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# A Regenerable Calcium-Based Core-in-Shell Sorbent for Desulfurizing Hot Coal Gas

## Abstract

A regenerable calcium-based sorbent was prepared by pelletizing either powdered limestone or calcium sulfate hemihydrate and then coating the pellets with an optimum mixture of powdered alumina and limestone. The pellets were subsequently calcined and treated at high temperature to produce pellets with a calcium oxide core surrounded by a strong, inert porous shell. The crushing strength of the core-in-shell pellets was directly proportional to the shell thickness. The performance characteristics of the sorbent were determined by employing a thermogravimetric analysis system to measure the rate of reaction of individual pellets with small concentrations of H<sub>2</sub>S at high temperature. The reaction was rapid and directly proportional to H<sub>2</sub>S concentration. The reaction rate was not affected greatly by the thickness of the pellet shell or by temperature in the range of 840–920 °C. However, the rate was more rapid for hemihydrate-based pellets than for limestone-based pellets. The hemihydrate-based pellets also had the advantage of withstanding repeated loading and regeneration without suffering a significant loss of reactivity, whereas the limestone-based pellets did suffer markedly.

## Keywords

Chemical and Biological Engineering

## Disciplines

Chemical Engineering | Materials Science and Engineering

## Comments

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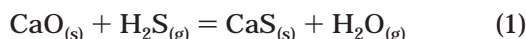
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A regenerable calcium-based sorbent was prepared by pelletizing either powdered limestone or calcium sulfate hemihydrate and then coating the pellets with an optimum mixture of powdered alumina and limestone. The pellets were subsequently calcined and treated at high temperature to produce pellets with a calcium oxide core surrounded by a strong, inert porous shell. The crushing strength of the core-in-shell pellets was directly proportional to the shell thickness. The performance characteristics of the sorbent were determined by employing a thermogravimetric analysis system to measure the rate of reaction of individual pellets with small concentrations of H<sub>2</sub>S at high temperature. The reaction was rapid and directly proportional to H<sub>2</sub>S concentration. The reaction rate was not affected greatly by the thickness of the pellet shell or by temperature in the range of 840–920 °C. However, the rate was more rapid for hemihydrate-based pellets than for limestone-based pellets. The hemihydrate-based pellets also had the advantage of withstanding repeated loading and regeneration without suffering a significant loss of reactivity, whereas the limestone-based pellets did suffer markedly.

## Introduction

Integrated coal gasification combined cycle (IGCC) power generation systems hold great promise for producing electric power efficiently and economically. However, to achieve maximum energy conversion efficiency, such systems need to include hot gas cleanup methods capable of operating close to gasifier outlet temperatures, which may range from 725 to 1325 °C.<sup>1</sup> While various sorbent materials have been proposed for desulfurizing hot coal gas, few will withstand or be effective at such temperatures.<sup>2–4</sup> At lower temperatures zinc-based sorbents are highly effective, but their use is limited to temperatures below 650–700 °C. At higher temperatures calcium-based sorbents may offer the most promise for the least cost because the following reaction is both thermodynamically and kinetically favorable:<sup>2,5</sup>



Because this reaction is exothermic, the reaction equilibrium becomes somewhat less favorable at very high temperatures, and of course, the reverse reaction is favored by large steam concentrations. Also, if the reaction temperature is not very high, reaction 1 has to compete with the endothermic reaction shown below because of the presence of CO<sub>2</sub> in coal gas:



Reaction 2 becomes less favorable thermodynamically as the temperature is raised. An earlier thermodynamic analysis of this reaction system showed that the gas produced by a typical air- and steam-blown coal gasifier

operating at 20 atm could be 95% desulfurized under equilibrium conditions over a temperature range of 770–1400 °C.<sup>2</sup> A more recent thermodynamic analysis indicated that the H<sub>2</sub>S content of gas produced by a Shell entrained flow gasifier could be reduced to 20 ppmv by contacting the gas under a total pressure of 30 bar with CaO under highly reducing conditions over a temperature range of 815–845 °C.<sup>6</sup>

Over the years much consideration has been given to sorbents based on limestone and dolomite because these materials are plentiful and inexpensive.<sup>6,7</sup> However, because these materials are soft and friable, they do not stand up well to handling and repeated use. Voss<sup>8</sup> claimed to overcome this problem by pelletizing pulverized limestone and a clay binder. Kamphius et al.<sup>9</sup> also reported making attrition-resistant sorbent pellets by agglomerating limestone particles with unspecified binders. The pellets were said to have an open porous microstructure that was highly favorable for gas absorption.

To improve the physical properties of pelletized limestone, Akiti et al.<sup>10</sup> utilized a two-step pelletizing process in which pulverized limestone was pelletized in the first step, and the pellets were then coated with a hydraulic cement in a second step. After steam curing, each pellet consisted of a weak but highly reactive core encased in a relatively strong and porous shell. It was found subsequently that the physical properties of the pellets were improved further by adding hydraulic cement to the pellet core and limestone to the shell.<sup>11,12</sup>

The present work was undertaken to further enhance the properties of the calcium-based, core-in-shell pellets and to demonstrate that the sorbent could be loaded and regenerated numerous times. Significant improvements were made by modifying the pellet core and shell compositions. Pellet cores were made either by pelletizing a mixture of pulverized limestone and alumina or by pelletizing calcium sulfate hemihydrate. The cores were subsequently coated with a mixture of powdered

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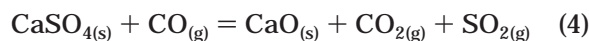
alumina and limestone, which was then converted into a relatively strong but porous shell material by heat treating at 1100 °C. While this treatment also converted CaCO<sub>3</sub> into CaO, an additional treatment step was required when pellet cores were made with hemihydrate to convert CaSO<sub>4</sub> into CaO. This step utilized a previously demonstrated cyclic process of reduction and oxidation.<sup>13,14</sup>

The sorbent pellets were characterized by measuring their crushing strength, apparent and bulk densities, and capacity for absorbing H<sub>2</sub>S. The effect of shell thickness on crushing strength and absorption capacity was investigated. Also, the effects of both loading temperature and H<sub>2</sub>S concentration on absorption rate and capacity were determined. In addition, a few pellets were subjected to multicycle loading and regeneration tests to evaluate potential sorbent performance and durability.

Regeneration was accomplished at a temperature somewhat above the loading temperature by employing a cyclic oxidation and reduction process.<sup>15,16</sup> In this process the loaded sorbent, which is largely in the form of CaS, is treated first with an oxidizing gas to convert a portion of the CaS to CaSO<sub>4</sub> by the following reaction:



The material is then treated with a reducing gas such as CO or H<sub>2</sub> to convert the CaSO<sub>4</sub> to CaO:



The cycle is repeated until all of the CaS has been converted to CaO.

## Experimental Section

**Materials.** Several materials were used in the preparation of the different sorbent formulations. These materials included limestone samples from both the Three Rivers Quarry located near Smithland, KY, and the quarry operated by Martin Marietta Aggregates located near Ames, IA. The Kentucky limestone typically contains 92.8% CaCO<sub>3</sub>, 5.9% MgCO<sub>3</sub>, and 1.1% SiO<sub>2</sub>, whereas the Iowa limestone contains over 99% CaCO<sub>3</sub>, according to the suppliers. The particle size of these materials used for pelletization ranged from 44 to 297 μm. Other materials used in the sorbent formulations included reagent-grade calcium carbonate from the Fisher Co. and calcium sulfate hemihydrate obtained as commercial-grade plaster of Paris. Both materials consisted of particles smaller than 37 μm. A combination of X-ray diffraction and X-ray fluorescence analysis showed the plaster of Paris to have the following composition by weight: 77% calcium sulfate hemihydrate, 15% calcite, 6% dolomite, and 2% other minerals. Sorbent pellet shells were made largely of a mixture of A-16 SG alumina powder and T-64 tabular alumina particles both supplied by Alcoa. The first material had a median particle diameter of 0.88 μm and the second a median particle diameter of 8.65 μm.

**Preparation Methods.** In the search for a suitable shell material, A-16 SG alumina powder, T-64 tabular alumina, and in some cases pulverized limestone were combined in various proportions and then mixed with water to form a very thick slurry. The slurry was poured into a mold to form cylindrical tablets having a diameter of 14.2 mm and thickness of 5.3 mm. The resulting

tablets were air-dried for 24 h and then calcined at 1100 °C for 2.0 h. The compressive strength of the tablets was determined as described later.

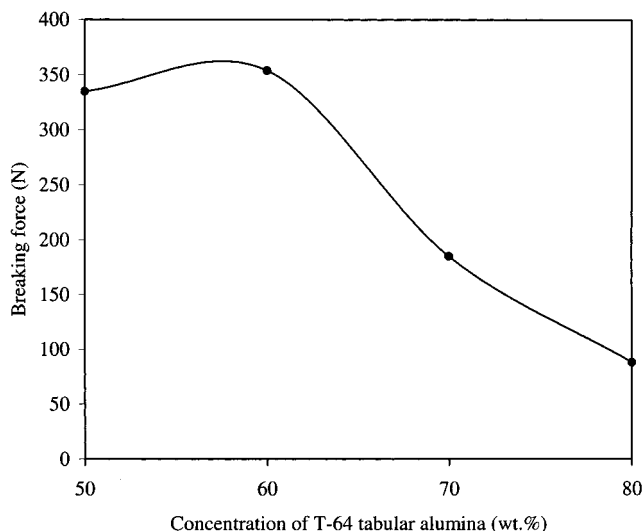
The core-in-shell pellets were prepared in two stages using a small bench-scale drum pelletizer that had a diameter of 25 cm and could be operated at various speeds. The pellet cores were prepared first by placing a measured amount of the appropriate powdered material in the drum, and as the drum revolved at a constant 60 rpm, the powder was sprayed at frequent intervals with water or a dilute lignin solution until pellets formed. Water was used for pelletizing plaster of Paris, whereas a lignin solution was used for pelletizing a mixture of limestone and A-16 SG alumina. The small pellets were grown into larger pellets by adding more material. When the pellets reached a desired size, they were allowed to tumble for 1.0 h to improve their sphericity and uniformity. The pellets were then separated into various sizes by hand screening with 5-, 6-, and 7-mesh screens. Pellets of a particular mesh size were reloaded into the pelletizer for coating with the optimum shell formulation. While the drum speed was kept constant, the coating material was added gradually as the pellets were sprayed with the dilute lignin solution. Once coated, the pellets were allowed to tumble for 2.0 h to consolidate the coating. During this time the pellets were sprayed at 5-min intervals with a dilute lignin solution. The coated pellets were subsequently removed and screened. Pellets of the desired size were then calcined at 1100 °C for 2.0 h.

The compressive strength of the pellets was determined by measuring the force required to fracture a single pellet when it was placed between the two plates of an Accuforce EZ250 test stand and the upper plate was lowered at a rate of 10 mm/min. The method was similar to that reported by Deng and Lin.<sup>17</sup> The determination was repeated several times for each batch of pellets to determine the average compressive strength. In the case of spherical pellets the compressive strength is generally reported as the ratio of the breaking force to pellet diameter.

Each pellet consisted of solid material with both open and closed pores. The bulk volume of the three constituents was determined by applying Archimedes principle while the apparent volume of the solid, which included both the solid and closed pores, was determined with a Mircomeritics model 1350 multivolume pycnometer using helium. These values together with the dry weight of the material provided the bulk density  $\rho_b$  and apparent density  $\rho_a$ , respectively, of the pellets. The apparent porosity was calculated by using

$$P_a = \frac{\rho_a - \rho_b}{\rho_a} \times 100 \quad (5)$$

The absorption characteristics of a sorbent pellet were determined by employing a thermogravimetric analysis (TGA) system to determine the gain in weight over time of the pellet exposed to a dilute stream of H<sub>2</sub>S at a predetermined temperature. The pellet was suspended in a quartz basket from a Cahn model 2000 electrobalance so that it could be weighed continuously as it was treated with the gas mixture inside of a vertical tubular reactor made of 25-mm-diameter quartz tubing. The reactor had an overall length of 61 cm and a heated length of 30.5 cm. The gas mixture of known composition was supplied to the reactor at a flow rate of 500



**Figure 1.** Effect of composition on the force required to break the calcined tablets made with a mixture of T-64 alumina and A-16 SG alumina powders.

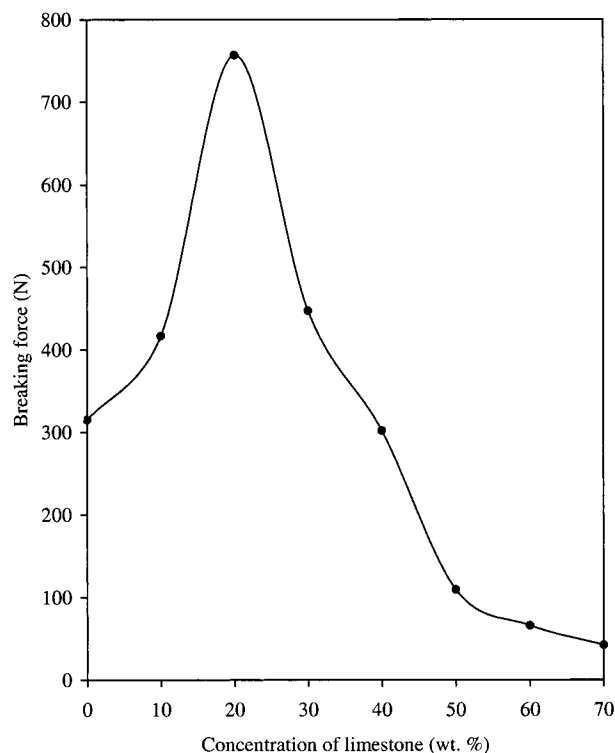
$\text{cm}^3/\text{min}$  measured at room temperature and pressure. The system temperature was determined with a thermocouple protected by a quartz thermowell located just below the suspended basket. The temperature was maintained by an electric furnace that surrounded the reactor.

To regenerate a sorbent pellet after it had been largely converted to CaS, the pellet was left in the TGA system, and as nitrogen was passed through the system, the temperature was normally raised to 1050 °C. Oxygen was then added to the flowing nitrogen to provide a mixture with 20 mol %  $\text{O}_2$  and having a total flow rate of 500  $\text{cm}^3/\text{min}$  at room temperature and pressure. After 1–5 min of oxidation, the composition of the gas mixture was changed to 30 mol % CO in nitrogen. Then, after 1–3 min of reduction, the cycle was repeated. The process was continued until the pellet approached a constant weight.

## Results and Discussion

**Shell Composition.** To develop a relatively strong but porous shell material, the finer size A-16 SG alumina powder was combined with the coarser T-64 tabular alumina and heated to 1100 °C to cause particle sintering. To determine the optimum proportion of the two materials, several batches of tablets were prepared by the previously described technique, and the force required to break the tablets was measured. The results are presented in Figure 1. Each point represents an average of five determinations of the crushing force for a given composition. It can be seen that the strength of the material was a maximum when the material contained about 60% T-64 alumina or, in other words, when the ratio of T-64 alumina to A-16 SG alumina was 3:2.

Several additional batches of tablets were prepared to study the effect of adding either pure calcium carbonate or Iowa limestone to the 3:2 mixture of T-64 alumina and A-16 SG alumina. The tablets were prepared and tested as described above, and the results with Iowa limestone are presented in Figure 2. Similar results that are not shown were obtained with pure calcium carbonate. It is apparent that the force required to break the material was a maximum when 20% limestone was incorporated in the formulation. For this formulation



**Figure 2.** Effect of limestone concentration on the force required to break the calcined tablets made with a 3:2 ratio of T-64 alumina to A-16 SG alumina.

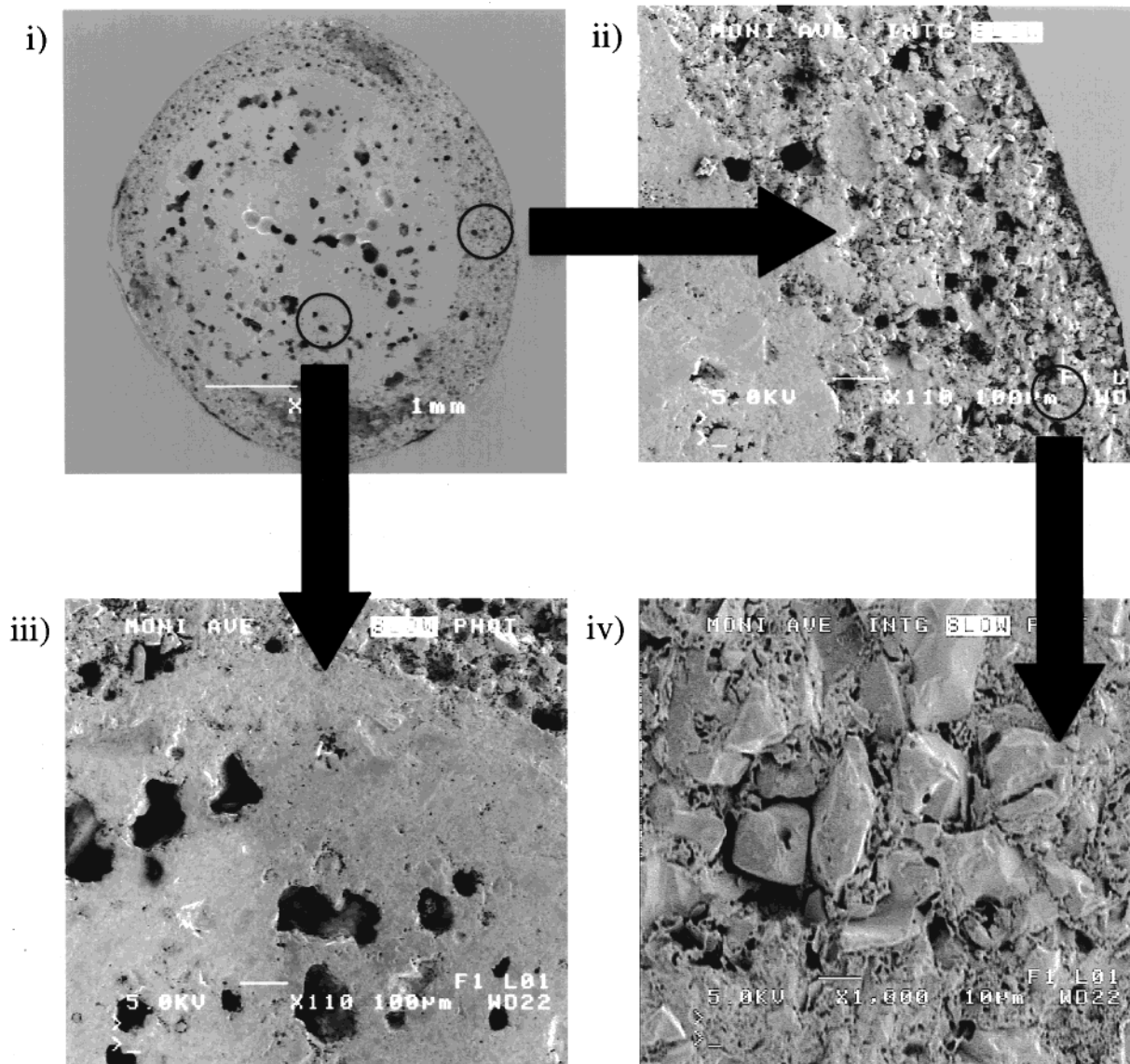
the force required to break a tablet was more than twice that of the formulation that did not contain limestone. However, when the limestone content was increased beyond the optimum level, the required crushing force decreased rapidly. The results suggest that with the optimum level of limestone a calcium aluminate compound formed upon sintering, which served as a particle bonding agent. However, when excess limestone was incorporated in the formulation, free CaO may have been present, which weakened the calcined material.

**Core-in-Shell Pellet Properties.** Numerous batches of core-in-shell pellets were prepared to investigate the effects of shell thickness and different core formulations on the physical properties of the sorbent pellets. All of the pellets were made with the optimum shell composition, that is, 48% T-64 tabular alumina, 32% A-16 SG alumina powder, and 20% Iowa limestone. The cores were made either of limestone or of calcium sulfate hemihydrate. Most of the limestone cores were made of Iowa limestone and most contained 10% A-16 SG alumina. The compressive strength of each batch of core-in-shell pellets was determined after the pellets had been calcined, and the batches that exhibited a compressive strength of 8.9 N/mm or more were characterized further. This value of the compressive strength is regarded as adequate for fixed-bed applications.<sup>18</sup>

Examples of pellet formulations that met the compressive strength criterion are shown in Table 1. The examples represent calcined pellets made from different core materials and made with shells of different thickness. For this set of measurements the pellet core diameter was kept within the range of 3.2–3.4 mm. The property values listed for each sorbent represent the mean of three batches of pellets. Because the crushing strength was measured on five different pellets selected at random from each batch, each value of compressive strength is based on the breakage of 15 different pellets.

**Table 1. Physical Properties of Typical Sorbent Pellets after Calcination at 1100 °C for 2 h**

	sorbent designation				
	A	B	C	D	E
initial core composition	90% Ames limestone + 10% A-16SG alumina	90% Kentucky limestone + 10% A-16SG alumina	90% Ames limestone + 10% A-16SG alumina	100% calcium sulfate hemihydrate	100% calcium sulfate hemihydrate
pellet diameter (mm)	4.20 ± 0.06	4.23 ± 0.13	4.80 ± 0.20	4.54 ± 0.14	5.14 ± 0.17
shell thickness (mm)	0.40 ± 0.04	0.42 ± 0.05	0.78 ± 0.03	0.62 ± 0.12	0.91 ± 0.15
fractional shell volume	0.47 ± 0.03	0.48 ± 0.03	0.69 ± 0.02	0.64 ± 0.01	0.73 ± 0.07
compressive strength (N/mm)	8.94 ± 1.39	8.57 ± 1.79	16.44 ± 0.48	12.10 ± 3.16	18.28 ± 3.09
bulk density (g/cm <sup>3</sup> )	1.60 ± 0.09	2.03 ± 0.15	1.95 ± 0.02	1.48 ± 0.06	1.86 ± 0.03
apparent density (g/cm <sup>3</sup> )	3.40 ± 0.05	3.30 ± 0.03	3.46 ± 0.04	3.39 ± 0.02	3.49 ± 0.11
apparent porosity (%)	52.7 ± 3.8	38.4 ± 4.8	43.6 ± 1.2	56.4 ± 2.2	46.7 ± 2.7



**Figure 3.** Micrographs of a freshly made limestone-based pellet: (i) section of an entire pellet at  $\times 17$ , (ii) the shell at  $\times 110$ , (iii) the core at  $\times 110$ , and (iv) the shell at  $\times 1000$ .

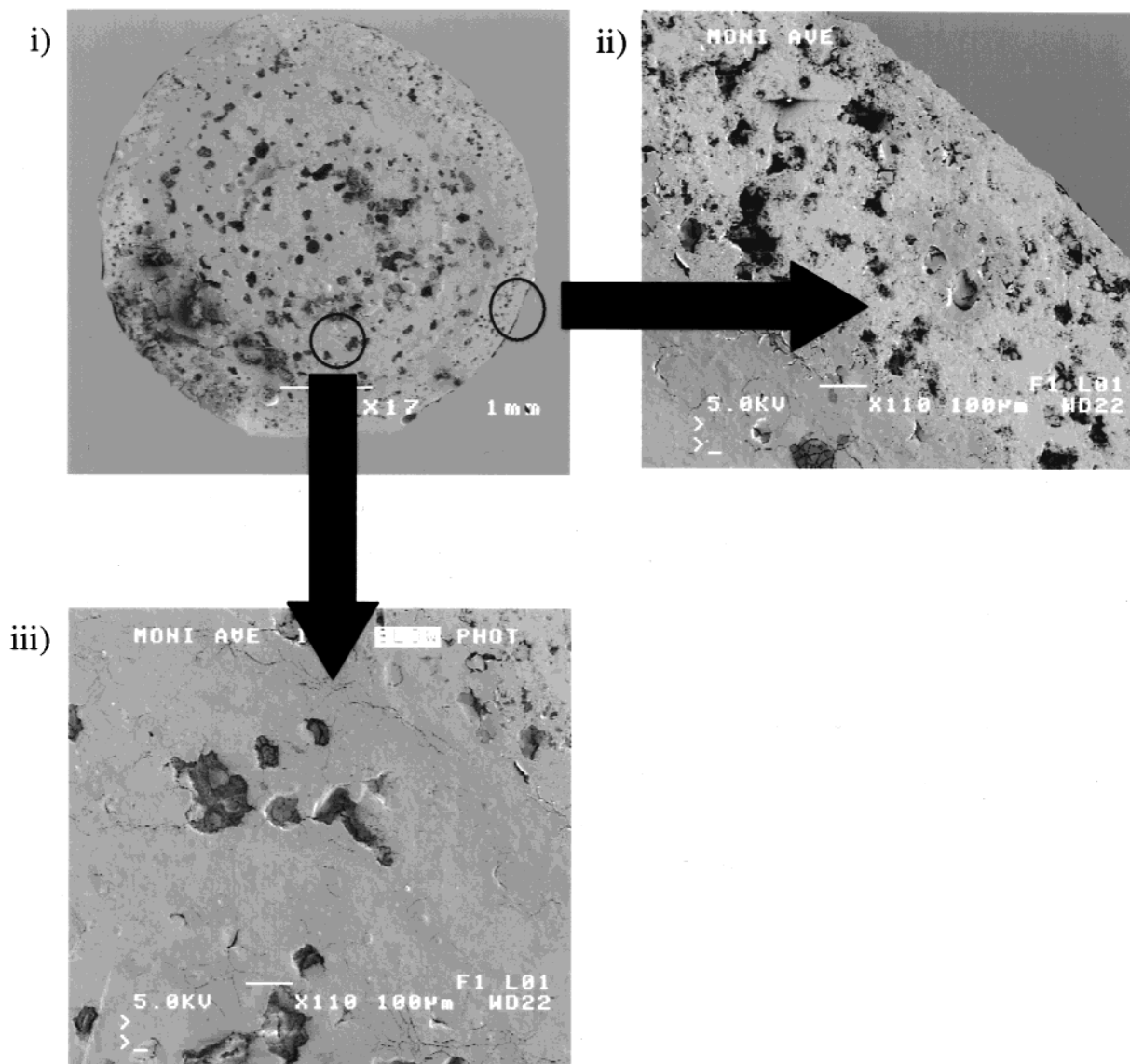
The crushing strength correlated extremely well with shell thickness. The following relationship between compressive strength  $S$  and shell thickness  $t$  was developed by applying linear regression:

$$S = 19.5t + 0.65 \quad (6)$$

Because the correlation coefficient  $r$  had a value of 0.993, this equation seemed to account for most of the variation in the compressive strength of the pellets.

Therefore, the composition of the core seemed to have relatively little effect on pellet crushing strength.

The variation in porosity among different sorbent formulations was due largely to the variation in bulk density of the pellets because the variation in apparent density was small. Also, because the apparent porosity tended to decrease as the shell thickness increased and made up a larger share of the total pellet volume, the porosity of the shells must have been smaller than the porosity of the cores. Because the porosity of sorbent C

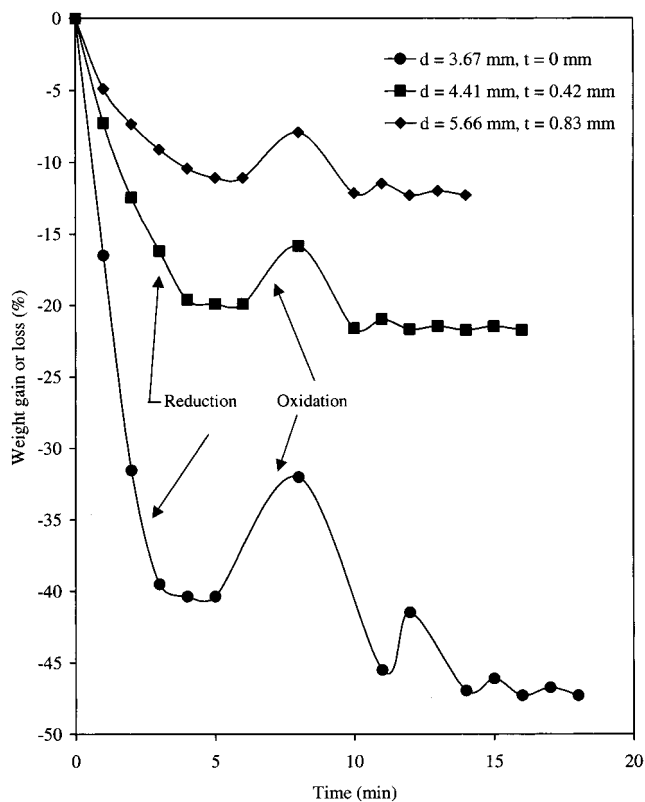


**Figure 4.** Micrographs of a fired limestone-based pellet: (i) section of an entire pellet at  $\times 17$ , (ii) the shell at  $\times 110$ , and (iii) the core at  $\times 110$ .

was less than that of either sorbents D or E with comparable fractional shell volumes, it is apparent that the porosity of the hemihydrate-based pellets was larger than that of the limestone-based pellets.

To examine the actual structure of the core-in-shell pellets, several pellets were cross-sectioned and viewed with a scanning electron microscope. The pellets were made with Iowa limestone cores and the optimum shell composition. The cores also contained 10% A-16 SG alumina. The structure of an uncalcined pellet is revealed in Figure 3. The core and shell are clearly delineated by the difference in texture of the two regions. The shell had a much coarser texture because of the presence of relatively large tabular alumina particles intermixed with much finer but discrete alumina and limestone particles. Also, the shell appeared to be slightly darker than the core, and the shell had fewer and smaller voids or holes than the core. Calcination produced a change in the structure that is revealed in Figure 4. The texture of the calcined shell material was much finer than before because of particle sintering. Consequently, it became more difficult to distinguish the shell from the core.

Because calcination alone did not convert pellets made with calcium sulfate cores into a calcium oxide-based sorbent, the pellets had to be subjected to the cyclic process of reduction and oxidation that had been developed previously.<sup>13,14</sup> However, for the present application one pellet at a time was treated in the TGA apparatus. The results of treating several different pellets are shown in Figure 5. The treatment was applied at 1070 °C using a nitrogen gas mixture containing 30% CO for reduction and 20% O<sub>2</sub> for oxidation. The cyclic treatment was continued until the pellets reached a constant weight. One of the pellets was a bare core without a shell that had only been heated to 1070 °C before the treatment was applied while two of the pellets had shells that were 0.42- and 0.83-mm thick, respectively, and had been calcined at 1100 °C. It can be seen that during each reduction step the pellets lost weight as CaSO<sub>4</sub> was converted into a mixture of CaO and CaS. Then, during the following oxidation step the pellets gained weight as CaS was converted into a mixture of CaO and CaSO<sub>4</sub>. Of course, the amount of weight gained or lost decreased with each cycle because of the SO<sub>2</sub> produced. It is also apparent that the

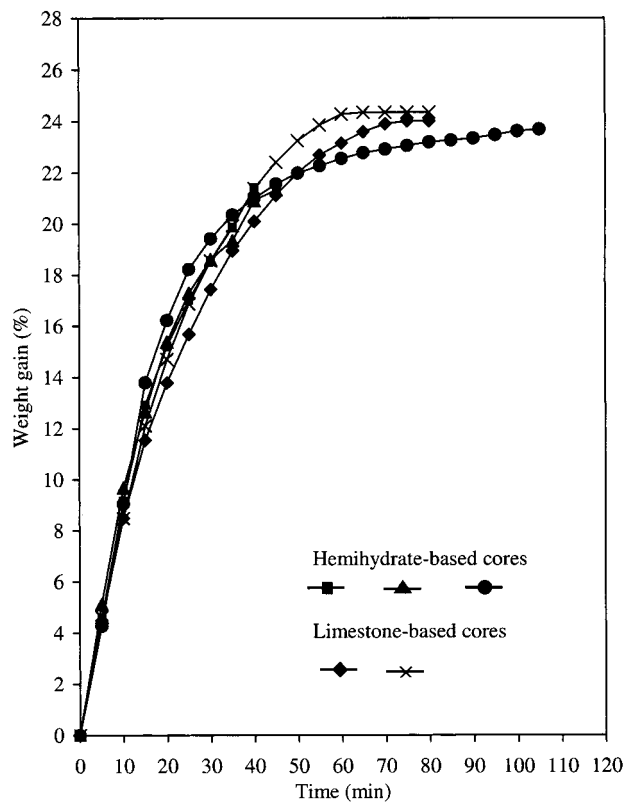


**Figure 5.** Decomposition of  $\text{CaSO}_4$  in various pellets by a cyclic oxidation and reduction process conducted at  $1070\text{ }^\circ\text{C}$ .

ultimate loss in weight on a percentage basis declined with increasing shell thickness because the core mass became a smaller fraction of the total pellet mass. For the bare pellet core the ultimate loss in weight of 47% was close to the theoretical maximum loss in weight of 50% if all of the  $\text{CaSO}_4$  in the impure material was converted into  $\text{CaO}$ .

**Sorbent Characteristics.** The absorption characteristics of pellets made from Iowa limestone or from calcium sulfate hemihydrate were determined after the limestone or hemihydrate had been converted to  $\text{CaO}$ . Pellets made with limestone cores always included 10% A-16 SG alumina in the core preparation mixture. Pellet shells were made with the optimum shell composition.

The absorption characteristics of several pellet cores were determined first to establish a baseline. Although the cores had not been precalcined at  $1100\text{ }^\circ\text{C}$ , they had been preheated sufficiently to convert the starting materials to  $\text{CaO}$ . The absorption tests were conducted at  $880\text{ }^\circ\text{C}$  with 1.1%  $\text{H}_2\text{S}$  in a nitrogen mixture. While some of the  $\text{H}_2\text{S}$  could have decomposed at this temperature, another work<sup>19</sup> suggests that the extent of decomposition would probably not have exceeded 7–10%. The results presented in Figure 6 indicate good agreement between repeated tests and virtually no difference in the absorption characteristics of pellets made from the different starting materials. The observed maximum gain in weight for either material was  $\approx 24\%$ , which corresponded closely to the theoretical gain in weight of the limestone-based pellets if all the  $\text{CaO}$  was converted into  $\text{CaS}$ . However, it was 10% less than the theoretical gain in weight of the hemihydrate-based pellets if all the calcium compounds had first been converted into  $\text{CaO}$  and all of the  $\text{CaO}$  had then been converted into  $\text{CaS}$ .

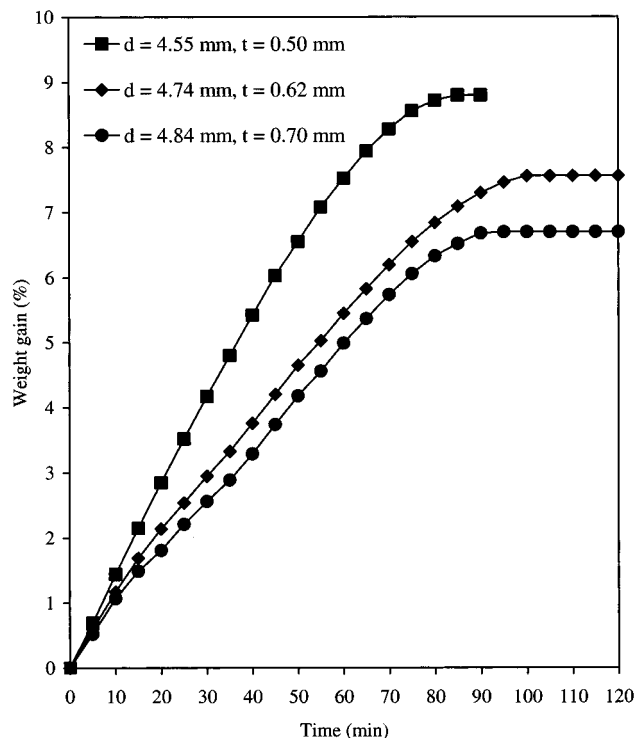


**Figure 6.** Replicate runs with pellet cores made of either calcium sulfate hemihydrate or limestone. Absorption was conducted with 1.1%  $\text{H}_2\text{S}$  at  $880\text{ }^\circ\text{C}$ .

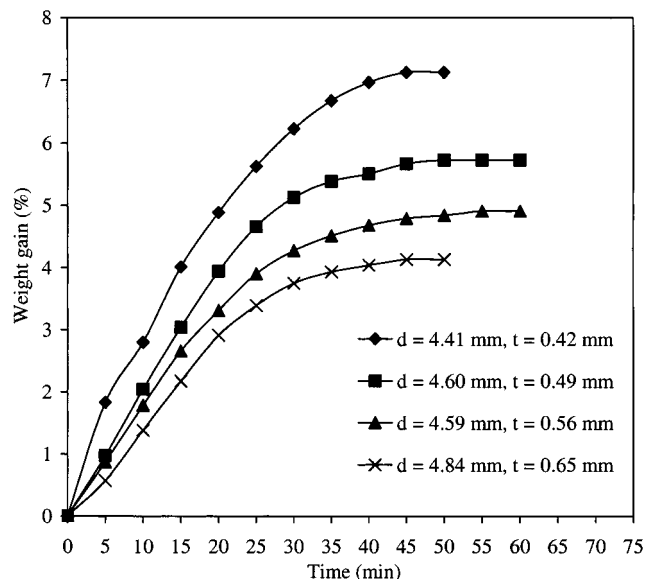
Several absorption tests were conducted with precalcined core-in-shell pellets to study the effect of increasing shell thickness. Again, the tests were conducted at  $880\text{ }^\circ\text{C}$  with 1.1%  $\text{H}_2\text{S}$  in a nitrogen mixture. Results obtained with limestone-based pellets are shown in Figure 7 and results with hemihydrate-based pellets in Figure 8. In both cases it is apparent that the ultimate gain in weight due to absorption decreased as shell thickness increased. Also, the ultimate gain in weight of limestone-based pellets was greater than that of hemihydrate-based pellets. These effects are the result of expressing the gain in weight as a percentage of the initial pellet mass. As the shell thickness increased, the reactive core mass became a smaller fraction of the total pellet mass because all of the pellets had approximately the same initial core diameter, 3.5 mm. Furthermore, the pellet cores derived from limestone had more  $\text{CaO}$  than those derived from hemihydrate because the molar volume of the limestone particles was less than the molar volume of the hydrated calcium sulfate particles.

While it is apparent from Figures 7 and 8 that the rate of weight gain decreased with increasing shell thickness, it is not so apparent that the rate of conversion of  $\text{CaO}$  to  $\text{CaS}$  was generally not greatly affected by shell thickness. This can be seen by comparing the conversion of the different pellets at a particular time assuming that the conversion was proportional to the fractional change in pellet weight based on the ultimate gain in weight at steady state. For example, after 20 min of absorption, most of the hemihydrate-based pellets registered a conversion of 68–69%. Only the pellet with the thickest shell registered a slightly higher conversion (71%). The difference is not considered significant. For the limestone-based pellets the results suggest that shell thickness had some effect. After 50





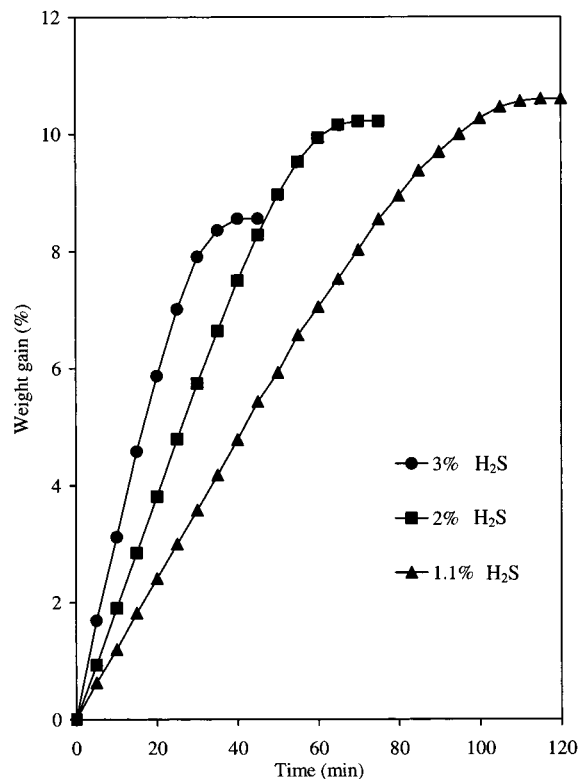
**Figure 7.** Effect of shell thickness on the absorption capacity of limestone-based core in shell pellets. Absorption was conducted with 1.1% H<sub>2</sub>S at 880 °C.



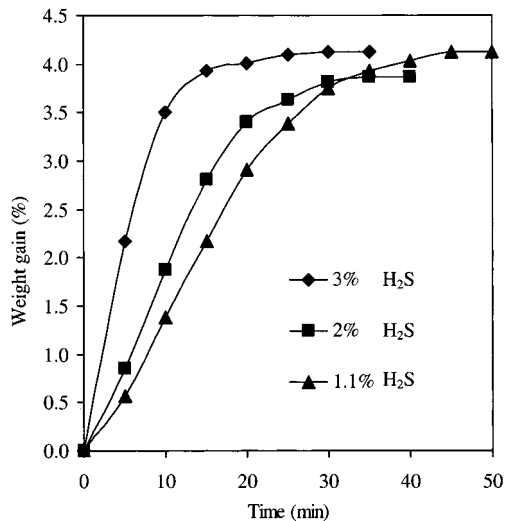
**Figure 8.** Effect of shell thickness on absorption capacity of hemihydrate-based core-in-shell pellets. Absorption was conducted with 1.1% H<sub>2</sub>S at 880 °C.

min of absorption, the pellet with the thinnest shell registered a conversion of 74% while the other two pellets having thicker shells registered conversions of 62 and 63%, respectively. Because the hemihydrate-based pellets in 20 min registered a conversion that was equal to or greater than that registered by the limestone-based pellets in 50 min with a comparable shell thickness, it is apparent that the hemihydrate-based pellets reacted more rapidly.

The difference in reactivity of the two types of core-in-shell pellets may seem surprising because the uncalcined pellet cores made of the different materials appeared to react equally rapidly with H<sub>2</sub>S (Figure 6).



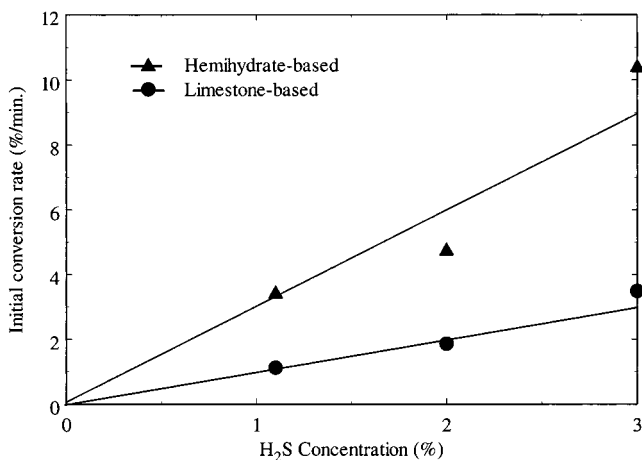
**Figure 9.** Effect of H<sub>2</sub>S concentration on absorption rate of limestone-based, core-in-shell pellets. Runs were conducted at 880 °C.



**Figure 10.** Effect of H<sub>2</sub>S concentration on absorption rate of hemihydrate-based, core-in-shell pellets. Runs were conducted at 880 °C.

However, the limestone-based cores initially contained 10% A-16 SG alumina that probably reacted with part of the lime when the core-in-shell pellets were calcined at 1100 °C, thereby changing the properties of the material.

Other absorption tests were conducted with precalcined core-in-shell pellets to investigate the effect of H<sub>2</sub>S concentration on the rate of absorption while holding pellet dimensions and other system parameters constant. The results obtained with limestone-based pellets are presented in Figure 9 and those obtained with hemihydrate-based pellets in Figure 10. Although the average diameter of both types of pellets was nearly the same (4.9–4.8 mm), the average core diam-

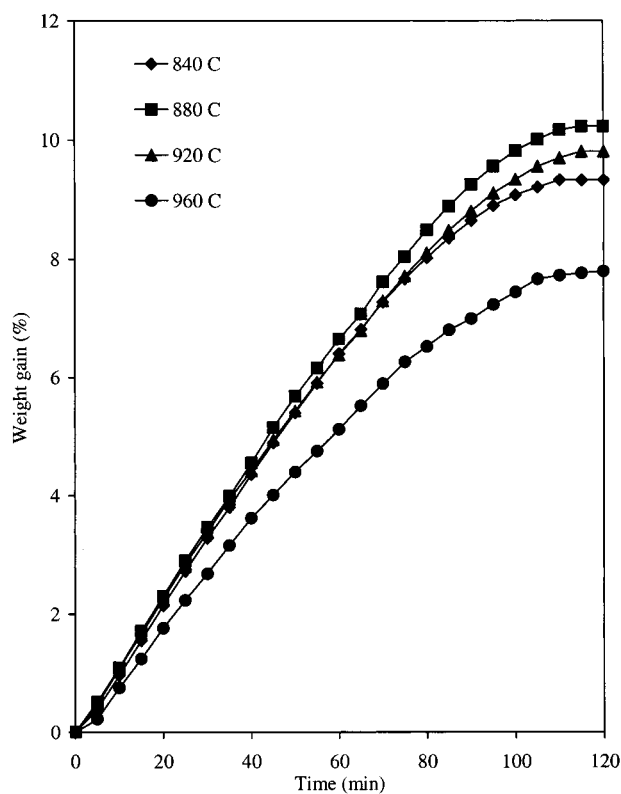


**Figure 11.** Effect of H<sub>2</sub>S concentration on initial global conversion rate for different types of core-in-shell pellets at 880 °C.

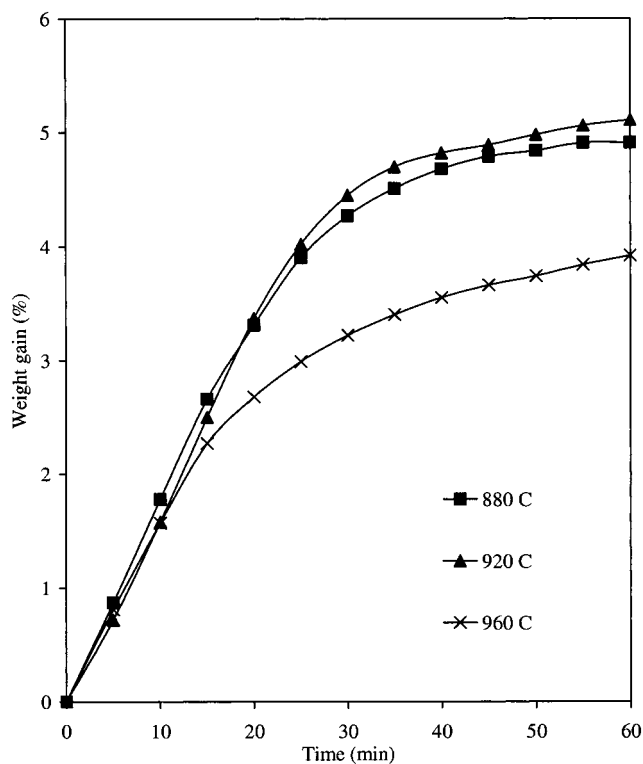
eters differed and were 4.0 and 3.5 mm, respectively. Consequently, the average shell thickness was 0.45 mm for the limestone-based pellets and 0.64 mm for the hemihydrate-based. For a given sorbent material the ultimate gain in weight of the sorbent appeared to be independent of H<sub>2</sub>S concentration with the exception of the result shown for a limestone-based pellet treated with 3% H<sub>2</sub>S (Figure 9). In this case the decline in ultimate capacity of the sorbent may have been due to pore closure.

For both sorbent materials the initial rate of absorption was greatly affected by H<sub>2</sub>S concentration. In Figure 11 it can be seen that the initial global rate of conversion of CaO to CaS was directly proportional to H<sub>2</sub>S concentration, which suggests that the process is governed at least initially by first-order kinetics. Furthermore, because the global rate of reaction was larger for the hemihydrate-based pellets, which also had the thickest shells, the results indicate that the hemihydrate-based cores reacted more rapidly than the limestone-based cores.

Additional absorption tests were conducted with precalcined pellets to study the effect of temperature on the rate of absorption of H<sub>2</sub>S. The results are shown in Figures 12 and 13, respectively, for the two types of pellets. For some of these tests, limestone-based pellets having an average overall diameter of 4.88 mm and a shell thickness of 0.48–0.55 mm were employed. Figure 12 indicates very little difference in the rate of absorption over the temperature range from 840 to 920 °C. The small differences in the final weight gain of the different pellets were probably due to differences in sorbent mass. However, the lower rate of absorption observed at 960 °C was clearly due to the increase in temperature. Similar results were observed with the hemihydrate-based pellets, which had an average overall diameter of 4.56 mm and average shell thickness of 0.53 mm (Figure 13). Again, the small difference in rate of absorption observed between 880 and 920 °C was not significant, whereas the lower absorption rate observed at 960 °C was significant. Considering that for the two cases the rate of absorption did not seem to be affected significantly by temperatures below 920 °C, the overall rate did not appear limited by chemical reaction. Therefore, the rate-controlling mechanism remained elusive. The marked decrease in absorption rate above 920 °C may have been caused by incipient sintering of the material with corresponding pore closure or it may



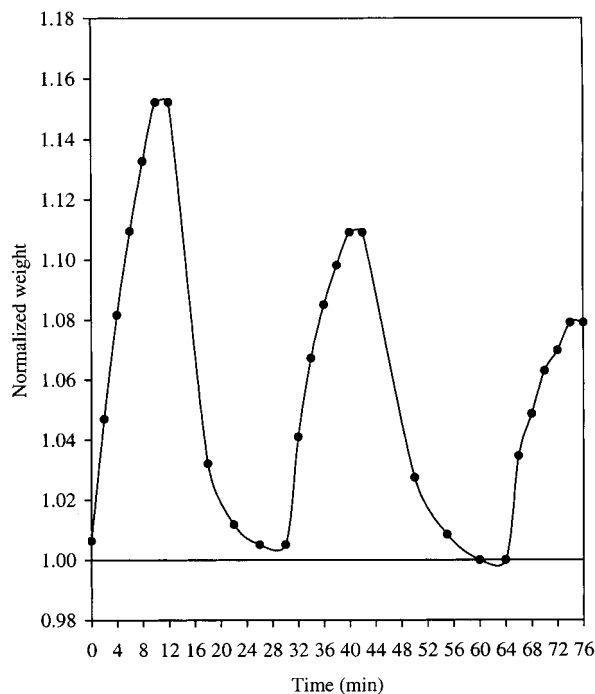
**Figure 12.** Effect of temperature on absorption rate of limestone-based, core-in-shell pellets. Runs were conducted with 1.1% H<sub>2</sub>S in nitrogen.



**Figure 13.** Effect of temperature on absorption rate of hemihydrate-based, core-in-shell pellets. Runs were conducted with 1.1% H<sub>2</sub>S in nitrogen.

have been caused by greater decomposition of the H<sub>2</sub>S with a corresponding decrease in the concentration of the reactant.

**Sorbent Loading and Regeneration.** To determine the effects of repeatedly loading and regenerating the

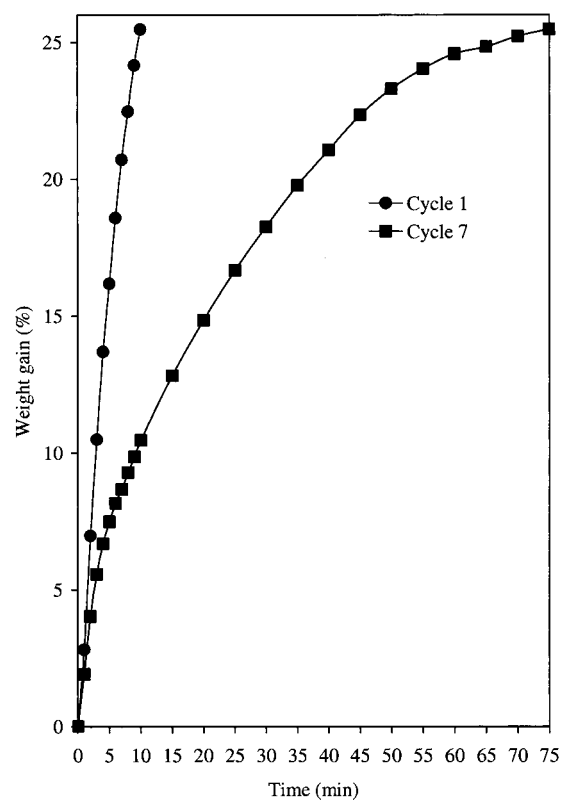


**Figure 14.** Results achieved when a limestone-based core was subjected to a multicycle absorption/regeneration test. Absorption was conducted with 3.0% H<sub>2</sub>S at 920 °C. Regeneration was conducted at 1050 °C.

different sorbent materials, several experiments were conducted with uncoated pellet cores and also with core-in-shell pellets. During the absorption phase a single pellet was treated at 920 °C with 3.0% H<sub>2</sub>S in nitrogen for a preset time. Then the flow of H<sub>2</sub>S was discontinued, and while the flow of nitrogen was continued, the temperature of the system was raised to 1050 °C for regeneration. Regeneration was conducted by subjecting the pellet to several cycles of oxidation and reduction as previously described. Regeneration was continued until virtually all of the weight gained during the absorption phase had been lost. The temperature of the system was then returned to 920 °C and the cycle of loading and regeneration repeated.

In one experiment an uncalcined limestone-based pellet core was first converted to CaO and then subjected to several cycles of loading and regeneration, and the results are shown in Figure 14. It can be seen that using a constant loading time of 10 min/cycle resulted in a systematic decrease in the quantity of H<sub>2</sub>S absorbed. Consequently, the gain in pellet weight during the third cycle was only half of the weight gained during the first cycle. The results indicate a loss in reactivity of the material, which could have been due to sintering.

To see if the presence of limestone impurities or 10% A-16 SG alumina in the mixture was responsible for the loss in reactivity of the previous pellet core, another experiment was conducted using a pellet core made entirely of reagent-grade calcium carbonate. The experiment was conducted as before and a steady decrease in the quantity of H<sub>2</sub>S absorbed was observed from cycle to cycle. During the seventh cycle the loading time was extended until the pellet had gained as much weight as during the first cycle. Figure 15 shows the gain in weight of the pellet core during the first and last cycles, and it is evident that it required 75 min for the pellet to gain as much weight during the last cycle as the pellet gained in 10 min during the first cycle. Therefore, it is



**Figure 15.** Comparison of the absorption rates achieved during the first and the seventh cycles for a pellet core made from reagent-grade calcium carbonate. Absorption was conducted with 3.0% H<sub>2</sub>S at 920 °C and regeneration was conducted at 1050 °C.

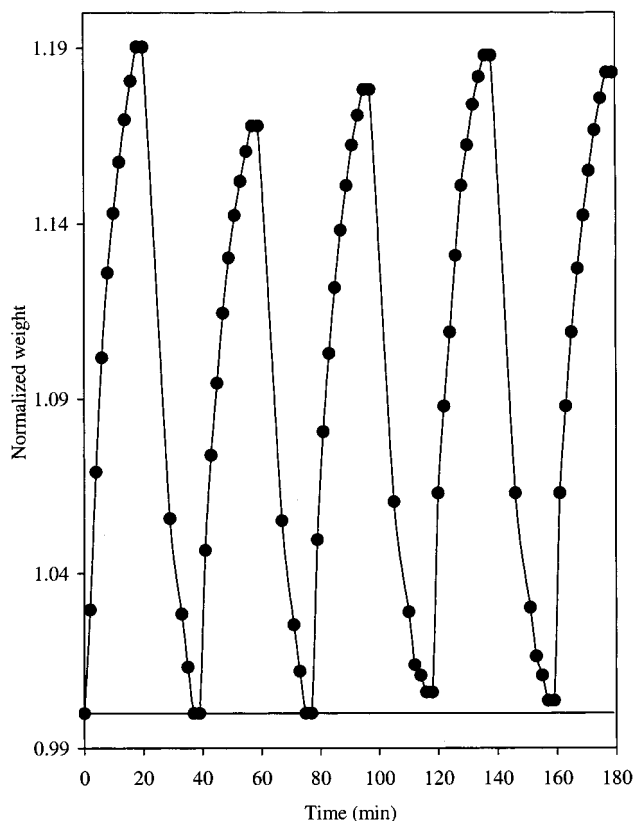
clear that even pellets made of pure calcium carbonate experienced a decline in reactivity when subjected to repeated loading and regeneration.

To see whether pellets made from calcium sulfate would behave similarly, an experiment was conducted with a pellet core made from the hemihydrate. Although the pellet had not been precalcined at 1100 °C, it had been converted to CaO before it was subjected to several cycles of loading and regeneration. The results presented in Figure 16 show that the sorbent experienced no loss in reactivity over five loading cycles. When a second pellet was subjected to the same treatment, similar results were observed.

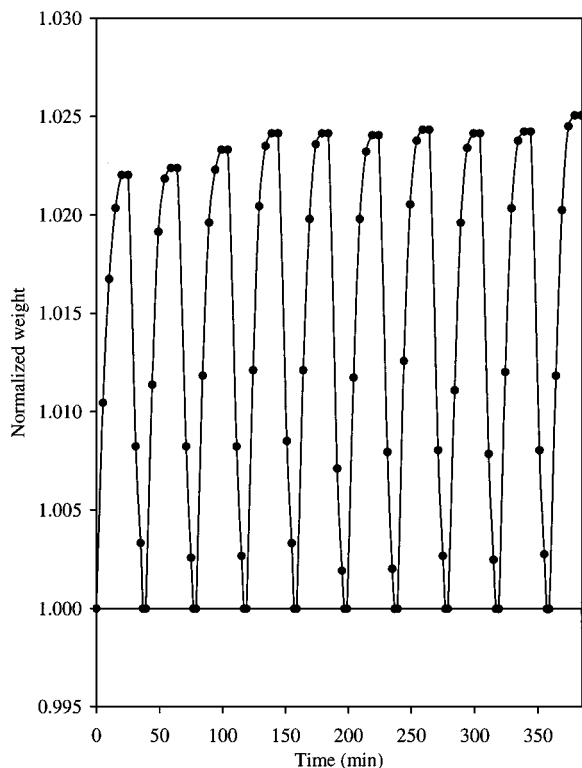
In a final experiment, a core-in-shell pellet having a hemihydrate-based core was treated to repeated loading and regeneration as described above. However, the pellet had first been precalcined at 1100 °C for 2 h and the core converted into CaO. The pellet had an overall diameter of 4.76 mm and an inner core diameter of 3.35 mm. The results presented in Figure 17 indicate no loss in reactivity over 10 loading cycles. In fact, the results show a slight increase in the weight gained from cycle to cycle. Of course, the amount of weight gained in each cycle was low compared to the weight gained by a bare core. The core-in-shell pellet had a relatively thick shell (0.70 mm), which limited the relative gain in weight due to reaction with H<sub>2</sub>S and also may have limited the rate of diffusion of H<sub>2</sub>S into the core.

## Discussion

The present results show how a promising regenerable sorbent for desulfurizing hot coal gas can be made by encasing a highly reactive but physically weaker material in a supporting shell of porous but stronger



**Figure 16.** Results achieved when a hemihydrate-based, 3.35-mm-diameter core was subjected to a multicycle absorption/regeneration test. Absorption was conducted with 3.0%  $\text{H}_2\text{S}$  at  $920^\circ\text{C}$  and regeneration was conducted at  $1050^\circ\text{C}$ .



**Figure 17.** Results achieved when a hemihydrate-based, core-in-shell pellet was subjected to a multicycle absorption/regeneration test. Absorption was conducted with 3.0%  $\text{H}_2\text{S}$  at  $920^\circ\text{C}$  and regeneration was conducted at  $1050^\circ\text{C}$ .

and largely inert material. While the method was demonstrated by pelletizing either powdered limestone

or plaster of Paris to form the pellet cores, it could be applied to other potential sorbents. Limestone or plaster of Paris have the advantage of being inexpensive compared to other proposed sorbent materials such as zinc or copper.<sup>3,4</sup> Although the pellet cores were encased in shells made largely of high-grade alumina, future work is expected to show that the shells can be made of a less costly material. The two-step method of pelletization and subsequent treatment steps are also expected to be relatively low in cost. Even though the method required to convert  $\text{CaSO}_4$  into  $\text{CaO}$  is more involved than that required to convert  $\text{CaCO}_3$  into  $\text{CaO}$ , the method has been demonstrated extensively and its cost should not be prohibitive.<sup>13,14</sup> Therefore, the cost of sorbent pellets made from limestone or plaster of Paris should compare quite favorably with that of other manufactured sorbents.

The calcium-based sorbent requires an unusual method of regeneration because oxidation alone converts part of the  $\text{CaS}$  into  $\text{CaSO}_4$ . Furthermore, when  $\text{CaSO}_4$  is subjected to strongly reducing conditions at high temperature, the conversion of  $\text{CaSO}_4$  back to  $\text{CaS}$  is favored thermodynamically more strongly than the conversion of  $\text{CaSO}_4$  to  $\text{CaO}$ . However, it has been shown that the kinetics and mechanism of reduction favor the second reaction.<sup>20</sup> Therefore, reduction tends to convert more  $\text{CaSO}_4$  into  $\text{CaO}$  than into  $\text{CaS}$ . But because both  $\text{CaO}$  and  $\text{CaS}$  are produced, the oxidation and reduction cycle must be repeated. Air can be employed for oxidation and various gases including  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{CH}_4$  can be used for reduction. Practical methods for converting either  $\text{CaS}$  or  $\text{CaSO}_4$  into  $\text{CaO}$  have been proposed and/or demonstrated.<sup>13-16</sup> These methods should produce a relatively rich stream of  $\text{SO}_2$  that is convertible into either  $\text{H}_2\text{SO}_4$  or elemental sulfur.

The results presented here are the product of an ongoing research effort directed toward the development of a superior and economical sorbent that is also regenerable. Because further improvements in the material are anticipated, the material has not been completely characterized. Further characterization will go hand in hand with product improvement.

## Conclusions

A promising calcium-based sorbent was prepared by pelletizing either powdered limestone or calcium sulfate hemihydrate and then coating the resulting spherical pellets with an optimum mixture of powdered alumina and limestone. Through calcination at  $1100^\circ\text{C}$ , the coating was partially sintered and converted into a strong porous shell. If limestone was present in the core, it was converted into  $\text{CaO}$  at the same time. However, if calcium sulfate was present, it was converted into  $\text{CaO}$  by applying a cyclic oxidation and reduction process. The crushing strength of the core-in-shell pellets was directly proportional to shell thickness regardless of core composition.

The hemihydrate-based pellets proved superior to the limestone-based pellets in two important respects. Under similar conditions the hemihydrate-based pellets reacted more rapidly with  $\text{H}_2\text{S}$  and their reactivity did not decline with repeated loading and regeneration. On the other hand, the ultimate absorption capacity of the limestone-based pellets was greater than that of hemihydrate-based pellets of equal size. The rate of reaction of the materials was directly proportional to  $\text{H}_2\text{S}$  concentration, but the rate was not affected greatly by

shell thickness over the range tested. The absorption rate did not appear to be controlled by chemical reaction because the rate was not affected significantly by temperature over the range from 840 to 920 °C. Above this range the rate declined markedly, probably because of sintering.

The loaded sorbent was readily regenerated by subjecting the material to a cyclic oxidation and reduction process conducted at 1050 °C. During regeneration CaS was completely converted back into CaO. The hemihydrate-based material appeared to withstand repeated loading and regeneration, whereas the limestone-based material suffered a decline in performance.

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