Project Title: COMPOSITION MODIFICATION OF ZINC TITANATE SORBENTS FOR HOT GAS DESULFURIZATION

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ABSTRACT

For new coal gasification systems, zinc titanate sorbents are being developed to remove sulfur from the hot product gas prior to its use in combined cycle turbines and high temperature fuel cells. Although most of the properties of these sorbents are very attractive, there are still concerns about durability over many sulfidation-regeneration cycles and zinc losses due to vaporization. Doping the zinc titanate with other metal ions could alleviate both concerns, which were the objectives of this project. Initial work consisted of parallel tasks to determine the solubilities of Ni, Cu, Cr, Mg, and Al in Zn₂TiO₄, and to screen sorbents containing these dopants for crush strength and chemical reactivity. All the dopants had high solubilities in Zn₂TiO₄, but only the sorbents containing Cr and Al had good reactivities. Cr was selected for comprehensive evaluation because it showed promise for increasing the sulfur capacity of the sorbents, while Al did not. A total of 13 formulations containing Cr were evaluated. A few of the 13 had a good combination of properties; the remainder suffered from poor reactivity, mainly when the Cr concentration was high. Successful fixed bed tests were carried out on the best formulation, which contained 1 part Cr to 4 parts Zn, at 650 and 725°C. At 725°C, no vaporization loss of Zn was detected, while an undoped formulation lost approximately one-third of its Zn under the same test conditions.
EXECUTIVE SUMMARY

Sulfur sorbents which contain zinc as the primary desulfurizing agent continue to show promise for coal gasification applications. Scale-up tests are now in progress for Integrated Gasification Combined Cycle (IGCC) systems. There are still concerns, however with sorbent durability over many sulfidation-regeneration cycles and with vaporization losses of zinc. Therefore research and development directed at these potential problems is continuing. Zinc titanate sorbents are among the few that have reached the stage of large scale testing.

An approach that has received little attention to date for improving the properties of zinc titanate is to dope the material with other metal ions. In principle, it should be possible to both strengthen the material and reduce zinc vaporization losses in this way. Based on ceramic crystal chemistry principles, it was decided to study the possible beneficial effects of Ni, Cr, Cu, Mg, and Al as dopants in zinc titanate. A series of solubility measurements were made at 900, 1000, and 1100°C, which demonstrated that all five dopants have high solubilities in the titanate spinel phase. In parallel with the solubility experiments, a screening study was conducted to determine which of the dopants offered the most promise. Bulk density, crush strength, X-ray diffraction, and thermogravimetric analysis (TGA) measurements were made. It was decided, primarily on the basis of TGA results of chemical reactivity, that emphasis in subsequent research should be placed on sorbent formulations containing Cr.

A total of 13 formulations containing Cr were prepared and evaluated. The preparation variables were chemical composition, sintering temperature, and initial oxide particle size. It was found generally that Cr additions had a retardation effect on reaction kinetics. This result is not surprising because the thermodynamic activity of Zn in the titanate spinel compound is reduced when Cr dissolves as a dopant. The same thermodynamic effect also reduces the vapor pressure of Zn, thereby reducing the susceptibility to vaporization losses. Thus there is a tradeoff between two important properties when Cr is added to the material.

In the TGA experiments, some of the sulfidation steps were carried out in a gas mixture of 1% H₂S in H₂ and others in simulated coal gas. In the 1% H₂S mixture, it was clear that both Zn and Cr in the sorbents were converted to sulfides. In simulated coal gas, the weight gain was less, and it was not clear whether or not the Cr was sulfidizing. The benefits of adding Cr were evident, however, when TGA experiments were carried out at 725 and 800°C. Vaporization losses of Zn were much less for Cr-doped than for undoped sorbents.

A database developed for the physical and mechanical properties of the 13 Cr-containing formulations allowed some correlations between properties to be made. The crush strengths of the sorbents decreased with increasing Cr concentration. This result is thought to be due to a retarding effect of Cr on sintering kinetics. A better correlation was found between crush strength and porosity. The crush strength increased linearly with decreasing porosity in the range of porosity from 62.8 to 45.3%.
The final task in the project was to carry out fixed bed tests on Cr-doped sorbents with the best combination of properties. The sorbent composition was 57.2 ZnO·7.1 Cr₂O₃·35.7 TiO₂ (molar basis). For one test, the material was prepared from fine (0.3 micron) oxide powders, and in another coarse powders (2 micron) were used. The first test was conducted for three cycles at a temperature of 650°C for both sulfidation and regeneration. The prebreakthrough concentration of H₂S in the gas exiting the bed was less than 1 ppmv. Breakthrough occurred suddenly at a reaction time of approximately 11 hours. Regeneration in a 5% O₂ in N₂ mixture was complete in two to three hours.

The second and third fixed bed tests were carried out at temperatures of 725 and 650°C for sulfidation and regeneration, respectively. Their main purpose was to determine the difference in Zn vaporization tendency between Cr-doped and undoped sorbents. For the undoped material, it was concluded from both breakthrough times and sorbent weight loss that one-third of the Zn in the sorbent was lost due to vaporization. The Cr-doped material, on the other hand, showed no evidence of Zn loss. It also exhibited a large increase in breakthrough time after the second cycle. This increase is attributed to a beneficial change in pore characteristics with successive cycles, an effect that was observed in prior studies in which the same sorbent preparation method was used.

The duration of the project was sufficiently short that some important questions could not be answered. The thermochemical conditions for which Cr will or will not sulfidize was not made clear. Also Al and perhaps Mg as dopants may prove to be attractive if studied further.
OBJECTIVES

The principal objective of the project was to improve the engineering properties of zinc titanate \((\text{Zn}_2\text{TiO}_4)\) sorbents by adding dopants such as Ni, Cu, Cr, Mg, and Al. A second objective was to develop an understanding of how these dopants substitute for Zn and Ti in the \(\text{Zn}_2\text{TiO}_4\) crystal structure.

INTRODUCTION AND BACKGROUND

All modern coal combustion and coal conversion processes must have provisions to meet strict specifications on emissions of \(\text{H}_2\text{S}\) and \(\text{SO}_2\). For many systems, removal of sulfur-bearing species from hot gases is also needed to prevent corrosive damage to materials and components. Both requirements apply to Integrated Gasification Combined Cycle (IGCC) and Molten Carbonate Fuel Cell (MCFC) systems. An important milestone in the development of IGCC systems was successful completion of the Cool Water Coal Gasification Program (Douglas, 1990). In this program, the fuel gas was cooled down for \(\text{H}_2\text{S}\) removal, then reheated before injection into the turbine combustor. To avoid the associated efficiency loss with cooling of the fuel gas, most of the active development projects now include hot gas desulfurization with regenerable sorbents.

Many metals, oxides, and other compounds have been evaluated for their ability to remove \(\text{H}_2\text{S}\) from hot, coal-derived gases. In recent years, one of the classes of compounds that has been studied extensively and continues to show promise is zinc titanate (Swisher, Yang, and Gupta, 1995; Gupta, Gangwal and Jain, 1993; Gupta and Gangwal, 1993; Datta, 1994; Mei, et al., 1993; Ayala, et al., 1993; and Grindley, 1990). The status of the technology has matured to the point where large scale testing in process development units and pilot plants is in progress (Bevan, et al., 1994; Konttinen, et al., 1994). Updates on some of these, as well as new projects on sulfur sorbents, will be published in the near future in the proceedings of a contractor review meeting hosted by the DOE Morgantown Energy Technology Center in June, 1995.

There are still a few concerns with zinc titanate sorbents which are being investigated in current projects. One of these is durability over many sulfidation cycles in fixed and fluidized bed reactors. Another is a concern with vaporization losses of zinc. In this regard, current sorbent formulations are adequate unless the sulfidation reaction is carried out above a temperature of approximately \(650^\circ\text{C}\).

In the project described here, the research was directed toward both problem areas. By the incorporation of a third metal ion into the zinc titanate crystal structure, the thermodynamic activity and vapor pressure of zinc was reduced. Also, the dopants were expected to alter the strength and durability of the sorbents. Scanty information has been found in the literature on this subject, so the present work is pioneering in nature.
EXPERIMENTAL PROCEDURES

The procedure used for sorbent preparation was the same as that used by Swisher, Yang, and Gupta, 1995. Reagent-grade oxide powders were blended in a 3% solution of starch in distilled water. Excess water was removed until the slurry had a consistency like toothpaste. Some of the material was extruded through a 1 cm dia. metal tube and cut to lengths of approximately 1.5 cm. The remainder was rolled by hand to form roughly spherical pellets with diameters of 0.7 to 1.0 cm. The sorbents were then dried overnight in an oven and sintered in air at temperatures in the range of 900 to 1100°C for 3 hours.

Several techniques were used to characterize the as-sintered pellets. Bulk density determinations were obtained from weight and volume measurements and from a hydrostatic method. Porosity values were calculated from x-ray diffraction and bulk density data. A Philips X-ray Diffractometer (PW1729) employing Cu Kα radiation was used for both lattice parameter measurements and phase identification. Operating conditions were normally 40kV and 25mA, with a goniometer scanning rate of 1°-2θ/minute/inch on the chart recorder.

Compressive strength measurements were made by applying the load to the ground ends of the cylindrical specimens. Initially, the tests were conducted on Material Test System (MTS-810) equipment at a crosshead speed of 0.025 cm/min. Toward the end of the project, an Instron model 4206 universal testing instrument was used. Six to ten specimens from each formulation were tested and the results averaged.

The chemical reactivity of the sorbents was studied using a Dupont model 951 thermogravimetric analyzer (TGA). Sulfidation was carried out either in a 1% mixture of H₂S in H₂ or in simulated coal gas at temperatures in the range of 650 to 800°C. Regeneration was carried out in a 5% mixture of O₂ in N₂.

To select a composition for the simulated coal gas, a calculation was made to obtain a modification of Texaco Gasifier product gas that would not cause an extensive amount of carbon deposition in the apparatus. Table 1 shows the initial composition of the mixture, fixed by metering the flow rates of individual gases, and the equilibrium composition at 650°C, as determined by computer calculation.

The last task entailed testing of the best Cr-doped formulation in a fixed bed reactor. The reactor was made from 3 cm ID quartz tubing, and a Hewlett Packard model 5890 gas chromatograph was used to measure the concentration of H₂S or SO₂ in the gas mixtures exiting the bed. For these tests, sorbent pellets were crushed to a particle size range of -6 to +30 mesh size (0.6 to 3.4 mm).
Table 1. Composition of Simulated Coal Gas

<table>
<thead>
<tr>
<th>Component</th>
<th>Starting</th>
<th>Equilibrium Composition (650° C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>49.5%</td>
<td>33.8%</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.0%</td>
<td>14.4%</td>
</tr>
<tr>
<td>CO</td>
<td>17.0%</td>
<td>26.0%</td>
</tr>
<tr>
<td>CO₂</td>
<td>32.0%</td>
<td>22.7%</td>
</tr>
<tr>
<td>CH₄</td>
<td>-</td>
<td>2.6%</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.5%</td>
<td>0.5%</td>
</tr>
<tr>
<td>O₂</td>
<td>-</td>
<td>1x10⁻²³ atm</td>
</tr>
<tr>
<td>S₂</td>
<td>-</td>
<td>2x10⁻⁹ atm</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

There were two discrete phases to the project. In the first, which might appropriately be called preliminary studies, the solubilities of 5 dopants in Zn₂TiO₄ were measured, and screening experiments were conducted to study the effects of the same dopants on physical properties and chemical reactivity. The second phase of the project was directed toward a more comprehensive evaluation of the effects of what was believed to be the most promising dopant, chromium. The results will be presented and discussed in this sequence.

Solubility Study

The solubility data were obtained from x-ray measurements on oxide powder samples reacted at temperatures of 900, 1000, and 1100° C. The holding time was 24 hours. The solubility was determined from plots showing the variation of the mixed titanate lattice parameter with composition. The results for the addition of normally divalent Ni, Mg, and Cu at 1000° C are shown in Figure 1. It is expected that these metals substitute directly for Zn in the spinel crystal structure. Since the dopants all have smaller ionic radii than Zn, they produce decreases in the lattice parameter. Only two data points are shown for Cu because of an experimental problem. At higher concentrations, a liquid phase formed between the samples and the Al₂O₃ crucibles. Figure 1 shows that all three dopants dissolve completely in the titanate over the entire range of compositions studied. Otherwise plateaus in the data plots would have occurred when solubility limits were reached.

Similar data are shown in Figure 2 for the addition of normally trivalent Al and Cr. There is an uncertainty in how the data for Cr should be interpreted. It is possible that a steeper line should be drawn through the first 6 points, and the 7th point at x = 1.0 exceeds the solubility limit. If so, one would conclude that the Cr solubility limit occurs at about x = 0.6. Regarding the mechanism of ion substitution, it is likely that 2 Cr or 2 Al ions replace 1 Zn ion and 1 Ti ion. In this way, ionic charge neutrality is maintained.
The solubility measurements at 1100° C produced essentially the same results. At 900° C, the reactions to form titanate solid solutions were not believed to be complete, so no solubility results will be given. Some additional results on Cr-doped materials will be presented later in another section.

Figure 1. Comparison of Mean $a_0$ for $\text{Zn}_2\text{TiO}_4\cdot\text{MO}_y$, $\text{M}=\text{Ni}$, $\text{Mg}$ and $\text{Cu}$ at 1000° C.
Figure 2. Comparison of Mean $a_0$ for Zn$_2$TiO$_4$-Mo$_x$, M=Al, Cr at 1000° C.

Sorbent Screening Study

In the screening experiments to obtain preliminary data on physical properties and chemical reactivity, one formulation for each dopant was prepared with compositions of 1 part dopant to 4 parts Zn. All the materials were sintered for 3 hours at 900° C. A summary of the results is given in Table 2. Included for comparison are the properties of a reference material taken from a publication by Swisher, Yang, and Gupta, 1995. It contained 50% excess TiO$_2$ for strength enhancement, but no dopant. The porosities ranged from 46.6 to 61.8%, and the crush strengths ranged from 73 to 229 N/mm. While the ranges are high, it should be understood that these properties can be altered easily simply by varying the sintering temperature. Of more importance is the chemical reactivity obtained by thermogravimetric analysis (TGA) experiments. The only two dopants which gave good results over two sulfidation-regeneration cycles were Cr and Al. A more detailed discussion of the TGA results is given in the following paragraphs.
Table 2. Results of Screening Study

<table>
<thead>
<tr>
<th>Composition</th>
<th>Estimated Porosity (%)</th>
<th>Crush Strength (N/mm)</th>
<th>TGA Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_2$TiO$_4$ + 50% TiO$_2$</td>
<td>46.6</td>
<td>73</td>
<td>Good</td>
</tr>
<tr>
<td>Ni Doped $^+$</td>
<td>49.5</td>
<td>187</td>
<td>Poor</td>
</tr>
<tr>
<td>Cr Doped $^+$</td>
<td>54.6</td>
<td>110</td>
<td>Good</td>
</tr>
<tr>
<td>Cu Doped $^+$</td>
<td>47.4</td>
<td>229</td>
<td>Poor</td>
</tr>
<tr>
<td>Mg Doped $^+$</td>
<td>56.0</td>
<td>83</td>
<td>Second Cycle Poor</td>
</tr>
<tr>
<td>Al Doped $^+$</td>
<td>61.8</td>
<td>89</td>
<td>Good</td>
</tr>
</tbody>
</table>

* Reference material  
+ All contained 1 part dopant to 4 parts Zn

The first set of TGA experiments were carried out with 1% H$_2$S in H$_2$ as the sulfidizing gas and 5% O$_2$ in N$_2$ as the regeneration gas. The temperature for both steps was 650° C. The results for a specimen containing Ni are shown in Figure 3. Exposure to the sulfidizing gas began at a point on the time scale of 60 min. There was an initial weight loss believed to be caused by reduction of the doped titanate to form metallic Ni as a separate phase. Then a weight gain occurred as the material began to sulfidize. However, the total weight gain was only 2.5%, compared to a theoretical value of 10.7% for conversion of all the ZnO to ZnS and 0.9% for conversion of the NiO to Ni$_3$S$_2$. Thus complete sulfidation of all the Zn and Ni corresponds to a weight gain of 11.6%. It is likely that sulfidation in the specimen proceeded until the pores became clogged with sulfide reaction products. The problem may have been compounded by the formation of a liquid nickel sulfide, which can form at temperatures as low as 637° C. Even if complete sulfidation had occurred, there would still be a problem in that reduction of the mixed titanate to form Ni metal negates a major potential advantage of sorbent doping; the Ni can no longer produce a reduction of the Zn vapor pressure. It is somewhat surprising that the regeneration reaction proceeded to completion, judging from a return to the original weight in approximately 100 min. of reaction time.

The TGA data for a Cu-doped specimen showed even worse behavior. There was again an initial weight loss due to copper oxide reduction and essentially no weight gain on sulfidation.

Results for an Al-doped specimen were much better, as can be seen in Figure 4. The weight gain on sulfidation corresponds to 80% of the theoretical value for complete conversion of ZnO to ZnS; no sulfidation of Al in the sorbent was expected. Completed regeneration occurred, and the second sulfidation produced nearly the same weight gain. The rate of reaction were also reasonably fast.
Figure 3. TGA results for Ni-doped specimen showing sulfdation in 1%H$_2$S and regeneration in 5%O$_2$ at 650° C.

Figure 4. TGA results for Al-doped specimen, showing 1.5 cycles of sulfdation in 1%H$_2$S and regeneration in 5%O$_2$ at 650° C.
Figure 5. TGA results for Mg-doped specimen, showing 1.5 cycles of sulfidation in 1%H₂S and regeneration in 5%O₂ at 650° C.

Figure 5 shows the results of the TGA experiment on the Mg-doped sorbent. The first cycle was good, both in terms of complete sulfidation and reaction rates. In the second half-cycle, however, sulfidation was incomplete, due presumably to a change in pore structure.

The Cr-doped material had both a high sulfur capacity and reasonably good reaction rates. Therefore it was decided to prepare additional Cr formulations and study their properties in more detail, as discussed in the following section.

Properties of Sorbents Containing Chromium

The principal basis for choosing Cr as the most promising of the five dopants was the TGA results shown in Figure 6. It is an analogue to the results for Ni, Al, and Mg presented in Figures 3-5. The weight gains for the first and second sulfidations were 13% and 12%, respectively. These values indicate that both Zn and Cr were being converted to sulfides, meaning that the sulfur capacity of the sorbent was very high. Regeneration was nearly complete during the first cycle and the reaction rates were good, except when the reaction approached complete sulfidation. TGA results for a specimen from the same formulation sulfidized at 725° C are given in Figure 7. This experiment was carried out to see if the sulfidation rate was higher at a higher temperature. Comparison of Figures 6 and 7 indicates the sulfidation rate was improved.
Figure 6. TGA results for Cr-doped specimen \((57.2\text{ZnO}\cdot7.1\text{Cr}_2\text{O}_3\cdot35.7\text{TiO}_2)\) showing 1.5 cycles of sulfidation in 1\%\(\text{H}_2\text{S}\) and regeneration in 5\%\(\text{O}_2\) at 650\(^\circ\text{C}\).

Figure 7. Similar results for sulfidation at 725\(^\circ\text{C}\).
It was then decided to prepare and evaluate additional Cr formulations in which the chemical composition and sintering temperature were varied. A summary of the properties of the 13 formulations prepared and evaluated is given in Table 3. The intent was to see if an improvement could be made in the combined crush strength and reactivity properties, and to determine the solubility of Cr in Zn$_2$TiO$_4$ over a wider range of sorbent compositions. Cursory examination of Table 3 leads to the conclusion that both the crush strengths and reactivities of many of the new formulations were much worse than the first one prepared. The reasons for this behavior will be discussed later.

With the wide range of sorbent compositions prepared, it was important to determine whether or not Cr dissolved completely over the entire range to form spinel solid solutions. Accordingly, X-ray diffraction measurements were made on all the formulations listed in Table 3. Except for small amounts of TiO$_2$, ZnO, and Cr$_2$O$_3$ present, due probably to incomplete reactions, all the samples were single-phase spinel solid solutions. Figure 8 is a schematic drawing (not to scale), which shows how Cr$^{3+}$ ions can substitute for Zn$^{2+}$ and Ti$^{4+}$ ions in the spinel structure in different ways. Most of the experimental compositions lie on joins in the phase diagram between Zn$_2$TiO$_4$ and either Cr$_2$TiO$_4$, ZnCr$_2$O$_4$, or Cr$_2$O$_3$. The shaded area in the diagram is meant to show that spinel solid solutions are stable along and between all three joins extending into the diagram from the point representing undoped Zn$_2$TiO$_4$.

The lattice parameters obtained from X-ray diffraction measurements decrease with Cr concentration along all three joins, as can be seen in Figure 9. The differences between the lines are small, but larger than the experimental uncertainty. Each of the three joins on the phase diagram corresponds to a different model for Cr substitution. In crystal chemistry notation, these models can be described as follows.

**Join 1**: Stoichiometric Substitution

\[ \text{Zn}_{2x} \text{Ti}_{1-x} \text{Cr}_{2x} \text{O}_4 \]

cationic arrangement: \[ \text{Zn}^{1+} (\text{Zn}^{1-x} \text{Ti}_{1-x} \text{Cr}_{2x})^{1+} \text{O}_4 \]

**Join 2**: Nonstoichiometric Substitution with Cation and Anion Vacancies

\[ \text{Zn}_{2x} \text{Ti}_{1-x/2} \text{Cr}_{x} \text{O}_{4-x/2} \]

cationic arrangement: \[ \text{Zn}^{1+} (\text{Zn}^{1-x} \text{Ti}_{1-x/2} \text{Cr}_{x})^{1+} \text{O}_{4-x/2} \]

**Join 3**: Nonstoichiometric Substitution with Anion Interstitials

\[ \text{Zn}_{2x} \text{TiCr}_{x/2} \text{O}_{4+x/2} \]

The results presented above demonstrated that Cr has a high solubility in zinc titanate at temperatures of 950 to 1100°C. However, the use temperature of the sorbent should be in the vicinity of 650°C. Therefore a series of experiments was conducted to determine whether or not the solid solutions prepared at higher temperatures were stable at 650°C. Specimens with 6 different Cr concentrations were simply held at 650°C for 5 days, then examined by X-ray diffraction. There was no detectable change in lattice parameter, nor did new phases form in any of the specimens. Therefore it was concluded that the sorbents have the same phase structure at 650°C as at the sintering temperatures.
Table 3. Results Summary for Sorbents Containing Chromium

<table>
<thead>
<tr>
<th>Formulation No.</th>
<th>Composition (Molar Basis)</th>
<th>Sintering Temp. (°C)</th>
<th>Estimated Porosity (%)</th>
<th>Crush Strength (N/mm)</th>
<th>TGA Reactivity</th>
</tr>
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<tr>
<td></td>
<td>ZnO</td>
<td>Cr₂O₃</td>
<td>TiO₂</td>
<td></td>
<td></td>
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<tr>
<td>1*</td>
<td>57.2</td>
<td>7.1</td>
<td>35.7</td>
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<td>20.0</td>
<td>950</td>
<td>59.5</td>
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<tr>
<td>13*</td>
<td>57.2</td>
<td>7.1</td>
<td>35.7</td>
<td>950</td>
<td>52.5</td>
</tr>
</tbody>
</table>

+Data from screening study
*Made from coarse (2 micron) oxide powders. Others made from fine (0.3 micron) powders.
Figure 8. Phase diagram for the ZnO-TiO₂-Cr₂O₃ system showing the three modes of substitution in the spinel phase.

Figure 9. Trends in the change in mean lattice parameter of the Zn₂TiO₄ phase with Cr substitution.
Turning now to thermogravimetric analysis results, examples rather than all of the data plots will be presented. Two sets of TGA sulfidation data are given in Figure 10 for Formulation No. 2 (66.5 ZnO·3.5 Cr₂O₃·31.0 TiO₂ sintered at 900° C). In part (a), the sulfidizing gas was 1% H₂S in H₂, and in part (b) it was simulated coal gas with an H₂S concentration about half as high (see Table 1). As one might expect from the H₂S concentrations, the reaction rate was roughly a factor of two slower in simulated coal gas. The theoretical weight gain for complete sulfidation of the Zn but none of the Cr is 12.5%. The weight gains reached in Figure 10 were less than this amount. From the data, it is not possible to tell whether just one or both metals are being converted to sulfides. With either possibility, it is clear that the reaction is fast initially but becomes slow after a weight gain of 9% is reached. It may be important to mention that the specimen sulfidized in 1% H₂S changed in color from pastel green to dark gray during the test. The specimen sulfidized in simulated coal gas remained pastel green. This observation may mean Cr was sulfidizing in 1% H₂S but not in simulated coal gas. This subject will be discussed again in connection with a thermodynamic calculation and with x-ray diffraction measurements on samples from fixed bed tests.

Regeneration data from the same experiment are presented in Figure 11. The weight losses match the weight gains from Fig. 10, and the regeneration rate was slightly faster for the specimen sulfidized in simulated coal gas. This faster rate would be expected if the pores were not constricted as much as a result of a smaller amount of sulfide in the material.

A computer calculation was carried out to analyze the tendency for Cr in the material to sulfidize under the experimental conditions. The results are shown as a phase stability diagram in Fig. 12. Caution should be used in drawing conclusions from the diagram in that it ignores the fact that Cr is present at reduced thermodynamic activity in compounds with Zn. In plotting the point labeled 1% H₂S, it was assumed that the impurity level of H₂O in the gas mixture was 10 ppmv. It can be seen that Cr should convert to a sulfide under these conditions. For the point on the diagram corresponding to the simulated coal gas composition used, the diagram predicts that Cr should remain in oxidized form. However, the experimental point lies close to the sulfide-oxide boundary, so the computational assumptions and experimental uncertainty make it risky to conclude that no sulfidation of Cr will occur in simulated coal gas.

Referring back to Table 3, the TGA reactivity of 8 of the 13 formulations were judged to be fair or poor. An example for Formulation 11 is given in Fig. 13. Sulfidation was less than 50% complete after about 6 hours of reaction time. This result was typical for the formulations having poor reactivity. Table 3 contains enough data to look for correlations between good or poor reactivity and other sorbent characteristics. The relationship between reactivity and Cr₂O₃ concentration is depicted in Fig. 14 for the sorbents sintered at 900 and 950° C. All of the sorbents with poor reactivity had Cr₂O₃ concentrations above 12 mole percent. This behavior is believed to be due mainly to a chemical effect. When the Cr content of the titanate material is high, the thermodynamic activity of Zn is reduced, which would normally be expected to have an adverse effect on the rate at which Zn reacts with H₂S.
Figure 10. TGA results of sulfidation on Formulation No. 2 (66.5ZnO·3.5Cr₂O₃·31.0TiO₂) at 650 °C in (a) 1%H₂S and (b) simulated coal gas.
Figure 11. Regeneration of specimens from Figure 10 in 5\%O_2 at 650\^\circ C (a) sulfidized in 1\%H_2S and (b) sulfidized in simulated coal gas.
Figure 12. Phase stability for Cr-O-S system at 650°C with points corresponding to experimental gas compositions.

Figure 13. TGA results of sulfidation of Formulation No. 11 (60ZnO-15Cr₂O₃-25TiO₂) in simulated coal gas at 650°C.
Figure 14. Correlation of TGA reactivity with $\text{Cr}_2\text{O}_3$ concentration for specimens sintered at 900 and 950° C.

However, this reduction in thermodynamic activity results in a lower Zn vapor pressure, which should translate into suppression of vaporization loss of Zn. A second reason for the lower reaction rate is the formation of a higher volume fraction of sulfide compounds, which would reduce pore sizes in the material as sulfidation proceeds. An attempt was made to correlate TGA reactivity with initial porosity from the data in Table 3, but there was no correlation, indicating that the chemical effect was dominant.

Other correlations were sought to obtain an understanding of high versus low crush strength. Fig. 15 shows there to be a rough inverse correlation between crush strength and $\text{Cr}_2\text{O}_3$ concentration for sorbents sintered at 950° C. The interpretation given to the decrease is that $\text{Cr}_2\text{O}_3$ in the material acts as a sintering inhibitor. If a high strength is needed in a sorbent with a high $\text{Cr}_2\text{O}_3$ content, the sintering temperature must be higher than 950° C. A better correlation was obtained when crush strength was plotted versus porosity, as shown in Figure 16. Except for one deviant point, which cannot be explained, the crush strength decreased in a regular way with increasing porosity, as one would expect.

Analysis of all the data on doped sorbents presented thus far leads to the conclusion that the main potential benefit of doping is suppression of Zn vaporization losses. There might be smaller benefits in strength and sulfur capacity, and there is undoubtedly a penalty in chemical reactivity. To study the suppression of Zn vaporization more directly, some TGA and fixed bed experiments were conducted at higher temperatures, where a clearer difference should be evident between Cr-doped and undoped sorbents.
Figure 15. Correlation of crush strength with \( \text{Cr}_2\text{O}_3 \) concentrations for specimens sintered at 950° C.

Figure 16. Correlation of crush strength with estimated porosity for all formulations containing Cr.
A TGA sulfidation curve is given in Figure 17 for an undoped sorbent of the same composition as the one listed at the top of Table 2. The temperature of 800° C was selected to exaggerate Zn vaporization effects. The initial weight loss is believed to be due to ZnO reduction. The weight gain during sulfidation was small, and rapid weight loss due to zinc vaporization became the dominant reaction after about 1 hour of reaction time.

Similar data for a Cr-doped specimen are shown in Fig. 18. The weight gain during sulfidation was much higher, and the weight loss due to Zn vaporization was much less than for the undoped specimen. The tendency for Zn vaporization will be discussed again in the next section.

Figure 17. TGA results for undoped zinc titanate specimen sulfidized in 1%H₂S at 800° C.
Fixed Bed Tests

The first test was carried out at 650° C to evaluate a sorbent formulation that gave good TGA results. Three sulfidation–regeneration cycles on Formulation No. 1 (57.2 ZnO·7.1Cr₂O₃·35.7TiO₂) were carried out. Simulated coal gas was used for sulfidation and 5%O₂ in N₂ was used for regeneration. The reacting gases were passed upward through the bed at a space velocity of 2,000 h⁻¹. The sulfidation breakthrough curves are plotted in Figure 19.

For the first several hours, there was no detectable amount of H₂S in the exit gas. Approximately 1 ppmv of H₂S was detected in all three cycles at a reaction time of 600 minutes or 10 hours. In the first, but not the second and third cycles, the test was shut down after 684 minutes and continued the following day. After restarting the test, there was a period of about 60 minutes before the gas chromatograph reached stable operation. Therefore, the time of the breakthrough event for the first cycle is probably not as accurate as for the other cycles. Note that breakthrough occurred over a very short time period. It was more sudden than in any prior investigation known to the authors. During regeneration, rapid evolution of SO₂ occurred during the first 15 minutes, and regeneration was complete in two or three hours.
A sulfur mass balance calculation was carried out to analyze the sorbent's capacity. For sulfidation of all of the Zn but none of the Cr, the ideal sulfur uptake of the bed was 0.21 g S/g sorbent or 7.67 g in the 36.0 g bed. The amount of sulfur supplied by the gas train was 4.64 g for a reaction time of 650 minutes. These data correspond to 60.5% utilization of Zn in the sorbent. However, x-ray diffraction data obtained on a sample of material extracted after 2.5 cycles of testing revealed that a small amount of Cr sulfide had formed also. This result raises the question again on the extent to which the Cr reacts with H₂S in the coal gas, and a clear answer was not obtained in the test.

It was stated earlier that the main advantage of doping is believed to be suppression of Zn vaporization losses at temperatures above 650 °C. Accordingly, the second and third fixed bed tests were planned to support this contention. The second test was conducted on undoped material. It had the same composition as the first entry in Table 2, but was prepared from coarser oxide powders and was sintered at 1000 °C for added strength (Swisher, Yang, and Gupta, 1995). The temperatures for sulfidation and regeneration were 725 and 650 °C, respectively. Test results are plotted in Figure 20. H₂S breakthrough during the first cycle occurred at a reaction time of 600 min. This breakthrough time is about what one would expect with little or no vaporization loss of Zn. The significance of the test became apparent during the second and third cycles. The breakthrough times were shorter by a factor of one third. The interpretation given to this result is that vaporization loss of Zn occurred, causing a reduction in the sulfur capacity of the sorbent. From the weight loss of the sample before and after the test, it was concluded that the Zn loss was 35.4%. Thus, there was consistency between the change in breakthrough time and weight loss indicators of Zn vaporization tendency.

![Figure 19. H₂S breakthrough curves for three-cycle fixed bed test at 650 °C for sample from Formulation No. 1 (57.2ZnO-7.1Cr₂O₃-35.7TiO₂).](image)
Figure 20. $\text{H}_2\text{S}$ breakthrough curves for three-cycle test on undoped zinc titanate material at 725° C for sulfidation and 650° C for regeneration.

The third fixed bed test was planned to evaluate a Cr-doped sample under the same test conditions. The material tested was Formulation No. 13 (57.2 ZnO·7.1Cr$_2$O$_3$·35.7TiO$_2$), which is the same as Formulation No. 1, except that it was prepared from coarse oxide powders and sintered at 950° C. The reason for the change in procedures was to try to obtain higher strength with comparable reactivity, as was accomplished with excess TiO$_2$ in undoped zinc titanate (Swisher, Yang, and Gupta, 1995).

The results are plotted in Figure 21. The breakthrough time for the first two cycles was about 700 min., compared to about 650 min. for cycles two and three in Figure 19, where material of the same composition was tested at a temperature 75° C lower. The small improvement in breakthrough time is probably due to better reaction kinetics at the higher temperature. Of greater significance is that there was no reduction in breakthrough time due to Zn vaporization, as was observed with the undoped material in Figure 20.
Figure 21. Test results under the same conditions as Figure 20 for Cr-doped Formulation No. 13 (47.2ZnO-7.1Cr₂O₃-35.7TiO₂).

Results for the third and fourth cycle in this test require careful explanation. An experimental problem occurred during the third cycle. The inlet to the gas chromatograph became clogged with water, and it was not discovered until a reaction time of 900 min. was reached. At this time, the odor of H₂S was first detected in the exhaust gas, which means the breakthrough time was approximately 900 min., 200 min. longer than for cycles one and two. When a fourth cycle was carried out, the breakthrough time increased to 1700 min. Such large improvements in breakthrough time have been observed before in studies where the same sorbent preparation method was used (Swisher, Yang, and Gupta, 1995, and Gasper-Galvin, Swisher, and Hammerbeck, 1994). Since the sorbents were prepared under one set of thermochemical conditions and test under a much different set of conditions, it is to be expected that the pore structure and other properties of the sorbents will change during testing. Fortunately, the properties improve rather than degrade when sulfidation–regeneration cycles are carried out. Here there may be another contributing factor that was not observed in prior investigations. The Zn and Cr in the sorbents may sulfidize at different rates, Cr being the slower specie to react. If so, it would explain why some of the TGA experiments in coal gas indicated that only the Zn was reacting. As with many relatively
short-duration projects like this one, insufficient time was available to develop a better understanding of many of the results obtained.

CONCLUSIONS AND RECOMMENDATIONS

Results of solubility measurements showed that Ni, Cu, Cr, Mg, and Al all dissolve readily in zinc titanate at high temperature. When sorbents were prepared with these metals as dopants, Cr- and Al-containing sorbents had better TGA reactivities than the others. Cr was selected for in-depth evaluation because it increased the sulfur capacity, while Al did not. After 13 Cr-containing formulations were evaluated for TGA reactivity, crush strength, and other properties, it was found that the best combination of properties were obtained when the composition was 57.2 ZnO·7.1Cr₂O₃·35.7TiO₂. From both TGA and fixed bed tests, it was concluded that the main advantage of Cr-doping was to reduce vaporization losses of Zn when the sorbent is used at temperatures above 650° C.

If follow-on research is conducted, it is recommended that a better understanding be developed of the relative reaction rates of Zn and Cr, structural changes in the sorbents during cycling, and the coal gas compositions for which Cr either will or will not convert from an oxide to a sulfide. It also should be mentioned that sorbents containing Al and perhaps Mg should be studied further because sufficient data were not obtained to conclude that they are inferior to Cr as dopants.

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REFERENCES


PROJECT MANAGEMENT REPORT
June 1 through August 31, 1995

Project Title: COMPOSITION MODIFICATION OF ZINC TITANATE SORBENTS FOR HOT GAS DESULFURIZATION

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 3)
ICCI Project Number: 94-1/2.2A-2M
Principal Investigator: James H. Swisher, Southern Illinois University at Carbondale
Other Investigator: Ranajit K. Datta, Virginia Polytechnic Institute and State University
Project Manager: Franklin J. Honea, Illinois Clean Coal Institute

COMMENTS

The two final technical milestones scheduled for the fourth quarter were completed. Both related to fixed bed tests. Three such tests were carried out and the samples characterized after testing. Regarding projected versus estimated expenditures, the project was completed at an estimated cost of $148,169, compared to $153,371 available in the contract. In the subaccounts, other direct costs were $5,202 less than projected, and salaries and wages were $2,951 more than projected. Differences in the other subaccounts were all $500 or less.
### PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

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*Cumulative by Quarter
COSTS BY QUARTER

Composition Modification of Zinc Titanate Sorbents for Hot Gas Desulfurization

Cumulative $ (Thousands)

0  20  40  60  80  100  120  140  160
Sept 1 Nov 30 Feb 28 May 31 Aug 31
Months and Quarters

● = Projected Expenditures  ————
▲ = Actual Expenditures

Total Illinois Clean Coal Institute Award $153,371
**SCHEDULE OF PROJECT MILESTONES**

Hypothetical Milestones:

A: Literature search; materials and equipment procurement (SIUC and VPI)
B: ZnTiO₄-MO₃ solubility experiments (VPI)
C: Sorbent preparation (VPI)
D: Bench-scale testing (SIUC)
E: Characterization of bench-scale samples (SIUC and VPI)
F: Reporting (SIUC)

Begin
Sept. 1
1994