In the study on zinc titanate by Swisher (Ref 7), the major objective was to increase strength by incorporating  $\text{Zn}_2\text{TiO}_4$  in a matrix of  $\text{TiO}_2$ . Even though the strength of the resulting sorbents was high compared to the formulations tested by the other investigators (Ref 5, 19), the dispersed Ni in  $\text{Al}_2\text{O}_3$  sorbents evaluated here are much higher in crush strength. The high strengths are due to the superior properties of  $\text{Al}_2\text{O}_3$  as a structural ceramic and its inert behavior in sulfidizing gases. One might argue that crush test results obtained with a Materials Testing Systems apparatus, as used here, should not be compared to those obtained with a traditional catalyst testing apparatus, as used by others. A direct comparison was made on a batch of zinc titanate pellets provided by Gupta (Ref 20). The average crush strength on 10 pellets was 18 N/mm on the MTS machine, compared to 14 N/mm on a catalyst testing apparatus. Thus, the difference does not negate conclusions drawn from Table 4.

The initial experiments to evaluate chemical reactivity involved thermogravimetric measurements. The results shown in Fig. 2 were obtained by carrying out  $4\frac{1}{2}$  sulfidation-regeneration cycles on several pellets in a controlled-atmosphere tube furnace under conditions derived from the results of prior work (Ref 16). The sulfidation treatments consisted of 2 h at 900 °C

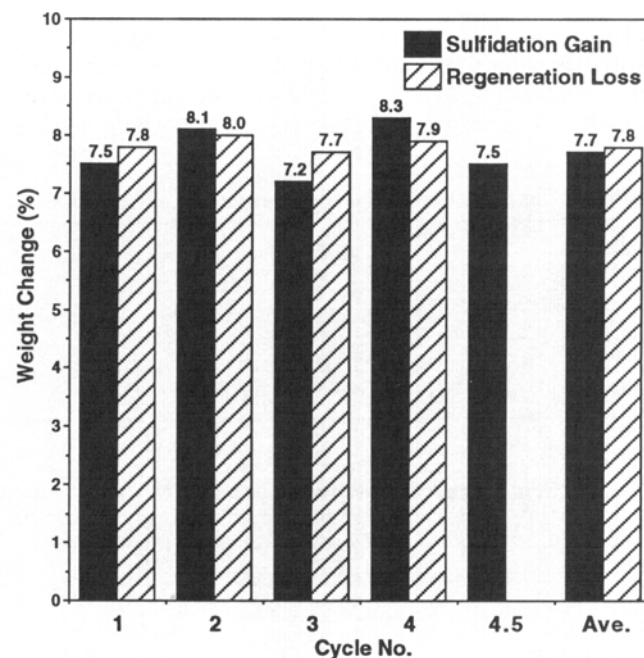
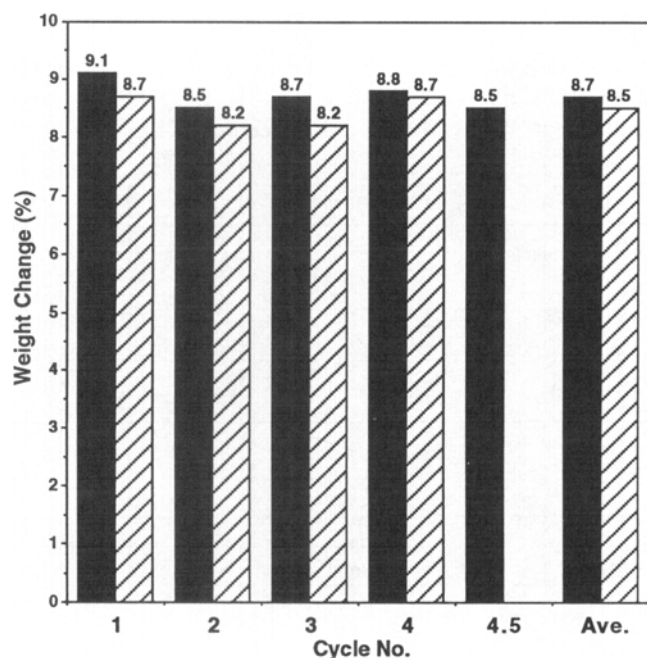
in a mixture of 1%  $\text{H}_2\text{S}$  in  $\text{H}_2$ . Regeneration was conducted for 3 h at 1000 °C in pure  $\text{H}_2$ . Two of the four formulations were evaluated this way. For the 26Ni- $\text{Al}_2\text{O}_3$  material, the average S capacity was 8.6 wt%, and no significant change occurred during the  $4\frac{1}{2}$  cycles. For the 24Ni-7Cu- $\text{Al}_2\text{O}_3$  material in Fig. 2(b), the S capacity was less by approximately 1 wt%. While there was more variation from cycle to cycle than shown in Fig. 2(a), there was no trend toward degradation.

Another set of thermogravimetric results is shown in Fig. 3. The measurements were made on single particles in a DuPont thermogravimetric analyzer (TGA). One plot is shown for each of the four sorbent formulations. In the first step,  $\text{H}_2$  reduction at 950 °C was used to produce dispersions of either Ni metal or a Ni-Cu alloy in the  $\text{Al}_2\text{O}_3$  matrix. The rates of  $\text{H}_2$  reduction in Fig. 3 were somewhat higher than rates of reduction of  $\text{NiAl}_2\text{O}_4$  powders obtained by Sridhar et al. (Ref 21). The same authors found that NiO could be reduced much faster.

In the second step in Fig. 3, Ni and Ni-Cu were sulfidized at 700 °C in simulated coal gas of the composition given in Table 1. In the third and final step, metal dispersions were again produced by regeneration in  $\text{H}_2$  at 950 °C. The main difference observed was that the time required for sulfidation and regeneration was longer for the Cu-containing sorbents in Fig. 3(c) and (d). Sulfur capacities for the Cu-containing sorbents were also slightly smaller, in agreement with Fig. 2. If the change in reactivity is attributed to the chemical effects of the Cu addition, then a compromise in sorption and regeneration rates must be accepted to take advantage of the larger temperature range over which a liquid sulfide is formed. Although not studied here, the formation of a liquid rather than a solid sulfide should result in less stress development as the chemical reactions proceed, which in turn should result in better sorbent durability.

**Table 4** Crush strength comparisons

Sorbent	Crush strength, N/mm	References
Dispersed Ni in $\text{Al}_2\text{O}_3$	186-866	This project
Zinc titanate in $\text{TiO}_2$	42-224	Swisher (Ref 7)
Zinc titanate	12-32	Ayala et al. (Ref 5)
Zinc titanate	36	Grindley (Ref 19)



**Fig. 2** Weight gain and loss behavior with sulfidation for 2 h in 1% $\text{H}_2\text{S}$ -99% $\text{H}_2$  mixture at 900 °C and regeneration for 3 h in  $\text{H}_2$  at 1000 °C

An alternate explanation for the reaction rate effect can be given if porosity differences are analyzed. From the data in Fig. 3, a parameter  $t_{1/2}$  is defined as the time required for 50% completion of the sulfidation or regeneration reaction. Values of  $t_{1/2}$  from Fig. 3 were plotted against porosity percent values from Table 2. Results are given in Fig. 4. Smooth curves fit the data, the reaction time increases with decreasing porosity, and the  $t_{1/2}$  values for regeneration are lower than for sulfidation. These inferences all make sense intuitively, even though the use of porosity percent as a parameter ignores the important effects of pore size distribution. The data suggest that the reaction rate is not enhanced significantly by increasing the porosity beyond 50%.

In the previously described experiments, there was no evidence for specimen decrepitation or the egress of liquid sulfide from the pores. A few specimens were also examined under a scanning electron microscope (SEM). Results for specimens of the 24Ni-7Cu-Al<sub>2</sub>O<sub>3</sub> material sintered at 1520 °C are shown in Fig. 5. In Fig. 5(a), the specimen was examined after the initial H<sub>2</sub> reduction treatment at 1000 °C. The bright, mostly faceted particles are metallic, and they vary in size from <1 μm to about 3 μm. The appearance of a single particle after sulfidation in a 1%H<sub>2</sub>S-99%H<sub>2</sub> mixture at 900 °C is shown in Fig. 5(b). At the experimental temperature, the particle was a Ni-Cu-S liquid droplet. A fraction of the surface of the particle appears to have ruptured either during the experiment or during SEM specimen preparation. There was no evidence that the liquid sulfide wetted the pores in the Al<sub>2</sub>O<sub>3</sub> matrix, which is consistent with the observation that no seepage occurred. The third SEM photograph in Fig. 5(c) was taken of a specimen after regeneration in H<sub>2</sub> at 1000 °C. The particle is similar to the metallic particles shown in Fig. 5(a), except that it is larger. The tendency for

larger particles to grow by subsuming small particles is expected from surface energy reduction principles. The SEM photographs of 26Ni-Al<sub>2</sub>O<sub>3</sub> material published in Ref 16 are similar to the ones shown in Fig. 5. The TGA reactivity data are also consistent with results reported in Ref 16. The results presented thus far, therefore, are a logical extension of the results of the earlier study and include evaluation of new processing and characterization methods.

In the remainder of the project, fixed-bed reactor tests were conducted to evaluate the dispersed Ni sorbents under conditions closer to expected practice. All except one of the fixed-bed tests were carried out in the apparatus shown in Fig. 1. Its only limitation was a maximum temperature capability of 927 °C (1700 °F) because of the metal reaction tube, and it was considered too risky to use a control temperature above 871 °C (1600 °F) because of possible exothermic sorbent reactions. Before presenting the experimental results, the results of equilibrium calculations are given to explain the tests and the possibility of having as many as three H<sub>2</sub>S breakthrough events.

As shown in Fig. 6, sulfidizing gas containing 3000 ppmv H<sub>2</sub>, which corresponds to H<sub>2</sub>S/H<sub>2</sub> =  $1.10 \times 10^{-2}$  for the test conditions, is passed downward through the fixed bed of particles. Near the top of the bed, equilibrium data (Ref 11) show that nonstoichiometric Ni<sub>3</sub>S<sub>2</sub> should form (denoted as Ni<sub>3</sub>S<sub>2+x</sub>). At the position in the bed where the H<sub>2</sub>S concentration is reduced to 1230 ppmv, liquid nickel sulfide should form. Further down in the bed, where the H<sub>2</sub>S concentration is reduced to 520 ppmv, another zone is reached where S capture must occur by chemisorption. The latter mechanism could reduce the H<sub>2</sub>S concentration to less than 1 ppmv, as demonstrated by Patel et al. (Ref 15). As time passes and the bed absorbs more S, the interfaces shown in Fig. 6 move downward

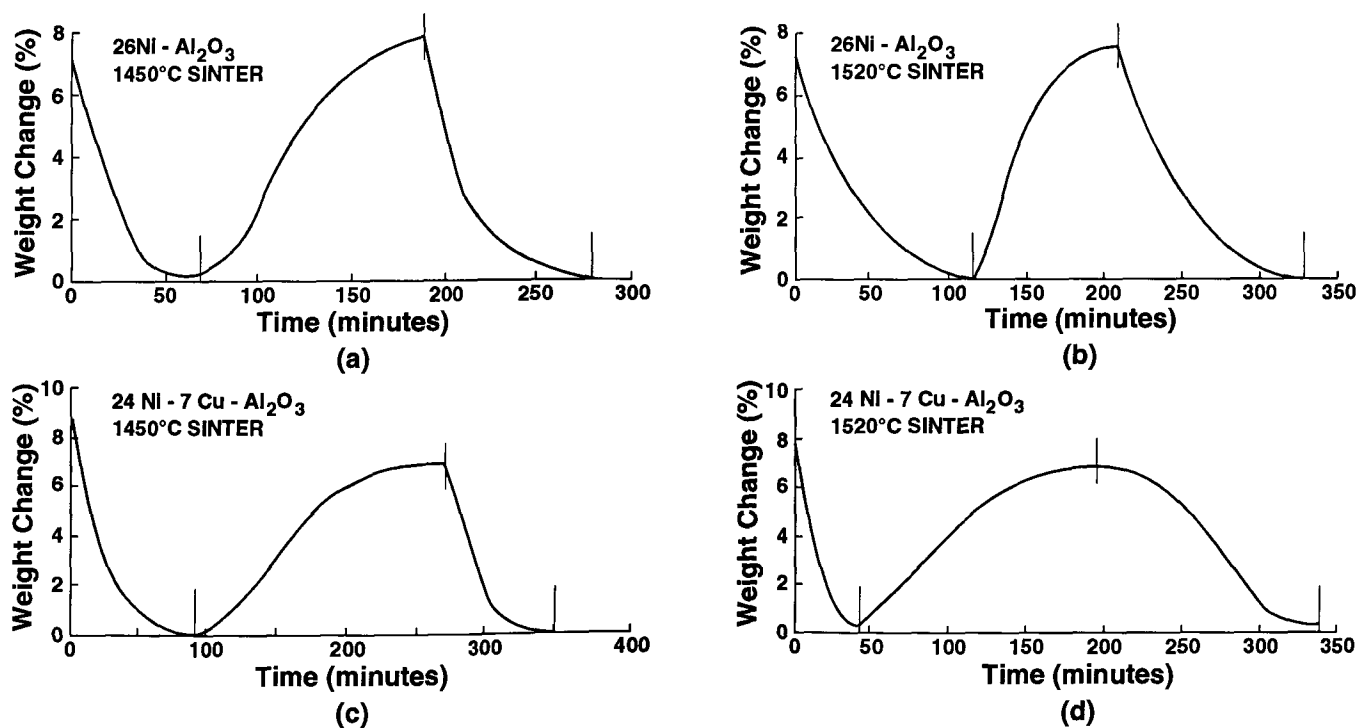


Fig. 3 TGA data showing H<sub>2</sub> reduction at 950 °C, sulfidation in simulated coal gas at 700 °C, and regeneration in H<sub>2</sub> at 950 °C

and eventually disappear. In principle, this model predicts that three  $H_2S$  breakthrough events should occur. In practice, however, blurring of the breakthrough events might occur because of deviations from local equilibrium in the bed. The concentration values shown in Fig. 6 were calculated rigorously from thermodynamic data. It was not possible to carry out the same calculation for adding Cu to the sorbent because needed thermodynamic data are not available. However, large differences from the pure Ni case are not expected.

Turning to the test data, Fig. 7 shows the  $H_2S$  breakthrough results on a dry basis for a  $6\frac{1}{2}$  cycle test on the 24Ni-7Cu- $Al_2O_3$  material sintered at  $1450^\circ C$ . For the first three cycles, a plateau appears in  $H_2S$  concentration at approximately 500 ppmv, which corresponds to the interface in Fig. 6, where the Ni-S liquid and chemisorbed S on Ni coexist. For cycles 4 through 7, the plateau is at approximately 100 ppmv, which does not correspond to any of the values shown in Fig. 6. The presence of 7% Cu in the alloy should not lower the equilibrium  $H_2S$  concentrations in the bed very much. It is possible that Cu segregates to the pore surfaces because of its higher affinity for S than Ni, but even pure Cu reacting to form  $Cu_2S$  would only reduce the equilibrium concentration of  $H_2S$  to 250

ppm at  $704^\circ C$  (Ref 22). Another possible explanation is that the prebreakthrough concentration is determined primarily by chemisorption of  $H_2S$ , but a value of 20 ppmv or less, as obtained by Patel et al. (Ref 15), was not obtained because of differences in experimental conditions (temperature, gas flow rate, sorbent porosity, etc.).

A striking feature in the data in Fig. 7 is that breakthrough time increased significantly with each successive cycle. This feature was also observed in a project on zinc titanate sorbents where a similar sorbent preparation procedure was used (Ref 8). The sorbents were prepared under one set of thermochemical conditions but are tested under a much different set of conditions. Therefore, it is not at all surprising that the structure and properties of the materials change during the tests. Fortunately, here the properties improve. It is not uncommon for the opposite to occur because of secondary sintering, decrepitation, or vaporization losses.

Direct evidence for structural changes is provided in Table 5. The reacted material has a much higher  $N_2$  pore volume and BET surface area than the fresh material. There was also a large decrease in the average pore diameter during the test. Thus, the pore structure became much finer as a result of the cyclic chemical transformations, giving rise to improved reactivity and longer time to  $H_2S$  breakthrough. There could also have been a beneficial redistribution of Ni and Cu to increase their concentrations near pore surfaces. It was not possible to prove this experimentally because available surface science techniques do not have the required resolution.

After the test, the sorbent was chemically analyzed for sulfur. The value obtained, 6.63 wt%, when compared to a calculated value for conversion of all the Ni and Cu to  $Ni_3S_2$  and  $Cu_2S$ , shows that the sorbent reached 71% of its theoretical capacity. The time for regeneration in  $H_2$  at  $871^\circ C$  ( $1600^\circ F$ ) was very long (25 to 120 h). Detailed data on this and other aspects of the test are given in Ref 23. If  $H_2$  regeneration were used in a commercial process, an all-ceramic or a ceramic-lined metal

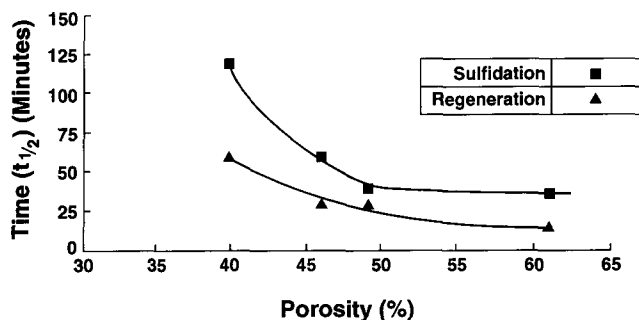


Fig. 4 Porosity dependence of half reaction time ( $t_{1/2}$ )

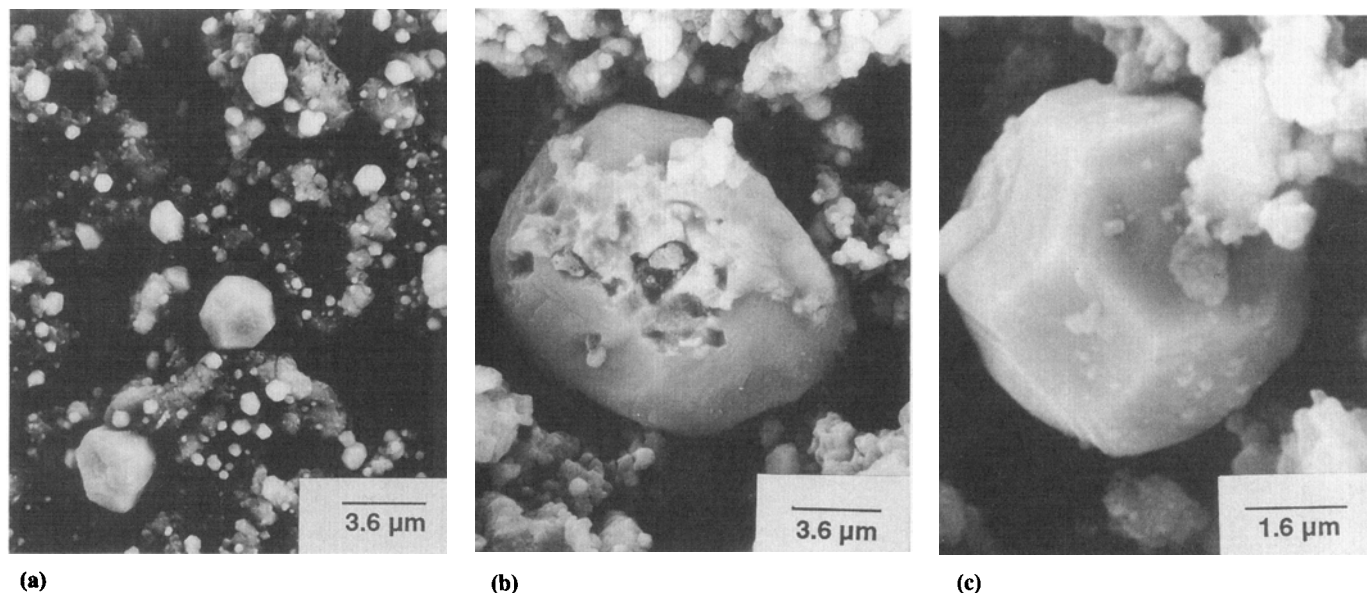


Fig. 5 Scanning electron micrographs of 24Ni-7Cu- $Al_2O_3$  specimens sintered at  $1520^\circ C$  (a) after oxide reduction in  $H_2$  at  $1000^\circ C$ , (b) after sulfidation in 1%  $H_2S$ -99%  $H_2$  mixture at  $900^\circ C$ , and (c) after regeneration in  $H_2$  at  $1000^\circ C$

reactor would be best for the needed temperature capability. A supplementary experiment in an apparatus with a quartz reaction tube was conducted to support this recommendation. It was a single-cycle fixed-bed experiment similar to the one discussed above, except that the temperature for H<sub>2</sub> regeneration was 1000 °C (1832 °F). The time for regeneration was 17 h, which was nearly the same as for H<sub>2</sub>S breakthrough during the first half of the cycle.

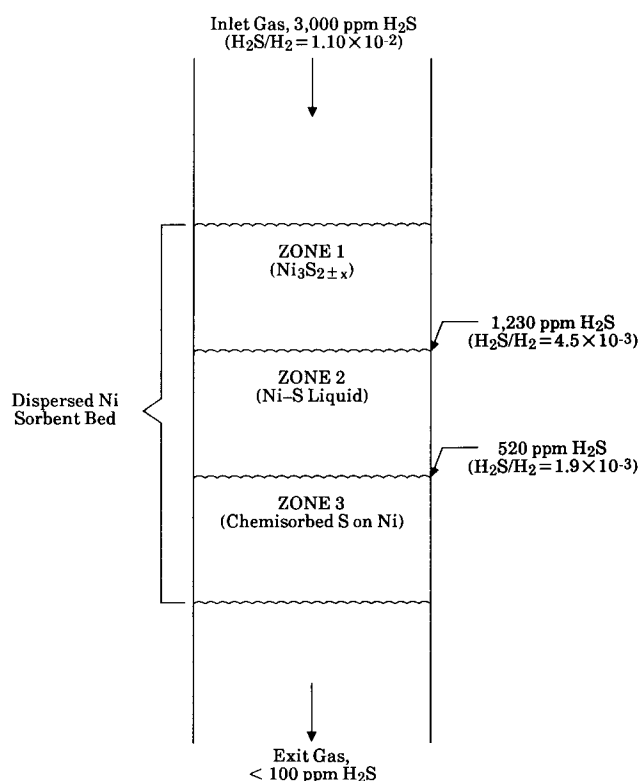
The results of another fixed-bed test are shown in Fig. 8. The material was 26Ni-Al<sub>2</sub>O<sub>3</sub> sintered at 1520 °C. The test temperature was 593 °C (1100 °F), and the duration was 3½ cycles. At this temperature, no liquid sulfide phase should form, and the H<sub>2</sub>S concentration corresponding to equilibrium between Ni and Ni<sub>3</sub>S<sub>2±x</sub> should be 270 ppmv (Ref 11). The results are similar to those given in Fig. 7 in that the breakthrough time increased with each cycle. The prebreakthrough H<sub>2</sub>S concentration after the first cycle, however, was much lower, about 25 versus 100 ppmv. Again, this concentration is very low compared to the predicted equilibrium concentration of 270 ppmv, so chemisorption of S on Ni surfaces is believed to be the dominant mechanism for fixing the concentration exiting the bed, but with Ni<sub>3</sub>S<sub>2±x</sub> formation being a major contributor to sulfur capacity of the bed. The lower temperature of this test is believed to account for the lower prebreakthrough concentration compared to the preceding test since stronger chemisorption is expected at the lower temperature.

The last fixed-bed test was designed to determine the feasibility of oxidative regeneration. Earlier, it was mentioned that oxidative regeneration was avoided initially because little or

no sorbent weight change would occur, and the reaction could not be studied with TGA measurements. This problem does not occur with fixed-bed tests, and oxidative regeneration is preferred to reductive regeneration by most developers due to cost considerations. The sulfidation data for the test are plotted in Fig. 9. The material was 26Ni-Al<sub>2</sub>O<sub>3</sub>, and the temperature was 593 °C (1100 °F). The H<sub>2</sub>S breakthrough times were much shorter than in the other tests, which indicates that Ni is a better sorbent than NiO. Therefore, another step should be used to reduce Ni to the metallic state after regeneration and before sulfidation.

The regeneration data shown in Fig. 10 are more interesting and encouraging than that for H<sub>2</sub> regeneration. Regeneration was carried out at a temperature of 871 °C (1600 °F) and with a gas composition of 50% air and 50% steam. Nearly all of the S was released as SO<sub>2</sub> in 1½ h of reaction time. Even though the sorbents were only partially sulfidized with the procedure used, the rapid release of SO<sub>2</sub> suggests that any future work on this system should explore this option further.

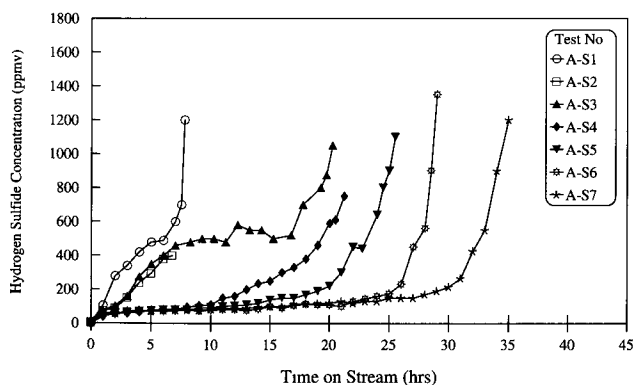
Metal analysis of both the fresh and reacted sorbents via atomic absorption (AA) was attempted after each of the three experiments for which H<sub>2</sub>S breakthrough curves are shown in Fig. 7 to 9. Although preliminary values for metal concentrations were given in a previous publication (Ref 23), since that time a greater number of analyses were performed. It is now concluded that, probably due to the complex chemistry of the solutions resulting from dissolving the sorbent samples in a mixture of six different acids, interferences in the AA analyses caused erratic and unreliable measurements of metal compositions. The previous values in question (Ref 23) suggested that Ni had volatilized and left the sorbent bed. An additional check



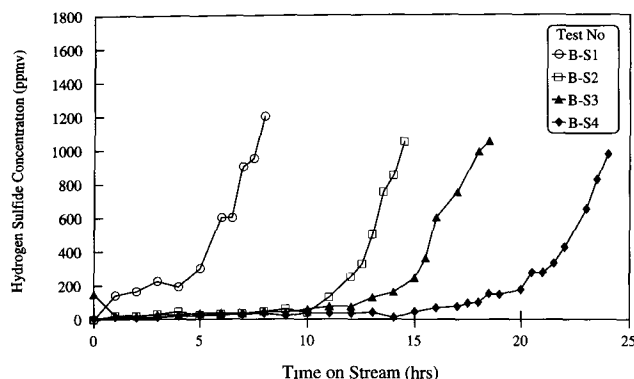
**Fig. 6** H<sub>2</sub>S concentrations in fixed bed of Al<sub>2</sub>O<sub>3</sub>-Ni sorbent from local equilibrium calculations at 704 °C (1300 °F)

**Table 5** Physical characteristics of fresh and reacted sorbents

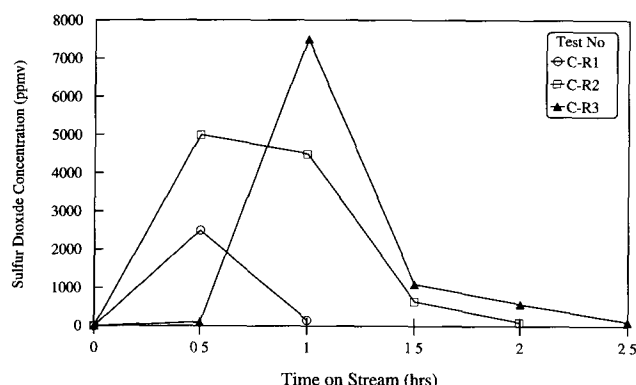
Item	Fresh	Reacted
N <sub>2</sub> pore volume, cm <sup>3</sup> /g	0.006354	0.04684
Hg skeletal density, g/mL	4.16	4.20
Hg bulk density, g/mL	2.38	2.37
Cum. Hg pore volume, mL/g	0.18	0.19
Surface area, m <sup>2</sup> /g	0.0963	3.21
Average pore diameter, μm	0.5858	0.1622
Porosity, %	42.79	43.76



**Fig. 7** Sulfidation of 24Ni-7Cu-Al<sub>2</sub>O<sub>3</sub> at 704 °C in a fixed-bed sorbent



**Fig. 8** Sulfidation of 26Ni-Al<sub>2</sub>O<sub>3</sub> at 593 °C in a fixed-bed sorbent screening unit with regeneration in H<sub>2</sub>

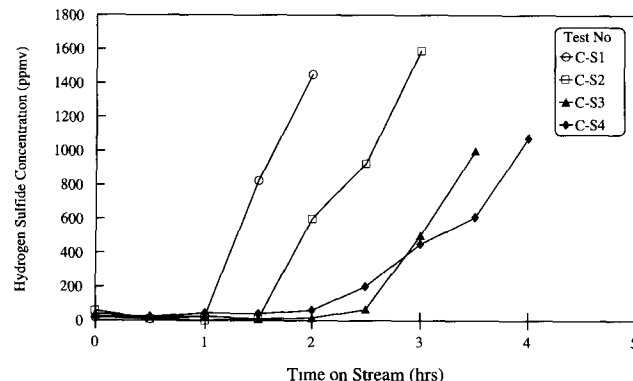


**Fig. 10** Oxidative regeneration results for the test described in Fig. 9. Temperature was 871 °C.

for Ni volatilization, using an electron microprobe to determine the Ni concentration on the walls of the reactor tube, both upstream and downstream from the sorbent bed (after the experiments shown in Fig. 8) showed no difference in Ni concentration. Therefore, no appreciable volatilization of Ni occurred during 3½ sulfidation/regeneration cycles at 593 °C.

## 4. Summary

In the second phase of a program on removal of H<sub>2</sub>S from coal gasification product gases with dispersed Ni sorbents, new results were obtained in several areas. The sorbents studied were pure Ni and a Ni-Cu alloy dispersed in an Al<sub>2</sub>O<sub>3</sub> matrix and sintered at two different temperatures. The crush strengths of the materials were very high compared to competing materials like zinc titanate. After promising chemical reactivity results were obtained by thermogravimetric analysis (TGA) measurements, a series of fixed-bed tests was conducted. Generally, the H<sub>2</sub>S breakthrough times were short at first but became progressively longer with each cycle. Evidence showed that this effect was due to beneficial structural changes occurring in the material. Another important result was that chemisorption of H<sub>2</sub>S played a major role in reducing its concentration in the exit gas to values as low as 20 ppmv. In most of the fixed-bed tests, sorbent regeneration was carried



**Fig. 9** Sulfidation of 26Ni-Al<sub>2</sub>O<sub>3</sub> at 593 °C in a fixed-bed sorbent screening unit with regeneration in an air-steam mixture

out in H<sub>2</sub>. The reduction reaction only occurred at a reasonable rate when the temperature was 1000 °C, which means that a ceramic-walled reactor is needed. In one test, oxidative regeneration was used, and the rate was fast at 871 °C (1600 °F).

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