Development of a regenerable calcium-based sorbent for hot gas cleanup

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Development of a regenerable calcium-based sorbent
for hot gas cleanup

By

Tetteh Akiti

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

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Major: Chemical Engineering
Major Professor: Thomas D. Wheelock

Iowa State University

Ames Iowa

2001
This is to certify that the Doctoral dissertation of

Tetteh Akiti

has met the dissertation requirements of Iowa State University

Signature was redacted for privacy.

Major Professor

Signature was redacted for privacy.

For the Major Program

Signature was redacted for privacy.

For the Graduate College
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ABSTRACT

Experiments were conducted to develop a regenerable calcium-based sorbent for hot coal gas desulfurization. Spherical sorbent pellets were fabricated in a novel core-in-shell configuration. All pellets were prepared using a bench-scale pelletizer. In accordance with the core-in-shell concept, a reactive calcium compound (CaO) was surrounded by a strong shell consisting of a composite material. Limestone (CaCO₃) and hemihydrate (CaSO₄ • 0.5 H₂O) were used as starting materials that were eventually decomposed to produce CaO. Different types of cements and aluminas were investigated as strength enhancing shell materials.

The sorbent pellets were characterized by measuring their compressive strength, surface area, pore volume and porosity. Sectioned pellets were also viewed with an electron microscope. A thermal gravimetric analyzer was used to determine the absorption rate, absorption capacity, optimum service temperature, concentration-initial rate relationship, and the regenerability of several sorbent formulations. Sulfidation runs were performed with 0.55 - 3.0% H₂S in nitrogen at temperatures of 840 - 1000°C. Regeneration of the spent sorbent was conducted at 1050°C using a cyclic oxidation/reduction scheme.

For all core-in-shell pellets tested, it was found that thicker shells provided greater strength, but reduced the absorption capacity. While Portland cement shells provided enormous strength after curing, most of this strength was lost at high temperature. Of the cement formulations, those containing high calcium aluminate concentrations provided the greatest high temperature strength. However, all cement formulations required a minimum curing time to obtain adequate calcined strength. On the other hand, a sintered alumina-
based shell produced pellets that met the strength requirements without the need for the extra curing step.

For most formulations, the initial reaction rate was directly proportional to the $\text{H}_2\text{S}$ concentration, and the optimum service temperature was found to be in the neighborhood of 920°C. Unlike the limestone-based formulations, the hemihydrate-based sorbents showed no loss in sorbent capacity when subjected to repeated sulfidation and regeneration cycles. The kinetics of sulfidation were represented well by a shrinking core reaction model that accounted for the effect of chemical reaction on the surface of the unreacted core.
CHAPTER 1. GENERAL INTRODUCTION

An Integrated Gasification Combined Cycle (IGCC) system provides a promising means for generating electrical power from coal. Figure 1 is a schematic diagram of an ideal IGCC plant. Much attention has been focused on the IGCC system in recent years because it is significantly more efficient than a conventional coal power plant system. Conventional coal power plants operate with a Rankine cycle that has a low thermal efficiency of about 35% (Gangwal et al., 1993). In addition, these plants carry out combustion under atmospheric pressure, which means that the gas flow rates are high, and thus costly to handle. In an IGCC system, coal is gasified at high temperature and pressure, typically between 700 and 1050°C at about 25 atmospheres. The smaller gas volumes obtained at these pressures, and the integration of air and gas streams can increase the thermal efficiency to as high as 50% (Gangwal et al., 1993).

When coal is gasified with steam and a limited amount of oxygen, the sulfur present in the coal is converted mostly into hydrogen sulfide (H$_2$S) and some carbonyl sulfide (COS). The amount of sulfur present in the coal dictates the H$_2$S concentration in the resulting coal gas. Ben-Slimane and Hepworth (1994) showed that H$_2$S levels can range from 0.1 to 3.0% by volume depending on the type of coal used. To prevent corrosion of the gas turbine and to ensure efficient power generation, the sulfurous gases need to be removed at the high temperature and pressure that exist in the gasifier. Some of the most effective and cheapest natural sorbents for coal gas desulfurization at high temperature are limestone (CaCO$_3$), dolomite (CaCO$_3$.MgCO$_3$) and lime (CaO). In the early nineteen seventies, Squires et al. (1971) suggested using limestone as a regenerable sorbent for hot gas desulfurization
Figure 1. Schematic diagram of an ideal Integrated Gasification Combined Cycle (IGCC) process (source: Ben-Slimane and Hepworth, 1994)
(HGD). However, due to the poor attrition resistance of natural limestones, the process was impractical. Another option was to dispose of the spent sorbent in a landfill. This posed a serious threat to the environment, as the sulfided compound would react with water (H$_2$O) and carbon dioxide (CO$_2$) to form H$_2$S. Regeneration of the spent sorbent was more desirable, as it would not only reduce the harm done to the environment, but also cut overall plant operating costs (Squires et al., 1971).

Other metal oxides have been studied for potential use as regenerable high-temperature sorbents (Westmoreland and Harris, 1976; Uysal et al., 1988). At present a commercially used sorbent is Z-Sorb™, a zinc-based sorbent. The typical operating range of temperature for Z-Sorb™ is from 315 to 515°C (Khare et al., 1995). Higher temperatures are not used due to sintering and reduction of zinc oxide (ZnO) by hydrogen (H$_2$). Therefore, when using a sorbent such as Z-Sorb™ in an IGCC system the coal gas is cooled, the contaminants are removed, and then the gas is re-heated before entering the gas turbine. The thermal efficiency of such a power plant could be increased by not cooling the gas before cleaning (Squires et al., 1971). Another major disadvantage of Z-Sorb™ is that it is currently a very expensive product. The ideal sorbent for HGD would be one with the ability to operate at gasifier outlet temperatures, with high strength and attrition resistance, with the ability to reduce the amount of acidic gases by over 99% (Gangwal et al., 1993), and which could be regenerated and reused for over 100 cycles without loss of desulfurization power, and which is inexpensive to manufacture.

Due to the effectiveness of calcium-based sorbents as desulfurizing agents, there has been continued research on the use of the natural sorbents that contain calcium. Westmoreland and Harris (1976) showed that the reaction between CaO and H$_2$S is
thermodynamically favorable between 800 and 1200°C. Furthermore, between these temperatures the reaction is also favored kinetically. Work has been done on the reaction of H₂S and other acidic gases with calcined and uncalcined limestone and with half and fully calcined dolomite (Heesink and Van Swaaij, 1995). Researchers have also investigated the use of these sorbents at elevated pressures (Yrjas et al., 1996; Zevenhoven et al., 1996).

Fenouil and Lynn (1995a) observed that uncalcined limestone had a very low overall calcium utilization, about 10%, whereas the calcium in calcined limestones could be fully utilized. Yet care should be taken when using lime as a sorbent at high temperatures. Borgwardt (1989a) showed that sintering of CaO derived from CaCO₃ or from calcium hydroxide [Ca(OH)₂] was significant between 950 and 1100°C in an inert atmosphere. He showed that sintering increased with an increase in temperature. Impurities present in the CaO lattice structure also promoted sintering. Sintering was also enhanced by the presence of H₂O and CO₂ gases (Borgwardt 1989b). In addition, the low attrition resistance of CaO has to be overcome in order for it to be reuseable. One method of improving the strength of CaO is to incorporate limestone or lime into a strong inexpensive ceramic material and fabricate a "synthetic" sorbent.

The goal of the research project described below was to engineer an inexpensive, regenerable "synthetic" calcium-based sorbent which is highly reactive with H₂S and possesses enough strength to withstand multiple sulfidation and regeneration cycles. The sorbent would need to retain its structural integrity and reactivity throughout these many cycles.
Dissertation Organization

This dissertation consists of 8 chapters and is organized in the following manner. In Chapter 1 a general introduction to the subject matter and the problem addressed in the rest of the manuscript are presented.

Chapter 2 is a literature review that focuses specifically on the problem addressed, that is, the engineering of structurally enhanced calcium-based sorbents for hot gas desulfurization. This chapter is divided into several sections. The first part looks at previous work conducted for making and/or testing structurally modified calcium-based sorbents for high temperature desulfurization. Following this is a review of work done on the sulfidation kinetics of CaO. The next section reviews several techniques developed for the conversion of CaS to CaO. The novel core-in-shell concept used as a basis for developing a superior synthetic calcium-based sorbent is introduced in Chapter 3.

Chapters 4 through 7 are manuscripts prepared for publication in technical journals. The first manuscript, Chapter 4, lays the foundation for further development of the core-in-shell idea. The results of preparing and testing sorbent pellets made with limestone cores and cement shells are presented. The effects of various parameters are described. The second manuscript, Chapter 5, builds on the first. A more refined core-in-shell pellet is described and its characteristics presented. The regenerability of the sorbent is also discussed. The third manuscript, Chapter 6, presents the results of work on pellets having shells made of a sinterable powder mixture consisting of alumina and limestone. Chapter 7 proposes a rate controlling mechanism for the reaction between a core-in-shell pellet and H₂S gas.

In Chapter 8 the general conclusions of this work are consolidated. Recommendations for future work are also addressed. The Appendices supply more detailed information about
the statistical methods employed for analyzing results. References cited in chapters 1 to 3 are listed after the appendices.
CHAPTER 2. LITERATURE REVIEW

In this section, a review of synthetic calcium-based sorbents is presented. Emphasis
is placed on the preparation methods for the various composite sorbents described in the
literature and the results obtained under the conditions tested. The preparation methods
encountered can be grouped into four categories: (1) direct impregnation, (2) a sol-gel
technique, (3) pelletization, and (4) casting. A major objective of this project was that the
sorbent developed be regenerable. Therefore, a review of the various methods for
regenerating calcium oxide (CaO) was conducted. Work done on the kinetics of the reaction
between calcined limestone and H₂S or COS was also reviewed.

Synthetic Calcium-Based Sorbents

Direct impregnation

The direct impregnation method for fabricating a calcium-based sorbent involves the
infusion of a strong inert porous substrate with a calcium compound. The calcium compound
is usually introduced into the carrier by refluxing the substrate in a calcium salt solution.
Upon subsequent heat treatment the calcium compound decomposes leaving CaO crystals
dispersed throughout the carrier.

Several previous workers experimented with calcium-based sorbents prepared by
direct impregnation. Some of the sorbents were prepared for absorbing SO₂ rather than H₂S.
One of these was prepared by Snyder et al. (1977) working with α-alumina as a carrier.
They impregnated 3.2 mm by 3.2 mm α-alumina cylindrical pellets with 3.3 to 16.5% CaO
by refluxing the substrate in a solution containing calcium nitrate for 8 hr. They showed that
the amount of calcium introduced into the carrier was directly proportional to the concentration of calcium in the impregnating solution. The samples were then heat treated at 1100°C, the highest temperature of utilization. This was done so that all possible calcium aluminates were formed prior to utilization. The authors suggested that calcium aluminate and not calcium oxide was the resulting active ingredient. The reaction believed to take place between the sorbent material and SO₂ is,

\[ \text{CaO} \cdot n\text{Al}_2\text{O}_3(\text{s}) + \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{CaSO}_4(\text{s}) + n\text{Al}_2\text{O}_3(\text{s}) \]  

(1)

Sulfation tests at 900°C with 0.3% SO₂, 5% O₂, and 94.7% N₂ showed that the conversion of CaO decreased with increasing concentration of impregnated CaO. A 90% conversion of CaO to CaSO₄ was obtained with a sample containing 3.3% CaO, whereas only a 40% conversion was achieved with a sample containing 14.8% CaO under the same conditions. Separate α-alumina pellets made from boehmite and impregnated with 11.1 and 12.5% CaO, respectively, were subjected to preliminary regeneration and reloading tests. Regeneration was performed with 3% H₂ in N₂ at 1100°C. The capacity of the sorbents containing 11.1 and 12.5% CaO dropped by 50 and 45%, respectively, after the 10th cycle.

Yang and Shen (1979) worked with silica pellets as an inert carrier for CaO. Silica pellets, -6/+16 mesh, were impregnated with CaO using solutions of calcium nitrate or calcium acetate. The samples made with calcium acetate were heat-treated at 1000°C and those made with calcium nitrate were heat-treated at 1075°C. Two samples heated to 1000°C contained 3.15 and 7.7 wt.% CaO, respectively, whereas those heated to 1075°C contained 1.2 wt. % beta calcium silicate (β-Ca₂SiO₄). Sulfation tests showed that the samples prepared using calcium acetate and heat-treated at 1000°C reached approximately 98%
conversion of CaO to CaSO\textsubscript{4} in less than one hour, compared to a 78% conversion after two hours for those prepared with calcium nitrate and heat treated at 1075°C. A regeneration run was performed with a sample which initially contained 7.7 wt. % CaO and another with a sample which initially contained 1.2 wt. % β-Ca\textsubscript{2}SiO\textsubscript{4}. The results showed that the latter sample was fully regenerated after 30 min., whereas the former was only 80% regenerated in a two-hour period.

Christoforou et al. (1995) used a dry impregnation technique to fabricate calcium-based sorbents. They impregnated magnesia with 7.0 - 8.5 wt.% CaO. Some formulations were treated with methanol to increase the pore volume prior to testing. Sulfidation tests were conducted at 600°C and 1 atm. using 0.2% H\textsubscript{2}S in a nitrogen atmosphere. The results showed that the methanol treatment improved the capacity of the sorbent by almost fourfold. Regeneration was performed with 12.4% CO\textsubscript{2}, 75.2% H\textsubscript{2}O, and 12.4% N\textsubscript{2} at 550 – 670°C. However, regeneration met with limited success, as some calcium sulfate remained in the sorbent after regeneration. This significantly reduced the capacity of the sorbent from cycle to cycle.

**Sol-gel technique**

An inert carrier can also be fabricated by a sol-gel process. Then a calcium compound can be introduced into the carrier. Calcium oxide can also be introduced during the preparation of the carrier by a process known as *in situ* impregnation. The sol-gel process starts with an aqueous solution called a sol. For the case where the carrier is alumina, the sol will consist of pseudo boehmite dispersed in an aqueous solution containing urea and nitric
acid. Hence, the boehmite particles are positively charged. The solution is then pipetted into a column containing an upper layer consisting of a non-polar medium such as kerosene where the boehmite spheres form and a lower layer consisting of an ammonia solution where gelation of the spheres occurs. If in situ impregnation is desired, the ammonia solution will also contain a calcium salt. Therefore, in the second step, gelation as well as the introduction of the calcium compound occurs. In either case the resulting spheres are calcined at high temperature to gain final strength.

Duisterwinkel (1991) fabricated calcium-based sorbents via in situ impregnation using a sol-gel process. Several formulations were made and the amount of impregnated CaO ranged from 3.2 to 15.4% by weight. The spherical pellets ranged from 2.3 to 3.54 mm in diameter, with crush strengths of 60 - 180 N per pellet. The authors suggested that approximately 8 wt. % of impregnated CaO is optimum. Sulfation and regeneration cycles were performed at 850°C. A 50-cycle test showed that the sorbent reactivity decreased significantly in the first 5 - 10 cycles. Thereafter, the authors suggested that the reactivity stabilizes at an “acceptable” value.

Wolff (1991) carried out similar work with sol-gel sorbents. A sample, designated as SG 105, consisted of spherical pellets which ranged from 2.8 to 3.4 mm in diameter and contained 8.2 wt. % of impregnated CaO. As with the sorbents prepared by Snyder et al. (1977), calcium aluminates were believed to be the active ingredients. The sorbent formulation had an initial crush strength ranging from 14 – 44 N/mm. Wolff deduced from sulfation tests performed in a fixed-bed reactor at 850°C that 89% of the available CaO was converted to CaSO₄ after 25 hr. A 10-cycle sulfation/regeneration test conducted at the same temperature with a regeneration gas mixture consisting of 25% H₂ in nitrogen showed a small
but steady decrease in sulfur capture from approximately 57% for the first cycle to just over 40% after the 10th cycle. The crush strength of the pellets was virtually unaffected by the cyclic test and ranged from 13 to 45 N/mm.

Deng and Lin (1996) prepared γ-alumina supports and impregnated them with CaO starting with calcium chloride (CaCl₂). Unlike the work by Duisterwinkel (1991) and Wolff (1991), the making of the carrier and impregnation were performed in two separate steps. After impregnation, the materials were first dried at 200°C for 10 hr. and then calcined at 550°C for 6 hr. The resultant sorbent had a very large surface area (100 - 300 m²/g) and contained 10 - 30 wt. % impregnated CaO. One important observation was that there was a large decrease in surface area when the sorbents were heat-treated to 850°C. Sorbents containing 10 and 20% CaO by weight experienced a 57 and 88% decrease in surface area, respectively. The authors did not report any absorption tests with their CaO sorbents.

**Pelletization**

Pelletization, due to its low cost, is an attractive means of sorbent preparation. Generally, to prepare a synthetic sorbent via pelletization, a powdered mixture of various constituents is loaded into a pelletizer which is in the form of a rotating drum. A liquid, usually water, is then sprayed on the powder to promote pelletization. To grow the pellets more powder is introduced into the revolving drum while spraying the surface of the pellets with liquid. When the pellets reach a desired size, the introduction of powder is discontinued. Depending on the binder, different methods are used to strengthen the pellets. In some cases high temperature sintering of the binding material within the individual pellets is responsible for final strength.
In a patent awarded to Voss (1982) of the Engelhard Minerals & Chemicals Corporation, a form of pelletization was described which produces structurally enhanced calcium-based sorbents. The sorbents in the form of -6/+60 mesh granules, are made by mixing limestone with clay and agglomerating the wet mixture with a pin mixer. Results of preparing several sorbents by this technique and subsequently testing them were reported. Sulfation tests were performed at 850°C and 1 atm. pressure with a gas consisting of 0.3% SO₂, 5% O₂, 13% CO₂ and 81.7% N₂. Voss claimed that the sorbents showed no loss of reactivity due to pore plugging by calcium sulfate. Of 16 different sorbents tested, a calcined “Chemstone” agglomerate with 15% attapulgite clay and 2% boric acid seemed to be best. Results showed that this sorbent had the highest sulfation capacity with 46% of the available CaO converted to CaSO₄ in a 5-hr. period. The same formulation also had the highest attrition resistance. Though no results were presented, Voss claimed that the sorbent could be put through several cycles of regeneration and reuse.

Yoo and Steinberg (1983) studied calcium silicates as potential sorbents. They pelletized Type III Portland cement and used it for H₂S absorption. The sorbent was called Agglomerated Cement Sorbent (ACS) and contained mostly tricalcium silicate (Ca₃SiO₅). The freshly made pellets were 1 - 3 mm in diameter and were frail and weak after pelletization. The pellets could only be handled after they had been air-dried for 16 - 18 hr. They were then cured for 28 days in an atmosphere of 100% humidity to gain final green strength. The resulting pellets were subjected to sulfidation tests carried out at 1000°C and 1 atm. with a simulated coal gas mixture consisting of 0.5% H₂S, 12.5% CO, 12.5% H₂, 8.0% CO₂ and 66.5% N₂. The following reaction was thought to be responsible for the weight gain of the sorbent:
(CaO)$_3$SiO$_2$($s$) + 3H$_2$S($g$) = (CaS)$_3$SiO$_2$($s$) + 3H$_2$O($g$).

(2)

The results showed that the ACS pellets had a 30% conversion to the sulfided material after two hours. Regeneration tests were performed at 1000°C and 1 atm. with a gas mixture containing 15% CO$_2$ in N$_2$. Repeated loading and regeneration runs showed that there was no loss in sorbent performance after four cycles. Other tests on the ACS pellets indicated that the sorbent performance was not affected by up to 10% steam in the bulk gas. Also, up to 8% CO$_2$ in the bulk gas did not alter the sulfidation capacity. The ACS pellets seemed to hold great promise. However, more regeneration/reuse runs were required to test the longevity of the sorbents.

Zhang et al. (1989) also fabricated calcium-based sorbents by pelletization. They used less than 90 μm limestone particles and agglomerated the mixture with a binder to produce pellets 2 - 9 mm in diameter. The nature of the binder was not given. They claimed that the method of preparation improved the microstructure of the sorbent which in turn enabled higher calcium utilization. Sulfation tests were performed with 0.3 - 0.9% SO$_2$ and undisclosed amounts of CO$_2$, CO, O$_2$ in nitrogen at various temperatures. The maximum attainable conversion of CaO was found to be approximately 70%. The conversion decreased slightly with an increase in pellet diameter, while it increased significantly with an increase in additive concentration. The nature of the additive was not given. The authors showed that the limestone grain size which ranged between 45 and 180 μm did not affect the conversion of CaO to CaSO$_4$ when tested under the same conditions. Although no results were presented, the authors suggested that the sorbents could be regenerated in a reducing atmosphere. Also, they suggested that adding a combustible material that would increase the
pore volume could enhance the capacity of the sorbent. However, this would be at the expense of strength.

Pelletization of a calcium-based sorbent was also explored by Ham et al. (1989). By agglomerating limestone with a suitable binder, they claimed that their sorbents had higher attrition resistance than natural limestone. They mixed 500 g of 150 μm limestone particles with 5-15 g of cement and 40 - 50 ml water. The mixture was then pelletized in a rotating disk agglomerator. The pellets produced ranged from 0.5 to 1.0 mm in diameter. They experimented with different types of binders, namely starch, carbonates, silicates and clays. Among these binders, the silicates and clays were found to be most effective. Sulfation tests of the sorbents were carried out at 850°C with 0.2% SO₂, and 2% O₂ in nitrogen. The best formulation achieved a 54% conversion of CaO to CaSO₄. Regeneration was carried out with 15% CO₂ in nitrogen at temperatures ranging from 1000 to 1100°C. A multi-cycle test showed that the capacity of the sorbent was reduced considerably between the first and the second cycle. They attributed this loss in capacity to sintering that may have occurred during regeneration.

**Casting**

Casting is yet another method of preparing a sorbent. In this method, the active ingredient is mixed with a binder in a dispersing liquid (usually water) to form a thick slurry or paste. The slurry is then poured into molds to produce small tablets. After drying, the tablets are either cured or heat-treated to gain final strength.

Shadman and Dombek (1988) cast flakes containing mixtures of calcium oxide and either kaolin, silica or alumina. The flakes were 6 mm × 10 mm in area and 1 mm thick. The
samples were dried at 65°C to gain green strength prior to testing. Absorption experiments were performed at 700°C and using 0.1% SO₂ in the bulk gas. Their results showed that the sorbents with structural modifiers performed better than those without. They observed that the amount and not the type of modifier increased the conversion. The best results were obtained when kaolin was used as a modifier. A 39% conversion was achieved after two hours. They attributed the better performance to the increased macro-porosity of a given material. However, cyclic regeneration and reuse of the material was not demonstrated.

Zhu (1999) also investigated casting as a means of fabricating a synthetic calcium-based sorbent. In this work, pure calcium carbonate was combined with a strength enhancer, namely A-16SG alumina powder and CA-14 calcium aluminate cement. Several tablets were made with varying amounts of CaCO₃. His results showed that the strength of all pellets decreased sharply with an increase in CaCO₃ concentration. However, for a given concentration of CaCO₃ in a formulation, pellet strength increased as the sintering temperature was increased.

Summary of preparation methods

Table 1 summarizes the characteristics of the synthetic calcium-based sorbents encountered in this review. Among these sorbents, only the Portland cement (Yoo and Steinberg, 1983) and the magnesia-impregnated sorbent (Christoforou et al., 1995) were tested with H₂S. The other materials were only tested with SO₂. A thorough investigation of the Al₂O₃ / CaO sorbent system was performed with SO₂ by Duisterwinkel (1991) and Wolff (1991). It is known however, that both H₂S and SO₂ react strongly with CaO. Thus the Al₂O₃ / CaO sorbents should also be effective for removing H₂S gas. The limestone / clay
system has also been studied by several researchers. However, only Ham et al. (1989) performed regeneration runs on their sorbents; again loading tests were performed with SO₂ gas.

The impregnated sorbents generally had low H₂S absorption capacities, column 4, and high strengths, column 7 (Table 1). Among the impregnated sorbents, those made by Deng and Lin (1996) achieved the highest theoretical weight gain, 8.57%. However, the pellet strength was not reported. Sorbents prepared via pelletization and casting exhibited high weight gains, column 4. However, the attrition results presented by Voss (1982) indicate that sorbents containing excessive amounts of lime are frail, as they showed a higher attrition loss than sorbents with less lime when tested under similar conditions. Also it can be seen that the rate of attrition loss of the best sorbent formulation prepared by Voss (1982) was 44 times that of the impregnated sol-gel sorbent prepared by Wolff (1991), column 8.

The Kinetics of CaO Sulfidation

Several researchers have studied the kinetics of CaO sulfidation. Westmoreland et al. (1977) reported that the reaction of CaO with H₂S is first order and that the activation energy is 22 kJ/mol. Attar and Dupuis (1979) reported an activation energy of 155 kJ/mol and Abbasian et al. (1991) reported a value of 160 kJ/mol. Contrary to the results of Westmoreland, Heesink and Van Swaaij (1995) determined the reaction order to be one-half with respect to H₂S concentration and the activation energy to be 160 kJ/mol. With the exception of the results obtained by Westmoreland there is good agreement between activation energy values. The substantially low value Westmoreland obtained indicates that mass transfer was a limiting factor in the earlier experiments.
<table>
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<th>Reference</th>
<th>Preparation method</th>
<th>Sorbent formulation</th>
<th>Theoretical maximum sulfur weight gain (%)</th>
<th>Gas sorbed</th>
<th>Regeneration? (number of cycles)</th>
<th>Crush strength (N/mm)</th>
<th>Attrition loss (%/hr)</th>
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<td>Synder et al. (1977)</td>
<td>Wet impregnation</td>
<td>α-alumina + 16.5 wt.% CaO</td>
<td>4.70</td>
<td>SO₂</td>
<td>No</td>
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<td>α-alumina with 3.3% CaO gave the highest conversion.</td>
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<td>2.20</td>
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<td>Silica with 3.15% CaO gave the highest conversion.</td>
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<td>Agglomeration</td>
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<td>SO₂</td>
<td>No</td>
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<td>H₂S</td>
<td>Yes (4)</td>
<td>---</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>Shadman and Dombeck (1988)</td>
<td>Mixing</td>
<td>CaO + 30% kaolin</td>
<td>20.00</td>
<td>SO₂</td>
<td>No</td>
<td>---</td>
<td>---</td>
<td>The amount of binder but not the type enhanced performance.</td>
</tr>
<tr>
<td>Ham et al. (1990)</td>
<td>Pelletization</td>
<td>Limestone + binder</td>
<td>27</td>
<td>SO₂</td>
<td>Yes (8)</td>
<td>---</td>
<td>---</td>
<td>Silicate and clay binders were best. Significant loss in capacity after first regeneration run.</td>
</tr>
<tr>
<td>Zhang et al. (1989)</td>
<td>Pelletization</td>
<td>Limestone + binder</td>
<td>---</td>
<td>SO₂</td>
<td>No</td>
<td>---</td>
<td>---</td>
<td>Burnable additives increased sorbent performance</td>
</tr>
<tr>
<td>Duisterwinkel (1991)</td>
<td>In situ impregnation via sol-gel technique</td>
<td>8 wt. % CaO + alumina</td>
<td>2.29</td>
<td>SO₂</td>
<td>Yes (50)</td>
<td>30</td>
<td>---</td>
<td>Cost of using the synthetic sorbent is 3 times that of a disposable one.</td>
</tr>
<tr>
<td>Wolff (1991)</td>
<td>In situ impregnation via sol-gel technique</td>
<td>8.2 wt. % CaO + γ-alumina</td>
<td>2.29</td>
<td>SO₂</td>
<td>Yes (50)</td>
<td>27</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>Christoforou et al. (1995)</td>
<td>Dry impregnation</td>
<td>8.54 wt. % CaO + Magnesia</td>
<td>2.44</td>
<td>H₂S</td>
<td>Yes (6)</td>
<td>---</td>
<td>---</td>
<td>Significant loss in capacity from cycle to cycle.</td>
</tr>
</tbody>
</table>
In order to develop an efficient process that utilizes a synthetic calcium based sorbent
to remove \( \text{H}_2\text{S} \), it would help to have a mechanistic model that describes the kinetics of the
reaction. For the reaction between \( \text{CaO} \) and \( \text{H}_2\text{S} \) and/or \( \text{COS} \), two mechanisms based on the
shrinking core model and the grain model respectively, have been used to describe the
reaction between the solid particles and the bulk gas. The second model is an extension of the
first model.

Yagi and Kunii (1955) first introduced the shrinking core model. This model
assumes that the reaction starts on the surface of the solid where the reacting solid turns into
a product layer leaving an unreacted core. As the reaction progresses the product layer grows
and the unreacted core shrinks. After final conversion only product remains. The grain
distribution model, which was first introduced by Szekely and Evans (1970), is an extension
of the shrinking core model. The grain model assumes that the bulk solid is made up of
many small grains, and upon reaction each of the individual grains follows a shrinking core
mechanism.

Several researchers have studied the kinetics of the reaction of calcined limestone
with \( \text{H}_2\text{S} \) and \( \text{COS} \); however, few have proposed a mechanism for the reaction. One of the
studies was conducted by Borgwardt et al. (1984) who suggested a mechanism for the
kinetics of the reaction. They used limestone particles having a size of 1 - 3 \( \mu\text{m} \), a surface
area of 2.2 \( \text{m}^2/\text{g} \) and about 8% porosity. The samples were calcined at 700\(^\circ\text{C} \) for 90 s prior to
reaction. Sulfidation with \( \text{H}_2\text{S} \),

\[
\text{CaO}_{(s)} + \text{H}_2\text{S}_{(g)} = \text{CaS}_{(s)} + \text{H}_2\text{O}_{(g)}
\]  

(3)
was conducted using a gas mixture containing 5000 ppm H$_2$S, 45% H$_2$ and 55% N$_2$ at 700°C.

Sulfidation with COS

$$\text{CaO}(s) + \text{COS}(g) = \text{CaS}(s) + \text{CO}_2(g)$$  \hspace{1cm} (4)

was conducted with 4300 ppm COS, 20% CO and 80% N$_2$ at temperatures ranging from 600 to 900°C. Two plausible models were postulated for the reactions:

Model 1 – Shrinking core model with reaction at the interface between CaS and CaO limiting the rate of reaction.

$$t = \frac{\rho_{\text{CaO}}}{kC} r_g [1 - (1 - X)^{1/3}]$$  \hspace{1cm} (5)

Model 2 – Shrinking core model with diffusion through the CaS product layer limiting the rate of reaction.

$$t = \frac{\rho_{\text{CaO}}}{6D_e C} r_g^2 [1 - 3(1 - X)^{3/2} + 2(1 - X)]$$  \hspace{1cm} (6)

In these models $\rho_{\text{CaO}}$ is the density of CaO, $k$ is the reaction rate constant, $C$ is the gas phase concentration of H$_2$S or COS gas, $D_e$ is the effective diffusivity through the product layer and $X$ is the conversion of CaO to CaS. The grain radius $r_g$ is given by

$$r_g = \frac{3}{S_g \rho_{\text{CaO}}}$$  \hspace{1cm} (7)

where $S_g$ is the specific surface area of CaO. From their results the authors suggested that Model 2 best describes the kinetics of both reactions.
Fernouil and Lynn (1995b) also studied the kinetics of the reaction between calcined limestone and $\text{H}_2\text{S}$ gas. In their work 20 - 30 mg of 1.75 mm limestone particles were used. The particles were first calcined in nitrogen at 915°C for 15 min. For some tests a gas mixture with 900 ppm $\text{H}_2\text{S}$ in nitrogen was used while for other tests a gas mixture with 9000 ppm $\text{H}_2\text{S}$ in hydrogen was employed. For these conditions they also concluded that Model 2 best describes the kinetics. Other observations were that the micro-structure of the lime, the gas mixture, and temperature did not affect the mechanism by which the reaction proceeded.

Heesink and Van Swaaij (1995) considered the kinetics of the reaction between calcined limestone and $\text{H}_2\text{S}$ and/or COS at temperatures ranging from 500 to 700°C. In their investigation limestone particles having a size of 150 - 210 µm and initial surface area of 16.8 m$^2$/g were used. The samples were calcined at 850°C for 10 min. before reaction. The grain distribution model of Szekely and Evans (1970) was considered for describing the kinetics of the sulfidation reactions. The mechanisms considered were:

Model 3 – Grain reaction limiting

$$\frac{dX}{dt} = \frac{3kC^n}{N_0R_o^2} (1 + KX)^{2/3}$$  \hspace{1cm} (8)

Model 4 – Solid state product layer diffusion limiting

$$\frac{dX}{dt} = \frac{3D_{c}C^n}{N_0R_o^2[(1 - X)^{-1/3} - (1 - X)^{-1/3}]}$$  \hspace{1cm} (9)

Model 5 – Core reaction limiting
\[
\frac{dX}{dt} = \frac{3kC^n}{N_0R_0} (1 + X)^{2/3}
\]  
(10)

In these equations, \( n \) is the reaction order, \( N_0 \) is the initial concentration of the reactant solid, \( R_0 \) is the initial grain radius, and \( K \) is the expansion factor defined as,

\[
K = N_0(V_{\text{sol,prod}} - V_{\text{sol,reac}})
\]  
(11)

where \( V_{\text{sol,prod}} \) and \( V_{\text{sol,reac}} \) are the molecular volumes of the product and reactant solids, respectively. In the presence of only \( \text{H}_2\text{S} \) or \( \text{COS} \) the authors suggested that Model 3 best describes the sulfidation kinetics. However, in the presence of both gases Model 4 provided a more accurate representation of the sulfidation kinetics.

### The Regeneration of Calcium-based Sorbents

Most metal oxides that form stable sulfides upon reacting with \( \text{H}_2\text{S} \) can be regenerated back to the metal oxide by direct oxidation at high temperature. Unfortunately, \( \text{CaS} \) is an exception. When \( \text{CaS} \) is oxidized, \( \text{CaSO}_4 \) as well as \( \text{CaO} \) form. The desired oxidation reaction is as follows:

\[
\text{CaS}_{(s)} + \frac{3}{2}\text{O}_{2(g)} = \text{CaO}_{(s)} + \text{SO}_{2(g)}.
\]  
(12)

However, at high temperatures (650-1100°C) and with excess oxygen the following reaction is thermodynamically and kinetically favorable:

\[
\text{CaS}_{(s)} + 2\text{O}_{2(g)} = \text{CaSO}_4_{(s)}.
\]  
(13)
The larger mole volume of the CaSO₄ eventually causes pore plugging and the formation of an impenetrable layer, Figure 2. This halts further oxidation of any remaining CaS. Christoforou et al. (1995) encountered this phenomenon during regeneration of calcium-based sorbents. Their work was done in a fluidized bed where the sorbent capacity was evaluated by measuring breakthrough times. After the fourth regeneration cycle, they observed a breakthrough time of approximately half that of the fresh sorbent. After the sixth cycle the sorbent capacity was reduced to 1/30th that of the fresh sorbent. Clearly a regeneration method that would alleviate this problem is required for calcium-based sorbents to be an economically attractive option. Several researchers have worked on the regeneration of calcium-based sorbents. Table 2 shows various proposed regeneration methods and the preferred conditions found by the respective authors.

Several researchers have suggested regenerating spent calcium-based sorbents with CO₂ gas. Yoo and Steinberg (1983) utilized 15 - 30% CO₂ in nitrogen at approximately 1000°C for the regeneration of Portland cement sorbents. They suggested that the reaction which took place was,

\[(\text{CaS})_3\text{SiO}_2(\text{g}) + 9\text{CO}_2(\text{g}) = (\text{CaO})_3\text{SiO}_2(\text{s}) + 3\text{SO}_2(\text{g}) + 9\text{CO}(\text{g})\, \text{.} \]  

(14)

Their results showed that there was no appreciable loss in sorbent capacity over four absorption and regeneration cycles.

Chou and Li (1984a) regenerated sulfided dolomite with CO₂. They chose to use 100% CO₂ at about 750°C and 14.6 atm. The reason for the CO₂-rich atmosphere was because the thermodynamics of CaS oxidation with CO₂ are not favorable at the temperatures investigated. Under their conditions they suggested that the following reactions took place:
Figure 2. Oxidation of CaS causes pore plugging and the formation of an impenetrable layer of CaSO₄.
Table 2. Summary of various regeneration methods for the recovery of CaO from CaS

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Preferred conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yoo and Steinberg (1983)</td>
<td>CO₂ atmosphere</td>
<td>15-30% CO₂ in N₂ at 1000°C</td>
</tr>
<tr>
<td>Chou and Li (1984)</td>
<td>CO₂ atmosphere</td>
<td>100% CO₂ at 750°C, 14.6 atm</td>
</tr>
<tr>
<td>Illerup et al. (1993)</td>
<td>CO₂ atmosphere</td>
<td>CO₂ in N₂ at 900°C</td>
</tr>
<tr>
<td>Van der Ham et al. (1996)</td>
<td>Alternating oxidation and inert</td>
<td>Step 1 - 10% SO₂ in N₂ at 700°C, 40 min</td>
</tr>
<tr>
<td></td>
<td>atmospheres</td>
<td>Step 2 - 1100-1200°C in N₂, 10 min</td>
</tr>
<tr>
<td>Jagtap and Wheelock (1996)</td>
<td>Alternating oxidation and</td>
<td>Step 1 - 20% O₂ in N₂, 1 min</td>
</tr>
<tr>
<td></td>
<td>reduction atmospheres</td>
<td>Step 2 - 30% CO in N₂, 1 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>950-1100°C</td>
</tr>
<tr>
<td>Qiu et al. (1998)</td>
<td>Alternating oxidation and inert</td>
<td>Step 1 - 5.5% O₂ in N₂ at 850°C, 45 min</td>
</tr>
<tr>
<td></td>
<td>atmospheres</td>
<td>Step 2 - 1000°C N₂, 15 min</td>
</tr>
</tbody>
</table>
CaS(s) + CO2(g) = CaO(s) + COS(g)  \quad (15) \\
CaO(s) + CO2(g) = CaCO3(s).  \quad (16)

Repeated absorption and regeneration showed that the CaO utilization dropped from 100% after the first cycle to about 50% after the 20th cycle. They attributed this loss in capacity to annealing and sintering of the sorbent particles. Pore plugging by CaCO3 crystallites may also have prematurely halted the regeneration reaction and, hence, reduced the sorbent capacity from cycle to cycle.

Illerup et al. (1993) also used CO2 to regenerate CaS. They investigated the reaction at 1 bar with undisclosed amounts of CO2 in nitrogen at temperatures ranging from 850 to 950°C. Under these conditions they claimed that the reaction which took place was

\[
CaS(s) + 3CO_2(g) = CaO(s) + 3CO(g) + SO_2(g). \quad (17)
\]

They concluded that a temperature of 900°C was optimum for regeneration since the degree of sulfidation was 80% after 10 cycles of sulfidation and regeneration. At 950°C the degree of sulfidation was only 30% after 10 cycles.

Van der Ham et al. (1996) took a different approach for the regeneration of CaS. The regeneration was performed via a two-step process. In the first step CaS was oxidized to form CaSO4:

\[
CaS(s) + 2SO_2(g) = CaSO_4(s) + S_2(g) \quad (18)
\]

which the authors suggested should be carried out at about 700°C with 10% SO2 for approximately 40 min. The oxidation step converted from 20 to 40% of the CaS to CaSO4 depending on the type of limestone used. This was followed by the solid-solid reaction,

\[
CaS(s) + 3CaSO_4(s) = 4CaO(s) + 4SO_2(g) \quad (19)
\]
at about 1000°C for only 10 min. Care should be taken when operating at temperatures above 1000°C as much sintering of the CaO may occur. Van der Ham et al. (1996) were only able to perform Reaction 10 at 980°C due to equipment limitations. Even so, a drop of 35% in sorbent capacity was observed over eight cycles.

Jagtap and Wheelock (1996) also proposed a method for regenerating calcium-based sorbents. They showed that the CaSO₄ layer that forms upon oxidation of CaS due to Reaction 4 can be broken down using CO according to the following reaction:

\[
\text{CaSO}_4(s) + \text{CO}(g) = \text{CaO}(s) + \text{CO}_2(g) + \text{SO}_2(g)
\]

Their results showed that alternating between oxidizing conditions where Reactions 3 and 4 take place and reducing conditions where Reaction 11 takes place, will convert CaS completely into CaO. The authors suggested that both oxidation and reduction reactions take place between 950 and 1100°C and that the switch between oxidative and reductive conditions be conducted at 1-min. intervals. No loss in reactivity was observed over seven absorption and regeneration cycles. The authors demonstrated that other reducing agents such as natural gas or propane can also be used for the reduction step.

Qui et al. (1998) introduced a modified form of the Van der Ham et al. (1996) regeneration scheme. They suggested a four-step procedure. In the first step, CaS is oxidized with 5.5% O₂ in nitrogen at about 850°C for 45 min. where Reaction 4 is predominant. Then at a temperature of approximately 1000°C in an inert atmosphere, Reaction 10 takes place for approximately 15 min. However, due to pore plugging the reaction does not go to completion. Therefore, the CaS is oxidized again, Reaction 4. This is
followed by Reaction 10 to obtain the final product. The authors state that by using this procedure the regeneration is greater than 98% complete.

With the exception of Yoo and Steinberg (1983) other researchers have used limestone or dolomite particles as the starting material for sulfidation and for regeneration tests. These materials most likely crumble during cyclic testing. These methods are yet to be tested on calcium based sorbents fabricated to maintain structural integrity over numerous cycles.

Conclusions

In this chapter some of the major factors which will affect the development of an improved calcium-based, regenerable synthetic sorbent for hydrogen sulfide have been considered. The first section concentrates on results of previous attempts to prepare synthetic calcium-based sorbents by various methods. Most of the sorbents were designed to capture sulfur dioxide rather than hydrogen sulfide. Although some researchers reported high conversions, the actual calcium utilization was often very low. Since the binding materials were often inert, sorbent absorption capacity in terms of weight gain was inevitably sacrificed for strength. Very few of the sorbent formulations were subjected to repeated regeneration and reuse. Most sorbents that underwent cyclic testing were tested with sulfur dioxide gas instead of hydrogen sulfide.

The next section focuses on the kinetics of calcium oxide sulfidation. A better understanding of the kinetic mechanism can aid the development of an efficient process that utilizes a calcium oxide based sorbent. There is general agreement on the magnitude of the activation energy for the reaction between lime and hydrogen sulfide. However, there is
disagreement about the reaction order with respect to hydrogen sulfide concentration.

Several mechanistic models have been suggested for the reaction. Borgwardt et al. (1984) and also Fernouil and Lynn (1995) suggested a shrinking core mechanism, whereas Heesink and Van Swaaij (1995) suggested a grain distribution model.

The regeneration of the spent sorbent after calcium oxide reacts with hydrogen sulfide is challenging. The third part of the review deals with this topic. Several investigators proposed different schemes for the regeneration. However, in all but one case lime particles were used for cyclic testing. Testing of these methods on a sorbent that retains its structural integrity over numerous cycles is yet to be performed.
CHAPTER 3. THE CORE-IN-SHELL CONCEPT

Of the various preparation methods encountered for the fabrication of a calcium-based sorbent, pelletization seems to be the most attractive option due to its relative lower cost. The pelletized sorbents encountered in the literature review consist of a binding material intermixed with a reactive ingredient. Although this configuration produces structurally enhanced sorbents, it has its drawbacks. Firstly, the matrix formed by the binding material may crack upon repeated loading and regeneration as there is a volume change between CaS and CaO and between these compounds other intermediates that may form (e.g., CaSO$_4$). Secondly, impurities are known to enhance sintering of lime, Borgwardt (1989a). Hence, the interaction of the binding material and the lime may promote sintering at an undesirably low temperature.

In an effort to eliminate these drawbacks a novel approach was used in this work to engineer a calcium-based sorbent. The idea was to separate the reactive ingredient from the binder, and yet combine the two components in such a way that each component serves its purpose; the binder providing strength and the reactive material serving as a sorbent. One way to achieve this is to have the sorbent material coated with a protective material that forms a tough shell. This novel configuration henceforth will be called a “core-in-shell” sorbent.

Various configurations of a core-in-shell sorbent are realizable and outlined in Table 3. The “ideal” core-in-shell sorbent is one which has a reactive core surrounded by an inert, light, porous, strong shell, Case 1. In this case the shell solely provides strength and undergoes no structural changes during repeated loading and regeneration. Also with the reactive material separated from the binder, sintering due to the interaction of the two
Table 3. Various configurations for a core-in-shell sorbent

<table>
<thead>
<tr>
<th></th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>Reactive material only</td>
<td>Reactive material and binder material</td>
<td>Reactive material only</td>
<td>Reactive material and binder material</td>
</tr>
<tr>
<td>Shell</td>
<td>Coating material only</td>
<td>Coating material only</td>
<td>Reactive material and coating material</td>
<td>Reactive material and coating material</td>
</tr>
<tr>
<td>Advantages</td>
<td>Unreactive shell undergoes no</td>
<td>Unreactive shell undergoes no</td>
<td>Core and shell both contribute to absorption</td>
<td>Core and shell both contribute to absorption</td>
</tr>
<tr>
<td></td>
<td>structural changes during</td>
<td>structural changes during</td>
<td>capacity.</td>
<td>capacity.</td>
</tr>
<tr>
<td></td>
<td>absorption and regeneration.</td>
<td>absorption and regeneration.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sintering of the reactive</td>
<td>Core offers strength; overall</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>material due to presence of</td>
<td>pellet strength can be significantly higher</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>binder is eliminated.</td>
<td>than Case 1.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disadvantages</td>
<td>Core is weak, pellet strength</td>
<td>Weight gain is sacrificed for strength.</td>
<td>Shell may undergo structural changes during</td>
<td>Core and shell may undergo structural</td>
</tr>
<tr>
<td></td>
<td>depends solely on the shell.</td>
<td></td>
<td>absorption and regeneration and, hence,</td>
<td>changes during absorption and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>may be weakened.</td>
<td>regeneration. Weight gain is sacrificed for</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>strength.</td>
</tr>
</tbody>
</table>
constituents is eliminated. The drawback of the ideal case is that the core may be very weak. Hence, any small defects in the shell may cause the pellet to fail under a crushing load. To alleviate this problem, some of the binding material can be incorporated into the core to increase the overall strength, Case 2. However, the reactivity of the core may suffer and the weight gain will be lower than in Case 1. Also premature sintering of the core may be a problem. Another realizable configuration is one that consists of a reactive core and a semi-reactive shell, Case 3. Here the overall absorption capacity is higher than for the ideal case. However, depending on the amount of reactive material in the shell, the shell may undergo undesirable structural changes that may cause the pellet to prematurely disintegrate. Case 4 is one that has varying amounts of both reactive and binding materials in the core and the shell. Therefore, the sorbent consists of a semi-reactive core and a semi-reactive shell. In this case, both core and the shell contribute to the strength and capacity. On the other hand, both parts undergo structural changes that may weaken the pellet. If the composition of the shell equals that in the core, then the pellet no longer has a core-in-shell configuration, rather it is a mixture of the two components.

Several researchers have studied the mechanism by which pellets form. Barlow (1968) identified three stages of pellet formation and growth: nucleation, transition and ball growth. In the nucleation stage, the powder and pelletizing liquid mix as the tumbling action proceeds. This causes particle-particle contact and bridging between the individual particles by the pelletizing liquid. In this stage several grains are consolidated to form a nucleus. In the transitional stage, several of the nuclei join together to form larger grains. At this point pellets of different sizes are formed. Although several mechanisms have been proposed for the ball growing stage, that by Capes and Danckwerts (1965) is the most acceptable
They suggested that the smaller pellets are crushed and material from these pellets loads onto larger pellets.

Butensky and Hyman (1971) identified several factors that affect pellet formation. They showed that the liquid sprayed onto the pellets needs to reach a threshold value before pelletization can occur. Thereafter, the amount of pelletized material increases exponentially with the addition of more liquid. According to Butensky and Hyman (1971), the mean particle size and particle size distribution also affect pelletization. Sastry and Fuerstenau (1977) fitted a model to their pelletization data to describe the ball growth stage. They concluded that the moisture content and pellet distribution affected pellet growth. Barlow (1968) pointed out that fines as well as large grains aid pelletization. Without one or the other pelletization is more difficult. In their experiments, Butensky and Hyman (1971) found that time, drum speed and drum loading did not affect the granule size. Sastry and Fuerstenau (1972) introduced a ballability index to describe the growth of pellets as a function of powder and moisture added.

In light of the mechanism by which pelletization occurs and some of the major factors that influence the pellet making process, a procedure was developed for the preparation of core-in-shell pellets. The procedure is outlined in Figure 3. In the first stage the core material is loaded into a pelletizer drum. Granules representing the core form when the tumbling powder is sprayed with a pelletizing liquid. Pelletization is discontinued at the transitional stage when pellets of different sizes are formed. The pellets are then screened and those of the same mesh size are either reloaded into the pelletizer for growing or set aside for coating. To grow the pellets, more powder is introduced as the granules are tumbled and sprayed with
Prepare core material (i.e., mix reactive material with binding material).

Pelletize core.

Prepare coating material (i.e., mix binding material with reactive material).

Coat pellets with the coating material.

Treat pellets, (i.e., fire pellets at high temperature to decompose compounds and to promote sintering.)

Product – strong porous shell with highly reactive core.

Figure 1. Preparation procedure for a core-in-shell sorbent
water. Once the pellets reach a desired mesh size, they are re-screened and set aside. If the pellets are very weak, they may be strengthened by allowing them to tumble longer in the drum without the further addition of powder. However, the pellets may be sprayed occasionally to keep them moist.

The second step in making core-in-shell pellets is to add the shell to the core. The pelletized cores are loaded into the pelletizer drum and their surface is moistened. These pellets should be approximately the same size. A powdered mixture of the shell materials is slowly sprinkled onto the tumbling pellets. The pellets then begin to be coated. When the pellets reach a desired size they are removed and screened. Again to minimize pellet enlargement in the ball growth stage, only pellets of the same mesh size are loaded into the pelletizer drum and allowed to tumble while spraying their surface occasionally with the pelletizing liquid. At this point no powder is added. After the formation of the pellets, further treatment to obtain final strength may follow. For example, firing the pellets at high temperature may cause the binding material to sinter and provide final strength.

In this work the core-in-shell approach was used to develop a structurally enhanced calcium-based sorbent for high temperature desulfurization. A combination of some of the conditions encountered in the literature review was exploited. Different suitable, inexpensive binders were investigated. The ideal binder is one that will enhance the strength of the sorbent and yet maintain high calcium utilization. Various formulations were tested for strength as well as reactivity with H₂S. The more promising formulations were subjected to repeated loading and regeneration. A cyclic oxidation and regeneration method proposed by Jagtap and Wheelock (1996) was used for regeneration. The preferred formulation was one
which provided a crushing strength of 8.9 N/mm or more and showed no loss in reactivity after 10 absorption and regeneration cycles.
CHAPTER 4. DEVELOPMENT OF AN ADVANCED CALCIUM-BASED SORBENT FOR DESULFURIZING HOT COAL GAS


T. T. Akiti, Jr.,¹ K. P. Constant,² L. K. Doraiswamy,¹ and T. D. Wheelock¹*

**ABSTRACT**

Modern coal power plants that employ an IGCC system provide an efficient means for power generation. However, toxic and extremely corrosive sulfurous gases produced in a coal gasifier need to be removed from the hot gas prior to combustion in gas turbines. Due to stringent environmental laws, a regenerable sorbent that can remove the unwanted gases at high temperature (e.g., 1170 K) is preferred. In this work, composite sorbents consisting of a limestone core and a cement shell were prepared by pelletizing the powdered materials. In some cases limestone was also incorporated in the shell. The sorbents were characterized by measuring their crushing strength and their adsorption capacity when exposed to $\text{H}_2\text{S}$ gas at high temperature. Several different hydraulic cements were tested including Type I, Type III, and Type IV Portland cements and CA-14 calcium aluminate cement. Other factors investigated included the shell thickness, concentration of limestone in the shell, and pelletization time. The results showed that formulations containing high concentrations of limestone in the shell had higher absorption capacities but at the expense of pellet strength. Longer pelletization times improved pellet strength. The best overall results were achieved

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when CA-14 cement was incorporated in the shell. While a foundation was laid for sorbents based on the core-in-shell pellet concept, further development is essential and is underway.

Key words: Sorbent, calcium-based, hydrogen sulfide, coal gas, desulfurization, sulfurous gases

INTRODUCTION

The development of advanced integrated coal gasification combined-cycle (IGCC) power generating systems would benefit significantly by the development of a sorbent capable of removing $H_2S$ and COS from coal gas at near gasifier operating temperature which can be 1200 K or more. Among various materials that have been proposed for this service, limestone offers several advantages including low cost and widespread availability. Moreover, after limestone is calcined, the resulting CaO in theory can capture 95% or more of the sulfurous species in the product of coal gasification with steam and air at 20 atm when applied within a temperature range of 1070 to 1570 K (Westmoreland and Harrison, 1976). However, lime is soft and friable, and the spent sorbent in the form of CaS is not easily regenerated. Therefore, it has been widely regarded as a material to be used once and then discarded. Unfortunately, materials containing CaS cannot be placed directly in a landfill since they will react slowly with moisture and CO$_2$ under ambient conditions to form $H_2S$.

These problems are not insurmountable. The sorbent can be regenerated by a new process which converts CaS to CaO by alternately oxidizing and reducing the material (Jagtap and Wheelock, 1996; Wheelock, 1995, 1997, and 2000). This process is designed to produce SO$_2$ as a by-product for conversion into sulfuric acid or elemental sulfur. The poor
physical properties of lime may be overcome by combining lime with a stronger material to create a composite structure which retains the chemical reactivity of lime and the strength of the second material. Previous investigations have employed the following general methods for producing a calcium-based composite: (1) infusion of a strong inert porous substrate with a calcium compound (Synder et al., 1977; Yang and Shen 1979; Christoforou et al. 1995), (2) pelletization of a powder mixture followed by partial sintering (Voss, 1982; Kamphius et al. 1989; Zhang et al., 1989), and (3) a sol-gel technique (Wolff, 1991).

The development of a fourth method was undertaken recently and preliminary results are reported below. This method involves first pelletizing powdered limestone in a revolving drum and then coating the pellets with a hydraulic cement in the revolving drum. A layered structure is produced which combines the adsorptive properties of the lime core with the strength of the porous cement shell. This structure may minimize pellet spalling. The method has been demonstrated with both Portland and refractory cements and is the subject of a patent application (Wheelock and Akiti, 2000). Since the pellets are approximately 5 mm in diameter and can be even larger, they are best utilized in separate moving bed or fixed bed equipment located downstream from a coal gasifier.

The possibility of utilizing Portland cement in a high temperature sorbent for sulfurous gases was suggested by the work of Yoo and Steinberg (1983). These workers pelletized Type III Portland cement by itself, and after curing, relatively strong pellets were produced which were capable of absorbing moderate amounts of H$_2$S from simulated coal gas at 1273 K. Consequently, Portland cement seemed to be a good material for use in a composite structure with limestone since it might contribute to both the strength and adsorption capacity of the product.
The reaction believed responsible for the uptake of H$_2$S by Type III Portland cement is the following:

\[
(CaO)_3SiO_2(s) + 3H_2S(g) = (CaS)_3SiO_2(s) + 3H_2O(g) \tag{1}
\]

By comparison calcined limestone would react with H$_2$S as follows:

\[
CaO(s) + H_2S(g) = CaS(s) + H_2O \tag{2}
\]

While the thermodynamic equilibrium of the first reaction is unknown, the thermodynamic equilibrium of the second reaction was reported by Van der Ham et al. (1996) to be represented by the relation,

\[
\ln K = 0.0596 + \frac{7658}{T} \tag{3}
\]

where $K = \frac{P_{H_2O}}{P_{H_2S}}$ and $T$ is the absolute (Kelvin) temperature. According to this relation, if a typical hot coal gas containing 4000 ppmv H$_2$S and 5 mol % H$_2$O were treated with CaO under equilibrium conditions at 1150 K and 20 atm (2027 kPa), the H$_2$S content of the gas would be reduced to 60 ppmv which represents a reduction of 98.5%.

Several types of Portland cement and a calcium aluminate cement designed for high temperature applications were investigated as pellet coating materials. In some cases, limestone was also incorporated in the coating. Limestone pellets were prepared with the different coatings and then tested to determine their compressive strength and capacity for absorbing hydrogen sulfide. Pellets made entirely of Portland cement or limestone were also prepared and tested for comparison. Because of the preliminary nature of the investigation, only screening tests were applied to guide further development.
MATERIALS AND EXPERIMENTAL PROCEDURE

Limestone was obtained from the Three Rivers Quarry located near Smithland, Kentucky. According to the supplier, the material typically contains 92.8% CaCO₃, 5.9% MgCO₃, and 1.1% SiO₂ after drying at 278 K (105°C). Samples of several types of Portland cement were obtained from various manufacturers including Type I (Lafarge Corp.), Type III (Holnam Inc.), and Type IV (Armstrong Cement Corp.). The following designations are used to represent the cements: PC-I for Type I, PC-III for Type III, and PC-IV for Type IV. PC-I and PC-III consisted mostly of tricalcium silicate, whereas PC-IV had a higher content of dicalcium silicate. Since Portland cements are not made for high temperature applications, a sample of hydraulically setting refractory cement was also tested. This material was CA-14 calcium aluminate cement produced by Alcoa Industrial Materials. The material is serviceable at temperatures up to 2253 K (1980°C).

The pelletized sorbent was prepared with a small bench-scale drum pelletizer which had a diameter of 25 cm and could be operated at various speeds. The procedure involved placing a measured amount of pulverized limestone in the drum and then turning the drum at a fixed speed between 60 and 80 rpm. Deionized water was added as a fine spray at frequent intervals until small spherical pellets formed. The small pellets were grown larger by introducing more limestone while spraying the pellets with water. When the pellets reached a desired size, they were allowed to tumble for an additional time to improve their sphericity and uniformity. During this time the surface of the pellets was kept moist by occasionally spraying with water. The pellets were then separated into various sizes by hand screening with 5, 6, and 7 mesh screens. For coating the pellets, a batch of uniformly sized pellets was returned to the pelletizing drum, and while the drum was turned at a constant speed, a
measured quantity of cement powder was added gradually as the pellets were sprayed with water. In some cases before the cement was applied it was premixed with some dry potato starch (2 wt.%) to enhance the porosity of the cement after the pellets were heated to the temperature at which they would be used. Alternatively, a mixture of cement and powdered limestone was used for coating the limestone pellets, and no starch was employed. In either case the coated pellets were tumbled for 15 min., unless stated otherwise to consolidate the coating. Afterwards, the pellets coated with cement were air-dried at room temperature for 20 hr to improve their green strength, and then the pellets were cured for 3 days in a steam atmosphere at 373 K (100°C). In the case of pellets coated with a mixture of cement and limestone, the air-drying step was omitted because of their greater green strength, but the pellets were still steam cured.

The cured pellets were tested to determine their crushing strength and capacity for adsorbing H₂S. The crushing strength of a single pellet was determined by measuring the force required to break the 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 determination was repeated with five different pellets selected at random from each batch of pellets. This method produced consistent results which were sufficient for screening purposes and it was also similar to the method used by Deng and Lin (1997).

In most cases the absorption capacity of the pelletized material was determined by using a thermogravimetric analysis (TGA) system to measure the gain in weight over time of a single calcined pellet exposed to a dilute H₂S stream at a predetermined temperature. The pellet was placed in a quartz basket which was suspended in a vertical tubular reactor made of 25 mm diameter quartz tubing and surrounded by an electric furnace capable of
maintaining a constant temperature. The pellet weight was determined continuously with a Cahn model 2000 electrobalance which could weigh with an accuracy of 0.1 mg. The cured but uncalcined pellets ranged in weight from 40 to 120 mg and in diameter from 3.35 to 5.62 mm. During an absorption test the reactor was supplied with a gas mixture of known composition at a flow rate corresponding to 500 cm³/min. measured at room temperature and pressure. The mixture was prepared by combining high purity nitrogen and technical grade H₂S supplied through calibrated rotameters. Initially pure nitrogen was supplied to the reactor as a pellet was heated from room temperature to approximately 1150 K over a 1.0 hr period. After the temperature had stabilized, H₂S was added to the gas stream and the nitrogen flow rate was readjusted. In most cases a gas mixture comprised of 1.1% H₂S and 98.9% N₂ was supplied to the reactor where the sorbent was held at 1153 K (880°C) under atmospheric pressure.

**EXPERIMENTAL RESULTS**

In order to establish a baseline for comparison, several batches of pellets with sorbent properties were prepared initially by using only a single component, Portland cement or limestone. Homogeneous pellets were produced without an outer shell made of a different material. Each batch was made with either a different type of Portland cement or pulverized limestone which passed a 297 μm (50 mesh) screen. Each batch of pellets was tested to determine the compressive strength and absorption capacity of the material.

The ratio of the breaking force to pellet diameter as well as the 95% confidence limits are indicated in Table 1 for the steam-cured but uncalcined cement pellets and also for the pellets calcined at 1273°K (1000°C). This ratio which ranged from 22 to 53 N/mm for the
cured cement pellets and from 12 to 24 N/mm for the calcined pellets was quite high which suggests that the pellets would be durable. The limestone pellets, on the other hand, were very fragile. A statistical analysis showed that the pellets made with either Type III or Type IV Portland cement were significantly stronger than those made with Type I cement. The pellet diameter reported in Table 1 and succeeding tables corresponds to the size of the standard testing screen opening which was very close to the spherical pellet diameter.

The absorption capacity of the pellets was determined by first heating a single pellet in a stream of nitrogen in the TGA system to 1153 K (880°C), and then as the temperature was held constant, the gain in weight of the sorbent was measured over a 1.0 hr period as it was treated with a gas stream consisting of 1.1% H₂S and 98.9% N₂. It should be noted that as the cement pellets were being heated to 1153 K, they experienced a weight loss of about 15% between 373 and 553 K (100 and 280°C) due to the decomposition of hydrated calcium silicates. Also as the limestone pellets were heated, they suffered a weight loss of about 44% at approximately 970 K (697°C) due to the decomposition of the carbonate minerals. Based on these weight losses, the materials appeared to be fully calcined when treated with the dilute H₂S stream. To check the reproducibility of the TGA data, spherical limestone pellets, 3.96 mm in diameter, made from -297 μm (-50 mesh) particles were tested. After calcination for two hours under nitrogen, the pellets were allowed to react with 1.1% H₂S at 1153 K (880°C) for one hour. The results of four replicate runs are shown in Figure 1. The average gain in weight in 1.0 hr. was 21.60% with a standard deviation of 1.44%. The percent gain in weight of the other materials due to reaction with H₂S is shown in Table 1. It can be seen that the gain in weight of the different cements was only 3 to 6%, whereas the average gain in weight of the limestone was 21.6%. Therefore, it is apparent that the average
adsorption of $H_2S$ by lime over 1.0 hr. is much greater than that of Portland cement. Furthermore, the results achieved with limestone were reasonably reproducible.

Yoo and Steinberg (1983) suggested that reaction 1 is responsible for the gain in weight as Type III Portland cement reacts with $H_2S$. On the other hand, reaction 2 would be responsible for the gain in weight as lime reacts with $H_2S$. If it is assumed that Type III Portland cement is largely tricalcium silicate, it would experience a gain in weight of 22% as it becomes fully reacted. By comparison, lime would experience a gain in weight of 29%. Consequently, the weight gains reported in Table 1 indicate that the conversion of Type III Portland cement was much lower than the conversion of lime under similar conditions, and, therefore, Portland cement is a much less effective sorbent than lime. For lime, the actual conversion was 83% of the theoretical value. The observed differences between Portland cement and lime could have been due to differences in the porosity and accessibility of the solid reactants or differences in the reactivity of the material.

In order to combine the advantages of cement and lime into a single material, several batches of pellets were prepared where each pellet consisted of a limestone core and a cement shell. Each batch was made with a different type of Portland cement or CA-14 refractory cement. The limestone core was made by pelletizing pulverized limestone that passed a 297 μm (50 mesh) screen. In most cases the limestone core had a diameter of 3.96 mm while the finished pellet had a diameter of 4.76 mm. Hence, the shell thickness was 0.40 mm. The exception was a second batch of pellets made with Type IV Portland cement where the core diameter was 2.35 mm and the shell thickness was 0.50 mm. The important properties of the different batches of pellets are indicated in Table 2. It can be seen that the force required to break the steam-cured but uncalcined pellets was much lower than observed
for the solid cement pellets (see Table 1). On the other hand, the force required to break most of the pellets was 9 N/mm or more which could be adequate for some applications. Also the strength of the pellets coated with CA-14 refractory cement was similar to that of pellets coated with Portland cement. In fact, a statistical analysis showed that the force required to break the cured pellets coated with CA-14 cement did not differ significantly from the force required to break the pellets coated with Type IV Portland cement. After the pellets were heated and reacted with H₂S, small shell cracks were observed on the surface of pellets coated with Type I or Type IV Portland cement. Such cracks were not observed on the surface of pellets coated with Type III Portland cement or CA-14 refractory cement. Also the cracks were not observed on pellets which had a thicker coating of Type IV Portland cement. The cracks could have been due to thermal stress or changes in cement structure as it was dehydrated upon heating. As before, the absorption capacity of the different batches of pellets was determined by measuring the 1.0 hr gain in weight of the calcined pellets exposed to a stream of gas containing 1.1% H₂S in nitrogen at 1153 K (880°C). The results presented in Table 2 show that the gain in weight ranged from 9 to 14% for the cement-coated pellets which was considerably better than the 3 to 6% noted for the pellets made entirely of cement but not as good as the 22% noted for limestone pellets. However, there seemed to be a negative correlation between adsorption capacity and breaking force. Therefore, a higher absorption capacity was achieved at the expense of a lower pellet strength.

Pellets made entirely of Type I Portland cement and pellets with a limestone core and Type IV cement shell were selected for further testing. The former were chosen because they had the highest absorption capacity of the cement only formulations and the latter because
they had a high absorption capacity without sacrificing much pre-calcined crushing strength. The PC-I pellets were assumed to react according to equation (1), whereas the composite core-in-shell pellets were assumed to react according to both equations (1) and (2).

Typical TGA runs for the two sorbent formulations are shown in Figure 2. The two lines indicate the changes in weight of single pellets as they were heated first in a stream of nitrogen and then in a gas mixture containing 1.1% H₂S. The lower line is for a pellet made entirely of Type I Portland cement, whereas the upper line is for a pellet with a limestone core and a Type IV cement shell. As the temperature rose between 373 and 553 K (100 and 280°C) both pellets experienced a loss in weight due to dehydration of the hydrated Portland cements. At a much higher temperature (973 to 1123 K) (700 to 850°C), the composite pellet also lost weight due to decomposition of the limestone. After these losses the weight of both pellets remained constant while the temperature was stabilized and until H₂S was introduced in 1.1% concentration. As the materials reacted with H₂S at a constant 1153 K (880°C), the weight of each pellet increased proportionally. Over a 60 min. period the PC-I pellet gained 6% in weight while the composite pellet gained 11.5%.

A series of absorption tests was conducted with each of the sorbent formulations to determine the optimum temperature for reaction with H₂S. Figures 3 and 4 show that the rate of reaction of the sorbents with H₂S, as indicated by the slope of the curves, was a maximum at a temperature of 1233 K (960°C) for a PC-I pellet and at a temperature of 1273 K (1000°C) for a composite core-in-shell pellet. The rate of reaction was lower either above or below these temperatures. The decrease in the rate of reaction which occurred when the temperature was raised above the optimum level was due most likely to sintering of the
material. A comparison of the results also showed that for a given temperature, the rate of reaction and/or absorption was much higher for the composite pellet than for the PC-I pellet.

Another series of absorption tests was conducted to study the effect of H$_2$S concentration on the rate of reaction of the two sorbents. These tests were conducted at the optimum temperatures for the respective materials. The results presented in Figures 5 and 6 show that for either material the rate of reaction increased substantially when the H$_2$S concentration was increased from 1.10 to 2.10%.

In an attempt to increase the absorption capacity of the cement-coated pellets, several batches of pellets were produced in which powdered limestone was mixed with Type III Portland cement and used as a pellet coating material. Pellets were prepared with two different coating or shell thicknesses and various concentrations of limestone in the shell. The properties of the different pellets are shown in Table 3. It is very apparent that adding limestone to the shell increased the percent gain in weight of the calcined pellets treated with 1.1% H$_2$S at 1153 K (880°C) for 1.0 hr. Furthermore, the absorption capacity increased in proportion to the limestone concentration in the shell. On the other hand, the force required to break the cured but uncalcined pellets decreased noticeably when limestone was added to the shell. However, this effect was counterbalanced by making the shell thicker. Therefore, there is probably an optimum shell thickness and limestone concentration which may be on the order of 0.8 mm and 60%, respectively.

Because of the large absorption capacity but low compressive strength of pellets made with 80% limestone in the shell, further consideration was given to shell strengthening. It was subsequently found that control of the limestone particle size and an extended pelletization time improved shell strength. To study the effect of pelletization time, several
more batches of pellets were produced in which the time allotted for tumbling after the limestone pellets were coated with a mixture of cement and limestone particles was varied. The limestone pellets were prepared from -297/+210 μm size particles and were thoroughly consolidated by allowing them to tumble for 1.0 hr before applying a coating. During this time the pellets were kept moist by occasionally spraying them with water. For the coating, -297/+210 μm limestone particles were premixed with cement powder, and then the mixture was applied to the pellets as they were treated with a fine water spray in the pelletizing drum. The coating procedure required about 5 min. The coated pellets were then allowed to tumble for either 15, 60, or 120 min. The product was subsequently steam-cured for 3 days and tested. Type III Portland cement was used for some batches and CA-14 refractory cement for other batches. The prepared pellets were characterized as before, and the results are shown in Table 4. It is apparent that with either type of cement the force required to break the cured but uncalcined pellets increased with tumbling time. Also the breaking force was considerably greater for pellets coated with a mixture of Portland cement than with a mixture of CA-14 cement. On the other hand, after calcination the pellets coated with a mixture of Type III Portland cement were weaker than those coated with limestone and CA-14 cement. Furthermore, the pellets coated with a mixture of CA-14 cement remained intact during reaction with H₂S whereas those coated with a mixture of Type III cement tended to crack and fall apart. In addition, pellets coated with a mixture of CA-14 cement exhibited larger weight gains when reacted with H₂S.

A statistical analysis showed that the apparent absorption capacity of the different formulations was not affected significantly by increasing the tumbling time from 60 to 120 min. Also the breaking strength of the calcined pellets coated with a mixture of CA-14
cement was not affected significantly by increasing the tumbling time from 60 to 120 min. Therefore, the only benefit gained by increasing the tumbling time from 60 to 120 min. was an increase in the strength of the cured but uncalcined pellets.

While these results are highly encouraging because they demonstrate the feasibility of incorporating a weak but highly reactive material in a pellet core surrounded by a much stronger but less reactive shell, they must be regarded as very preliminary. Sorbent development is continuing based on the core-in-shell concept. In the future other promising materials will be utilized for the shell, and the resulting sorbents will be characterized more completely. Eventually the most promising sorbents will be subjected to attrition tests as well as compression tests and subjected to many loading and regeneration cycles.

CONCLUSIONS

The results of this study indicate that a composite material can be prepared from limestone and a hydraulic cement which has considerable promise as a sorbent for H$_2$S at high temperature. By applying the cement as a coating on limestone pellets, a product is produced which combines the high reactivity of lime with the strength of cement in a novel core-in-shell configuration. The coating can be made almost entirely of cement or of a mixture of cement and limestone particles. Although the addition of limestone particles to the coating tends to weaken the compressive strength of the final product, it increases the absorption capacity of the material. In addition to the relative concentrations of cement and limestone in the coating, other important parameters are the coating thickness, the type of cement, and the time provided in the pelletizer for strengthening the coating. The best overall results were achieved with a coating of CA-14 refractory cement and limestone.
particles, which was strengthened by 1.0 hr. of tumbling. While pellets with a coating of Portland cement were very strong initially, they tended to break apart when heated and reacted with H$_2$S. This work has laid the foundation for further development of sorbents based on the core-in-shell concept.

ACKNOWLEDGEMENT

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REFERENCES


Table 1. Breaking force and adsorption capacity of various pelletized materials.

<table>
<thead>
<tr>
<th>Sorbent material</th>
<th>Pellet diameter (mm)</th>
<th>Force/diameter (N/mm)</th>
<th>Weight gaina (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cured</td>
<td>Calcined</td>
</tr>
<tr>
<td>PC-I</td>
<td>3.35</td>
<td>22 ± 6</td>
<td>12 ± 5</td>
</tr>
<tr>
<td>PC-III</td>
<td>3.35</td>
<td>52 ± 9</td>
<td>22 ± 6</td>
</tr>
<tr>
<td>PC-IV</td>
<td>3.35</td>
<td>53 ± 6</td>
<td>24 ± 4</td>
</tr>
<tr>
<td>Limestone</td>
<td>3.96</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

aIn presence of 1.1% H2S at 1153°K for 1 hr

Table 2. Breaking force and adsorption capacity of cement-coated limestone pellets.

<table>
<thead>
<tr>
<th>Coating material</th>
<th>Shell thickness (mm)</th>
<th>Pellet diameter (mm)</th>
<th>Force/diameter (N/mm)</th>
<th>Weight gaina (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-I</td>
<td>0.40</td>
<td>4.76</td>
<td>1.8 ± 0.5</td>
<td>13.8</td>
<td>Shell cracks</td>
</tr>
<tr>
<td>PC-III</td>
<td>0.40</td>
<td>4.76</td>
<td>12.8 ± 1.7</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>PC-IV</td>
<td>0.40</td>
<td>4.76</td>
<td>9.3 ± 1.7</td>
<td>9.2</td>
<td>Shell cracks</td>
</tr>
<tr>
<td>PC-IVb</td>
<td>0.50</td>
<td>3.35</td>
<td>13.8</td>
<td>10.1</td>
<td></td>
</tr>
<tr>
<td>CA-14</td>
<td>0.40</td>
<td>4.76</td>
<td>10.9 ± 1.8</td>
<td>8.9</td>
<td></td>
</tr>
</tbody>
</table>

aIn presence of 1.1% H2S at 1153°K for 1 hr.
bLimestone core contained 2% starch.
Table 3. Breaking force and adsorption capacity of limestone pellets coated with a mixture of limestone and Type III Portland cement. The concentration of limestone in the coating is indicated.

<table>
<thead>
<tr>
<th>Pellet diameter (mm)</th>
<th>Coating Thickness (mm)</th>
<th>Concentration (%)</th>
<th>Force/diameter, (N/mm)</th>
<th>Weight gain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.76</td>
<td>0.40</td>
<td>0</td>
<td>12.8 ± 1.7</td>
<td>10.3</td>
</tr>
<tr>
<td>4.76</td>
<td>0.40</td>
<td>20</td>
<td>7.8 ± 6.5</td>
<td>11.2</td>
</tr>
<tr>
<td>4.76</td>
<td>0.40</td>
<td>40</td>
<td>8.9 ± 4.6</td>
<td>13.0</td>
</tr>
<tr>
<td>4.76</td>
<td>0.40</td>
<td>80</td>
<td>5.8 ± 1.4</td>
<td>20.7</td>
</tr>
<tr>
<td>5.60</td>
<td>0.83</td>
<td>20</td>
<td>9.8 ± 1.5</td>
<td>8.6</td>
</tr>
<tr>
<td>5.60</td>
<td>0.83</td>
<td>40</td>
<td>11.1 ± 1.7</td>
<td>11.3</td>
</tr>
<tr>
<td>5.60</td>
<td>0.83</td>
<td>60</td>
<td>12.5 ± 2.5</td>
<td>13.0</td>
</tr>
<tr>
<td>5.60</td>
<td>0.83</td>
<td>80</td>
<td>5.2 ± 1.1</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Table 4. Breaking force and adsorption capacity of limestone pellets coated with a mixture of 80% limestone and 20% cement.

<table>
<thead>
<tr>
<th>Pellet coating Cement</th>
<th>Thickness (mm) 0.40</th>
<th>Pellet diameter (mm) 4.76</th>
<th>Tumbling Time (min.)</th>
<th>Force/diameter (N/mm) Cured 5.8 ± 1.4</th>
<th>Weight gain a (%)</th>
<th>Calcined &lt;1</th>
<th>16.0 ± 2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC-III</td>
<td>0.40</td>
<td>4.76</td>
<td>15</td>
<td>5.8 ± 1.4</td>
<td>&lt;1</td>
<td>16.0 ± 2.5</td>
<td></td>
</tr>
<tr>
<td>PC-III</td>
<td>0.40</td>
<td>4.76</td>
<td>60</td>
<td>16.1 ± 2.2</td>
<td>&lt;1</td>
<td>9.9 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>PC-III</td>
<td>0.40</td>
<td>4.76</td>
<td>120</td>
<td>18.7 ± 4.9</td>
<td>&lt;1</td>
<td>8.3 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>CA-14</td>
<td>0.40</td>
<td>4.76</td>
<td>15</td>
<td>4.8 ± 0.2</td>
<td>1.5 ± 0.2</td>
<td>17.5 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>CA-14</td>
<td>0.40</td>
<td>4.76</td>
<td>60</td>
<td>7.6 ± 1.6</td>
<td>2.6 ± 0.4</td>
<td>14.1 ± 1.3</td>
<td></td>
</tr>
<tr>
<td>CA-14</td>
<td>0.40</td>
<td>4.76</td>
<td>120</td>
<td>12.1 ± 1.9</td>
<td>2.1 ± 0.4</td>
<td>13.7 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>CA-14</td>
<td>0.83</td>
<td>5.62</td>
<td>120</td>
<td>20.7 ± 1.4</td>
<td>2.5 ± 0.3</td>
<td>11.4 ± 1.0</td>
<td></td>
</tr>
</tbody>
</table>

*a* In presence of 1.1% H₂S at 1153°K for 1 hr
Figure 1. Results of four adsorption tests conducted with limestone pellets under similar conditions: 3.96 mm diameter, 1.1% H₂S and 1153°K
Figure 2. Typical TGA runs made with single pellets made with different formulations.
Figure 3. Effect of temperature on the rate of adsorption of PC-I pellets treated with 1.1% H₂S
Figure 4. Effect of temperature on the rate of adsorption of core-in-shell pellets treated with 1.1% H₂S
Figure 5. Effect of H$_2$S concentration on rate of adsorption of PC-I pellets at 1233 K.
Figure 6. Effect of H$_2$S concentration on rate of adsorption of core-in-shell pellets at 1273 K.
CHAPTER 5. AN IMPROVED CORE-IN-SHELL SORBENT FOR DESULFURIZING HOT COAL GAS

A paper accepted by Advances in Environmental Research

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ABSTRACT

Work on an advanced calcium-based sorbent for desulfurizing hot coal gas has led to the development of a unique material in the form of spherical pellets which have a limestone-based core encased in a strong supporting shell. Strong pellets are made by incorporating some calcium aluminate cement in the core and a larger amount in the shell together with limestone. The pellets are prepared by a two step pelletizing method followed by steam curing and heat treatment. The pellets are capable of absorbing relatively large amounts of hydrogen sulfide at high temperature (e.g., 1150 – 1200 K) and can be regenerated by a cyclic oxidation and reduction process.

Key words: Sorbent, calcium-based, hydrogen sulfide, coal gas, desulfurization, sulfurous gases, limestone, calcium aluminate cement

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INTRODUCTION

Although various materials have been proposed for desulfurizing hot coal gas, there is a continuing need for an efficient sorbent which is also reusable and inexpensive. Such a material is needed specifically for hot gas cleanup in new integrated coal gasification, combined-cycle (IGCC) power systems (1). A broad survey of potential sorbent materials has been provided by Van der Ham, et al., (2). Recently a very promising zinc-based sorbent became commercially available but its use is limited to temperatures in the range of 260 to 600°C (3). Above this range of temperature, calcium-based materials seem to offer the most promise for the least cost (2,4,5).

An unusual calcium-based sorbent was prepared recently by pelleting powdered limestone and then applying a coating of cement and limestone to the pellets (6,7). Various hydraulically setting cements were investigated for this application including different types of Portland cement and a calcium aluminate cement. The coatings were strengthened by extended tumbling in a drum pelletizer followed by steam curing to hydrate the calcium silicates and aluminates. In this way spherical pellets were made with a highly reactive core encased in a stronger supporting shell. However, when the core-in-shell pellets were heated to temperatures that would be employed in coal gas cleanup, there was a marked decline in pellet crushing strength, more so for pellets coated with Portland cement than for pellets coated with the calcium aluminate cement. On the other hand, the coated pellets displayed a strong affinity for $\text{H}_2\text{S}$ at high temperature due to the following reaction:

$$\text{CaO}_\text{(s)} + \text{H}_2\text{S}_\text{(g)} = \text{CaS}_\text{(s)} + \text{H}_2\text{O}_\text{(g)}$$ (1)
The thermodynamic equilibrium of this reaction is such that 95% or more of the H$_2$S in a typical coal gas should be captured within a temperature range of 1070 to 1570 K, providing that the reaction kinetics are not a controlling factor (5).

The present work was undertaken for the purpose of improving the properties of the core-in-shell sorbent pellets by investigating the effects of different preparation conditions on the compressive strength and apparent absorption capacity of the material. The calcium aluminate cement which had provided the best results previously was chosen as a strengthening material. The effects of curing time, shell composition, and shell thickness were investigated. The material representing the best compromise between crushing strength and absorption capacity was characterized more completely by measuring various properties of the material and by subjecting samples to repeated loading and regeneration. Regeneration was accomplished by treating the loaded sorbent with a cyclic oxidation and reduction process which converts CaS to CaO by means of the following two reaction steps (8-10):

\[
\text{CaS} (s) + 2\text{O}_2 (g) = \text{CaSO}_4 (s)
\]  
\[
\text{CaSO}_4 (s) + \text{CO} (g) = \text{CaO} (s) + \text{CO}_2 (g) + \text{SO}_2 (g)
\]

**EXPERIMENTAL**

The limestone used for preparing sorbent pellets was obtained from the Three Rivers Quarry located near Smithland, Kentucky. The dried material typically contains 92.8% CaCO$_3$, 5.9% MgCO$_3$, and 1.1% SiO$_2$, according to the supplier. The limestone was ground and screened to provide particles between 210 and 297 μm for pelletization. The other principal ingredient of the pellets was type CA-14 calcium aluminate cement supplied by
Alcoa Industrial Materials. This material is a lime-free hydraulically setting cement designed for high temperature refractory applications. The material has a particle size distribution such that 90% of the particles by weight are smaller than 60 \( \mu \)m and 50% smaller than 9 \( \mu \)m.

The core-in-shell pellets were prepared in two stages. First the pellet cores were prepared by placing a known quantity of dry limestone and cement particles in a pelletizing drum having a diameter of 25 cm, and as the drum revolved at a fixed speed between 60 and 80 rpm, deionized water was applied as a fine spray at frequent intervals. The material balled up rapidly into small seed pellets which were subsequently removed and separated with a 16 mesh screen (i.e., a screen with 1.19 mm openings). The pellets retained on the screen were returned to the pelletizing drum and were grown larger by introducing more limestone or a mixture of limestone and cement while applying a water spray. When the pellets reached a desired size, they were allowed to tumble for 1.0 hr to improve their sphericity and uniformity. During this time the surface of the pellets was kept moist by spraying the pellets occasionally. The pellets were subsequently screened carefully, and the pellets between 3.96 and 4.76 mm were returned to the pelletizer drum for coating in a second stage. The coating was applied by adding a mixture of limestone and cement particles to the tumbling pellets and by applying a fine water spray as needed. While the pellets were completely coated within a few minutes, they were kept in the revolving drum for 2.0 hr to improve their physical strength and uniformity. During this time a fine water spray was applied at 6 – 8 min. intervals to keep the pellets moist. Afterwards the pellets were screened again, and the 5.83 \( \times \) 4.76 mm and 6.68 \( \times \) 5.63 mm sizes were selected for testing. These pellets were generally air-dried for one day and then steam cured at 373 K for up to three days to complete the hydration of the calcium aluminates. Usually some of the cured pellets were set
aside for various physical tests while the others were calcined at 1273 K for 2.0 hr before testing.

The crushing strength of the prepared pellets was determined by measuring the force required to break 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 employed by Deng and Lin (11). Each determination was repeated with five different pellets selected at random from each batch of pellets. This method produced consistent results which were considered adequate for initial screening purposes and for statistical inference. Attrition testing was reserved for a later stage of development.

Generally the absorption capacity of a material was determined by using a thermogravimetric analysis (TGA) system to measure the gain in weight over time of a single calcined pellet of the material exposed to a dilute H₂S stream (typically, 1.1 vol.% H₂S and 98.9 vol.% N₂) at a predetermined temperature. The pellet was suspended in a quartz basket from a Cahn model 2000 electrobalance which could weigh the pellet continuously with an accuracy of 0.1 mg. The basket was contained within a vertical tubular reactor made of 25 mm diameter quartz tubing which was surrounded by an electric furnace capable of maintaining a constant temperature. The reactor was supplied with a gas mixture of known composition at a flow rate of 500 cm³/min. measured at room temperature and pressure.

In some cases the electrobalance was not employed, and the gain in weight of a sorbent was determined by measuring the weight of the material with a sensitive analytical balance before and after exposure to a dilute H₂S stream for 1.0 hr in the same manner as described above. In using this method, three sorbent pellets were suspended separately in quartz
baskets inside the same vertical tubular reactor which was operated as before without monitoring weight change during the run.

To regenerate a sorbent pellet after it had been largely converted to CaS in the TGA apparatus, the temperature of the system was generally raised to a higher level as pure nitrogen was passed through the system. When this temperature was reached, the pellet was subjected to a cyclic oxidation and reduction process (8) in which the material was alternately treated with 20 vol.% O₂ for oxidation via reaction 2 and 30 vol.% CO for reduction via reaction 3. In each case, nitrogen made up the balance of the gas mixture. Each phase of the cycle lasted from 1 to 3 min., and the cycle was repeated until the sorbent lost all of the weight gained during loading, showing that all of the CaS formed during loading had been converted back to CaO.

The open pore volume and apparent porosity of the prepared sorbent pellets were determined by application of a combination of gas pycnometry and Archimedes principle. Gas pycnometry provided a measure of the volume of actual solid material in a sample, while weighing a dry sample in air and then weighing the sample submerged in water in a fully saturated state provided a measure of the combined volume of closed pores and solid material.

The specific surface area of an individual pellet was determined with a Quantachrome Autosorb 1 surface area analyzer. The BET method was employed with nitrogen as the adsorbate at liquid nitrogen temperature (77 K).
RESULTS AND DISCUSSION

Early in the development of an improved sorbent material based on the core-in-shell pellet structure it was discovered that the shell tended to develop small cracks if the core was made entirely of limestone or the shell was made entirely of a calcium aluminate cement. The cracking tendency was overcome by adding cement to the core and limestone to the shell. For example, cracking was avoided when the core contained 20 wt.% calcium aluminate cement and the shell contained 60 wt.% limestone. To investigate the importance of shell composition further, pellets were produced with 40, 60 and 80 wt.% limestone in the shell while holding the limestone content of the core at 80 wt.%. Half the pellets were made with a shell thickness of approximately 0.40 mm and half with a shell thickness of approximately 0.83 mm. Since the pellet core diameter was 3.96 mm in both cases, the overall pellet diameter was 4.76 mm in the first case and 5.63 mm in the second case. The pellets were steam cured for three days and then calcined at 1273 K for 2.0 hr.

The crushing strength of the pellets before and after calcination and the apparent absorption capacity of the calcined pellets are indicated in Table 1. The crushing strength is reported as the ratio of the force required to break a single pellet to the pellet diameter. Also reported are the 95% confidence limits based on five determinations in each case. The apparent absorption capacity is reported as the percent gain in weight of three pellets over a 1.0 hr period when the pellets were treated at 1153 K with a stream of gas containing 1.1 vol.% H₂S.

It can be seen that the force required to break the calcined pellets was much less than that required to break the cured but otherwise untreated pellets (Table 1). The decrease in breaking force was probably due in part to dehydration of the calcium aluminate cement.
since it is known that the hydraulic bond in calcium aluminate cements breaks down in the range of 1073 to 1273 K (12). It was also probably due in part to decomposition of the limestone which would have taken place in this range of temperature. Furthermore, the breaking force decreased markedly as the limestone concentration of the shell rose. This effect was statistically significant for both the cured and calcined pellets. The effect of shell thickness was less pronounced. While it appeared that the breaking force increased with shell thickness for both cured and calcined pellets, the effect was highly significant for the cured pellets but only marginally significant for the calcined pellets. Furthermore, pellet strength was affected by a significant interaction between shell composition and thickness in the case of cured pellets but not calcined pellets. Consequently, the relative difference in pellet strength increased as the limestone content of the shell was reduced in the case of cured pellets.

It can also be seen that the absorption capacity of the pellets increased markedly as the initial limestone content of the shell rose (Table 1). The effect of shell thickness on absorption capacity seemed to be due largely to a significant interaction between shell composition and thickness. It is noteworthy that the overall lime content of the pellets was higher for the pellets with the thinner shell.

The preceding results indicated that the pellets with the thinner shell made with 60 wt.% limestone offered the best compromise between crushing strength and absorption capacity. Therefore, this pellet formulation was selected for the more complete characterization which follows.

To study the microstructure of core-in-shell pellets made with the selected formulation, several were cross-sectioned before and after calcination and reaction with H$_2$S and then
examined with a scanning electron microscope. Figure 1 is a photomicrograph of a pellet after it had been calcined and then reacted at 1153 K with 1.1 vol.% H₂S for 1.0 hr. The pellet was approximately 4.6 mm in diameter. The lighter core and darker shell are easily distinguished, and it is evident that the microstructure of the two regions differed. Less easily discerned is the pellet nucleus or initial seed pellet which was about 1.2 mm in diameter. The microstructure of the region immediately surrounding the nucleus appears more porous than that of other regions, and several large voids can be seen along the boundary between the core and shell.

To determine the effect of steam curing time on pellet compressive strength, a number of pellets were prepared with the selected formulation. Different pellets were then subjected to different curing times ranging from 0 to 72 hr. Some of the cured pellets were tested directly while others were tested after being calcined at 1273 K for 2 hr. Pellets which had been steam cured but not calcined developed a maximum compressive strength after only 8 hr of curing, whereas pellets which had been cured and calcined continued to gain strength as the curing time was prolonged for up to 72 hr (see Figure 2). However, any additional gain in strength achieved by extending the curing time from 24 to 72 hr was not statistically significant. Figure 2 indicates the effect of curing time on the ratio of the force required to break a single pellet to the pellet cross-sectional area and each point is an average of five determinations.

To more fully characterize the core-in-shell pellets, five more batches were prepared with the selected formulation. After the pellets had been steam cured for three days and then calcined at 1273 K for 2.0 hr in air, they were characterized by various methods and the results are indicated in Table 2. The pellets had a shell thickness of 0.4 mm and an outside
diameter of 4.76 mm based on screen size and confirmed by direct measurement with a pair of calipers. The compressive strength is reported both as the breaking force per unit diameter and the breaking pressure based on the pellet cross-sectional area. The breaking force is an average for five different batches and five determinations per batch. After curing the average breaking force was 33.2 N/mm, whereas after both curing and calcining it was 11.5 N/mm. Again the decrease in pellet strength was probably due to a combination of dehydration and decomposition. These results are believed to be more reliable than those reported in Table 1 which were based on only a single batch of pellets for each different shell composition. Although the crushing strength of the pellets was greatly reduced by the heat treatment, the force required to break the calcined pellets was still greater than 8.9 N/mm which is regarded as the lower limit for fixed bed applications (13). Other pellet properties were affected much less by the heat treatment, although calcining did cause the apparent porosity to rise and the surface area to fall. These effects were probably due to the evolution of carbon dioxide and the conversion of smaller pores into larger pores by sintering.

When several of the calcined pellets were treated at 1153 K for 1.0 hr with a gas stream containing 1.1 vol.% H₂S, the pellets experienced an average gain in weight of 7.8% which was 58% of the theoretically possible gain in weight of 13.5%. The theoretical value is based on the assumption that the gain in weight would be due entirely to reaction 1 and, therefore, neglects any gain in weight which might occur because of the reaction of H₂S with MgO derived from the limestone or with the calcium aluminate cement.

To compare the relative rate of absorption or reaction of a core-in-shell pellet having the selected formulation with that of other types of pellets, a series of absorption tests was conducted with the TGA apparatus. The different types of pellets included a core-in-shell
pellet, a pellet made entirely of limestone, a pellet made entirely of calcium aluminate cement, and a pellet made with 80 wt.% limestone and 20 wt.% cement. The last one represented the uncoated core of a core-in-shell pellet. All of the pellets except the core-in-shell pellet had an overall diameter of 3.96 mm. The core-in-shell pellet had an overall diameter of 4.76 mm and shell thickness of 0.4 mm. Except for the all limestone pellet, the pellets were steam cured for three days. The pellets were subsequently calcined at 1273 K and then treated at 1153 K with 1.1 vol.% H₂S in the TGA apparatus. The relative rate of reaction of H₂S with the different materials can be inferred from the data presented in Figure 3. It is apparent that the pellet made entirely of limestone reacted most rapidly, and that the rate of reaction declined as the initial limestone content of the pellets was reduced. It is also apparent that the pellet made entirely of calcium aluminate cement reacted slowly. Since this material contained an insignificant amount of free lime according to the manufacturer, the results suggest that the cement is capable of reacting with H₂S to some extent.

To determine the reproducibility of such tests and to determine the effects of temperature and gas concentration on the apparent rate of conversion of core-in-shell pellets, additional absorption tests were conducted with the TGA apparatus using pellets prepared with the selected formulation. The 4.76 mm diameter pellets were steam cured for three days and calcined at 1273 K for 2 hr before testing. Two runs made under similar conditions of treatment with 3.0 vol.% H₂S at 1153 K produced nearly identical results (see Figure 4). Therefore, the results were highly reproducible. While it appears that the ultimate gain in weight of the pellets exceeded the theoretical maximum possible gain in weight, the latter is based on the assumption that only reaction 1 takes place which clearly is not the case.
The results of other absorption tests conducted with core-in-shell pellets at 1153 K indicate the effect of H$_2$S concentration on the apparent rate of conversion (see Figure 5). Since for a given H$_2$S concentration the rate of conversion is proportional to the slope of the corresponding curve in Figure 5, it is apparent that rate of conversion increased with increasing H$_2$S concentration. This effect is seen clearly in Figure 6 which shows that the initial rate of conversion was directly proportional to H$_2$S concentration. This figure suggests that the intrinsic rate of the reaction represented by equation 1 is first order with respect to H$_2$S concentration which is in general agreement with results reported by Abbasian (4).

To determine the effect of temperature on the apparent rate of conversion, other absorption tests were conducted with core-in-shell pellets at different temperatures using 1.1 vol.% H$_2$S in the treatment gas. The results presented in Figure 7 indicate that the highest rate of absorption over 60 min. was observed at 1193 K. Either higher or lower temperatures produced a lower rate of adsorption.

To determine how well the core-in-shell sorbent can be regenerated after it has been largely converted to CaS, several experiments were conducted in which individual pellets were first loaded by reaction with H$_2$S and then regenerated by cyclic oxidation and reduction. The process of loading and regeneration was carried out with the TGA apparatus, and it was usually repeated several times with each pellet. Typical results are shown in Figure 8 for a pellet which was subjected to ten cycles of loading and regeneration. In this case the pellet was loaded at 1193 K by reaction with an H$_2$S/N$_2$ gas mixture containing 3 vol.% H$_2$S. A loading time of 20 min. was employed in each cycle. After loading, the pellet was surrounded by pure nitrogen and the temperature was raised to 1323 K for regeneration. During regeneration the pellet was alternately oxidized with 20 vol.% O$_2$ and
reduced with 30 vol.% CO until nearly all of the weight gained during loading was lost. For the first four cycles of loading and regeneration, a regeneration cycle consisted of 1.0 min. of oxidation and 1.0 min. of reduction. These times were extended to 3.0 min. for oxidation and 3.0 min. for reduction in subsequent loading and regeneration cycles. The results show that after each loading, the sorbent was subsequently fully regenerated except for two cycles where regeneration was discontinued prematurely. Although regeneration was not a problem, it can be seen that the sorbent gained less and less weight from cycle to cycle which indicated a decline in reactivity that may have been due to sintering. By the tenth cycle the sorbent loading was only 39% of what it had been in the first cycle. To compensate for the loss in reactivity, the loading time could have been extended from cycle to cycle.

Improving the high temperature stability of the sorbent material and thereby extending the useful life of the sorbent is a remaining problem which will continue to be addressed. A promising avenue for exploration is the elimination of impurities which are known to promote sintering of the primary materials. Another possibility is to reduce the regeneration temperature. Both of these remedies are indicated by previous work which showed that the sintering rate of CaO derived from impure limestone was much greater than the sintering rate of pure CaO and that the sintering rate of CaO increases rapidly with temperature (14).

CONCLUSIONS

The development of a reusable calcium-based sorbent for desulfurizing hot coal gas was advanced by improving the properties of a pelletized sorbent in the form of small spherical pellets. Each pellet had a limestone-based core encased in a supporting shell made from both limestone and calcium aluminate cement. The best overall results were achieved
by incorporating 20 wt.% cement in the core and 40 wt.% cement in the shell and by making the shell relatively thin (i.e., 0.4 mm thick). The resulting pellets appeared to have adequate crushing strength and absorption capacity. Increasing the cement content of the shell produced stronger pellets but at the expense of reduced absorption capacity. Reducing the cement content had the opposite effect. The initial rate of reaction of the sorbent appeared to be first order with respect to H$_2$S concentration. The maximum rate of reaction was observed at 1193 K. After the pellets were loaded by reaction with H$_2$S, they were readily regenerated by a cyclic oxidation and reduction process. However, repeated loading and regeneration of the sorbent resulted in a gradual loss of reactivity which was probably due to sintering. Improving the high temperature stability of the material will be addressed in the future.

ACKNOWLEDGEMENT

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REFERENCES


Table 1. Properties of core-in-shell pellets made with different concentrations of Kentucky limestone in the shell. Results of replicated tests with 95% confidence intervals.

<table>
<thead>
<tr>
<th>Diameter, mm</th>
<th>Shell Thick., mm</th>
<th>Limestone conc., wt.%</th>
<th>Breaking force, N/mm</th>
<th>Wt. gain, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cured</td>
<td>Calcined</td>
</tr>
<tr>
<td>4.76</td>
<td>0.40</td>
<td>40</td>
<td>47.5 ± 5.7</td>
<td>18.8 ± 3.5</td>
</tr>
<tr>
<td>4.76</td>
<td>0.40</td>
<td>60</td>
<td>26.7 ± 2.6</td>
<td>12.9 ± 0.5</td>
</tr>
<tr>
<td>4.76</td>
<td>0.40</td>
<td>80</td>
<td>7.5 ± 1.6</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>5.60</td>
<td>0.83</td>
<td>40</td>
<td>55.0 ± 6.7</td>
<td>20.1 ± 1.1</td>
</tr>
<tr>
<td>5.60</td>
<td>0.83</td>
<td>60</td>
<td>33.4 ± 7.0</td>
<td>13.2 ± 6.1</td>
</tr>
<tr>
<td>5.60</td>
<td>0.83</td>
<td>80</td>
<td>8.1 ± 1.8</td>
<td>2.5 ± 0.2</td>
</tr>
</tbody>
</table>

*Treated with 1.1% H₂S at 1153K for 1.0 hr.

Table 2. Properties of core-in-shell pellets with 80 wt.% limestone in the core and 60 wt.% limestone in the shell. Results of replicated tests with 95% confidence intervals.

<table>
<thead>
<tr>
<th>Property</th>
<th>Cured</th>
<th>Calcined</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breaking force, N/mm</td>
<td>33.2 ± 3.5</td>
<td>11.5 ± 1.0</td>
</tr>
<tr>
<td>Breaking pressure, kPa</td>
<td>8470 ± 1100</td>
<td>3070 ± 260</td>
</tr>
<tr>
<td>Breaking pressure, lb/in²</td>
<td>1230 ± 160</td>
<td>445 ± 38</td>
</tr>
<tr>
<td>Pore volume, cm³/g</td>
<td>0.59 ± 0.02</td>
<td>0.61 ± 0.02</td>
</tr>
<tr>
<td>Apparent porosity, %</td>
<td>48.0 ± 1.9</td>
<td>65.5 ± 3.1</td>
</tr>
<tr>
<td>Surface area, m²/g</td>
<td>8.2 ± 2.2</td>
<td>6.7 ± 1.8</td>
</tr>
<tr>
<td>Theoretical maximum weight gain, %</td>
<td>---</td>
<td>13.5 ± 0.7</td>
</tr>
<tr>
<td>*Actual weight gain, %</td>
<td>---</td>
<td>7.8 ± 0.6</td>
</tr>
</tbody>
</table>

*Treated with 1.1% H₂S at 1153K for 1.0 hr.
Figure 1. Cross-section of a core-in-shell pellet after calcination and reaction with H$_2$S.
Figure 2. Effect of curing time on the breaking pressure of calcined core-in-shell pellets made with 80 wt.% limestone in the core and 60 wt.% limestone in the shell.
Figure 3. A comparison of the relative rates of reaction of different pelletized materials with 1.1 vol.% H₂S at 1153 K.
Figure 4. The gain in weight of a core-in-shell sorbent exposed to a gas stream containing 3% H₂S at 1153 K.
Figure 5. Effect of $\text{H}_2\text{S}$ concentration on the rate of gain in weight of the core-in-shell sorbent at 1153 K.
Figure 6. Effect of $\text{H}_2\text{S}$ concentration on the initial rate of conversion of core-in-shell pellets at 1153 K.
Figure 7. Effect of temperature on the rate of gain in weight of the core-in-shell sorbent treated with 1.1% \( \text{H}_2 \text{S} \).
Figure 8. Results of repeated loading and regeneration of a core-in-shell pellet with regeneration conducted at 1323 K.
CHAPTER 6. A REGENERABLE LIME-ALUMINA CORE-IN-SHELL SORBENT FOR HIGH TEMPERATURE H₂S REMOVAL

A paper to be submitted to Industrial and Engineering Chemistry Research

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Abstract

A novel core-in-shell pellet structure was achieved while fabricating lime-alumina based sorbents for hot gas desulfurization (HGD). A suitable shell formulation was developed by combining ultrafine alumina powder with coarser alumina powder and some limestone. The cores were made starting with either limestone (CaCO₃) or calcium sulfate hemihydrate (CaSO₄·0.5H₂O). Several sorbents with varying core composition and shell thickness were made and tested for crushing strength and H₂S absorption capacity.

Absorption tests were performed at temperatures ranging from 840 - 960°C with 1.1- 3.0 % H₂S in nitrogen. Regeneration was performed via a cyclic oxidation and reduction procedure at 1050°C. Pellet strength was found to increase sharply with fractional shell volume while the absorption capacity decreased sharply. The most promising formulation was calcium sulfate hemihydrate-based, as it showed no signs of deactivation during a 10-cycle absorption and regeneration test.

Keywords: Sorbent, calcium-based, core-in-shell, desulfurization, pelletization, regenerable, synthetic

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Introduction

Modern power plants that employ an integrated coal gasification combined-cycle (IGCC) system provide an efficient means of generating electrical power. However, gaseous contaminants, mainly H₂S, need to be reduced to less than 100 ppm before the coal gas enters a gas turbine.⁷ To maximize the efficiency of an IGCC power cycle, a sorbent material capable of removing these contaminants at gasifier exit conditions (≈ 900°C) is needed.¹¹ Although now used for hot gas cleanup, zinc-based sorbents such as Zsorb® have an operating temperature limit of approximately 650°C.⁷ In addition, zinc-based sorbents are expensive. Therefore, an inexpensive material able to operate at higher temperatures is needed.

Lime (CaO) which is derived by the decomposition of limestone (CaCO₃) or calcium sulfate (CaSO₄) is an excellent sorbent for hot gas cleanup at the exit conditions of most coal gasifiers. However, in order to employ lime as a regenerable sorbent, it needs to be strengthened to reduce its friability. Structural modifiers such as alumina have been used to try and achieve this. Snyder et al.¹² introduced CaO into porous alumina pellets by refluxing the substrate in a calcium nitrate solution. By this method up to 15% CaO was impregnated in the carrier. Duisterwinkel⁶ used a different method to arrive at a similar product. In his work the alumina and CaO were combined in-situ by using a sol-gel technique. A sorbent formulation that contained approximately 6% Ca was produced. Although sorbents fabricated using these two methods produce extremely strong pellets, the preparation methods are expensive, and the sorbents are more costly than the disposable type.¹⁵

Pelletization provides a cheaper means for manufacturing a sorbent. The traditional sorbent pellet preparation method involves pelleting a mixture of CaO and a binder.¹⁰,¹⁴
Akiti et al.\textsuperscript{1} introduced an alternative pellet configuration where the reactive sorbent material is incased in a strong shell that is made up of a binder material. In their investigation different hydraulic cements were used as shell materials. They found that, although the cement shells were extremely strong after curing in a moist atmosphere at low temperature, when fired to temperatures in excess of 1000°C most of this strength was lost. Wheelock and Akiti\textsuperscript{14} found that in order to manufacture a good cement-based core-in-shell sorbent, some of the binding material had to be incorporated into the core and some of the sorbent material had to be incorporated into the shell. This was necessary to avoid cracking of the pellets upon calcination. Hence, they arrived at a compromise that consisted of a semi-reactive core and a semi-reactive shell. The ideal core-in-shell sorbent, however, would consist of a reactive core and an inert shell. This would prevent the shell from undergoing drastic structural changes, which may cause the sorbent to spall, crack and eventually disintegrate.

In this work, alumina was chosen as the shell material. Several alumina-based shell formulations were made and tested for strength. The best formulation was used for the shell of the core-in-shell sorbents. The core was made either with limestone only or with limestone and a small quantity of alumina. Alternatively the core was made entirely of hydrated calcium sulfate. The best sorbent formulations were characterized by measuring their crushing strength, apparent density and bulk density. The dependence of strength and absorption capacity on shell thickness was investigated. The effects of loading temperature and H\textsubscript{2}S concentration on absorption rate and capacity were also determined. Samples were also viewed with an electron microscope after they had been pelletized and fired at high temperature. Cyclic absorption and regeneration tests were performed to evaluate sorbent reusability.
Experimental Section

Materials. Several materials were used for the preparation of the different sorbent formulations. Two principal starting materials were used as the reactive component of the sorbent. The first was limestone which was obtained either from the Ames, Iowa, quarry of Martin Marietta Aggregates or from the Three Rivers Quarry located near Smithland, Kentucky. The second was DURABOND® Plaster Of Paris produced by DAP Inc. According to the suppliers, the Iowa limestone contained over 99% CaCO₃, whereas the Kentucky limestone typically contained 92.8% CaCO₃. Both limestone samples had particles in the 44 to 297 μm range. The Plaster of Paris sample contained mostly calcium sulfate hemihydrate (CaSO₄·0.5H₂O) and consisted of particles less than 37 μm in size. Reagent grade CaCO₃, (<37 μm), from the Fisher Co. was also used in certain shell formulations and for some regeneration tests. Mixtures of A-16 SG alumina powder and T-64 tabular alumina particles were used for the shell formulations. Both materials consisted of particles less than 37 μm in size. The first material had a median particle diameter of 0.88 μm and the second a median particle diameter of 8.65 μm. Both materials were supplied by Alcoa.

Preparation methods. To test various shell formulations, A-16 SG alumina and T-64 tabular alumina were combined in various proportions and then mixed with approximately 30% water to form a thick slurry which 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 hr. and then calcined at 1100°C for 2.0 hr.

To study the effect of different core compositions on the properties of core-in-shell pellets, the pellets were prepared with a small bench-scale drum pelletizer which 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 limestone or a mixture of limestone and A-16 SG alumina or calcium sulfate hemihydrate in the drum. While the drum revolved at a constant 60 rpm, the powder was sprayed at frequent intervals with a dilute lignin solution until small pellets formed. 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 hr. 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 shell formulation. While the drum speed was kept constant, a measured amount of 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 hr. 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 hr.

**Characterization methods.** The overall diameter and shell thickness of the various core-in-shell pellets were determined with a hand held caliper. The fractional shell volume was calculated by using the following equation:

\[ V_f = \left(1 - \frac{d_e^3}{d^3}\right) \]  

(1)

where \(d_e\) is the core diameter and \(d\) is the overall pellet diameter. Several determinations were made for each sorbent formulation.

The compressive strength of a sample was determined by measuring the force required to break the pellet. The procedure used was similar to that described by Deng and
Lin.  A single sample was placed on the base plate of an Accuforce EZ250 test stand. The upper plate was then lowered at a constant rate of 10 mm/min. The force required to fracture the pellet was taken to be the breaking force of the pellet. For the spherical sorbent pellets investigated in this work, the crush strength was determined by dividing the breaking force by the pellet diameter. Several determinations were made to represent the crush strength of a particular sorbent formulation.

Kinetic studies were performed using a thermal gravimetric analyzer. The instrument consisted of a vertical quartz reaction tube in which a quartz basket holding the sorbent was suspended from a Cahn model 2000 electrobalance. The reactor was surrounded by a high temperature furnace that was equipped with a temperature controller. A gas mixture of a known composition was introduced at a constant flow rate of 500 ml/min into the reaction tube. The reactor temperature was measured with a thermocouple encased in a protecting tube that extended from the bottom of the reactor to a location just below the quartz basket. The thermocouple was connected to a temperature reading device to display the reactor temperature. The sorbent weight gain was monitored with a strip chart recorder and a digital multi-meter. The instrument was operated under atmospheric pressure.

A Micrometrics model 1350 multivolume pycnometer was used to measure the apparent solid volume of a sorbent formulation. The weight of the same sample was measured with a sensitive electronic balance. This weight divided by the apparent solid volume yielded the apparent density. Archimedes principle was used to determine the bulk density of the sorbent material. The apparent porosity was determined using the following equation:
\[
P_a(\%) = \left(1 - \frac{P_b}{P_s}\right) \times 100.
\]  
(2)

Where \( P_a \) is the apparent density and \( P_b \) is the bulk density.

Selected samples were studied by scanning electron microscopy. The pellets were sectioned and mounted in an epoxy resin. After hardening for about a day, the samples were polished to improve imaging. The samples were then coated with gold using a sputter coater. A JEOL 6100 scanning electron microscope was used to view the sectioned samples.

**Reaction schemes.** The decomposition of \( \text{CaCO}_3 \) in the core of the limestone-based pellets occurred upon heat-treatment to 1100°C. At about 850°C, thermodynamics favors \( \text{CaCO}_3 \) decomposition according to the following reaction:\textsuperscript{13}

\[
\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g).
\]  
(3)

After calcination at 1100°C most of the \( \text{CaSO}_4 \) in the calcium sulfate hemihydrate-based pellets had not decomposed to \( \text{CaO} \). Therefore, prior to testing as an absorbent the material was converted to the \( \text{CaO} \) by employing the regeneration technique of Jagtap and Wheelock.\textsuperscript{9}

Part of the \( \text{CaSO}_4 \) was reduced to \( \text{CaO} \) at 1070°C by using 30 % CO in \( \text{N}_2 \) according to the following reaction:

\[
\text{CaSO}_4(s) + \text{CO}(g) = \text{CaO}(s) + \text{SO}_2(g) + \text{CO}_2(g).
\]  
(4)

Another part of the \( \text{CaSO}_4 \) was reduced to \( \text{CaS} \) by the side reaction,

\[
\text{CaSO}_4(s) + 4\text{CO}(g) = \text{CaS}(s) + 4\text{CO}_2(g).
\]  
(5)

The residual \( \text{CaS} \) was then oxidized with 20% \( \text{O}_2 \) in \( \text{N}_2 \) at the same temperature to form \( \text{CaSO}_4 \) by the following reaction:
\[ \text{CaS}_2(s) + 2\text{O}_2(g) = \text{CaSO}_4(s) \]  

(6)

The reduction and oxidation steps were repeated several times until only CaO remained.

For absorption studies, the gain in weight of a sample was monitored when it was exposed to a stream of gas containing a known concentration of H$_2$S at a preset temperature for a selected time period. For both calcium sulfate hemihydrate and limestone-based samples, after decomposition, the gain in weight was primarily due to the following reaction:

\[ \text{CaO}_2(s) + \text{H}_2\text{S}_2(g) = \text{CaS}_2(s) + \text{H}_2\text{O}_2(g) \]  

(7)

For the regeneration phase, again the cyclic process of Jagtap and Wheelock$^9$ was used. The regeneration took place isothermally at 1050°C. First the product, CaS, was oxidized with 20% O$_2$ in N$_2$ for a chosen time period, Equation 6. The CaSO$_4$ was then reduced for a selected time period at the same temperature with 30% CO in N$_2$, Equation 4. The cyclic process was repeated until the sample weight reached that of the fresh pellet or no weight change in the sample was detected. This suggested complete regeneration.

Results and Discussion

Shell Formulations. To study the effect of composition on the strength of the pellet shell formulation, the finer size A-16 SG alumina was combined with the coarser T-64 alumina in various proportions. It was hypothesized that when such a mixture was heated to a sufficiently high temperature, the smaller A-16 SG particles would sinter preferentially and form bridges or bonds between the larger T-64 particles. It was further hypothesized that by adjusting the proportion of coarse and fine particles a cohesive but porous structure could be produced.
To test this theory several different batches of tablets were prepared by combining the two grades of alumina in different proportions and using the previously described procedure to mold small cylindrical tablets. After the tablets had been heat-treated, the force required to break the tablets was measured and the results are presented in Figure 1. Each point represents an average of five determinations of the breaking 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 of formulations containing Iowa limestone are presented in Figure 2. The results obtained with calcium carbonate, which are not shown, were very similar and in some cases identical to those obtained with Iowa limestone. It is apparent that the crushing strength of the material is a maximum when 20% limestone is incorporated in the alumina mixture. For this formulation the breaking force was nearly twice that of the formulation which did not contain limestone. However, when the limestone content was increased beyond the optimum level, the crushing strength decreased rapidly. The results suggest that with the optimum level of limestone a calcium aluminate compound, probably (2CaO·3Al₂O₃), forms between the limestone and the A-16SG upon sintering because the ratio of CaO to Al₂O₃ in this compound is nearly the same as that in the optimum formulation. The additional strength gained with the optimum formulation could be due to particle bonding by the calcium
aluminate. When excess limestone was incorporated in the formulation, free CaO could be present in the calcined product which served to weaken the material.

**Core-in-Shell Sorbent Pellets.** Numerous batches of core-in-shell pellets were prepared using the previously described pelletization procedure. All of the pellets were made with the optimum shell composition. Pellets were made with differing core sizes and shell thickness for both calcium sulfate hemihydrate and limestone formulations. In some limestone-based samples A-16SG alumina was incorporated in the core. Also two different limestones were used for core formulations. Each formulation was tested for strength. Formulations that produced a crushing strength of 8.9 N/mm or more, a value considered sufficient strength for fixed-bed applications, were considered for further study.

Table 1 shows the important properties of the formulations which qualified. Sorbents A through C were limestone-based, D and E were calcium sulfate hemihydrate-based. The cores of all the limestone-based pellets were prepared with 90% limestone and 10% A-16SG alumina. Sorbents A and C were similar in that they were both made with Iowa limestone. The difference is that C had on average a thicker shell than A. Sorbent B differed from A in that the core was made with Kentucky limestone. For the calcium sulfate hemihydrate samples, D differs from E in that E possessed on average a thicker shell. The crush strength increased with shell thickness as expected, sorbents A and B vs. C and D vs. E. The pellet strength did not vary significantly between the Iowa and Kentucky limestones, sorbent A vs. B. Notice that despite the difference in shell thickness and core materials the apparent densities were similar. For both limestone and calcium sulfate hemihydrate-based pellets the porosity decreased with an increase in shell thickness. The calcium sulfate hemihydrate formulations had the higher porosities. It should be noted that, although the calcium sulfate
hemihydrate-based pellets had been heat-treated to the same temperature as the limestone-based pellets, the CaSO$_4$ core had not fully decomposed. Hence, it is conceivable that the porosity of the decomposed calcium sulfate hemihydrate pellets was even higher than the values reported in Table 1.

Limestone-based core-in-shell pellets were cross-sectioned and examined with a scanning electron microscope both before and after calcination at 1100°C for 2 hr. Figures 3a and 3b are micrographs of the sectioned pellets. In both cases, Figures 3a (i) and 3b (i) show that there was a pronounced difference in the texture of the material constituting the core and shell. However, the difference in texture was much greater before calcination than afterwards. Before calcination the texture of the shell material appeared very coarse due to the presence of relatively large tabular alumina particles intermixed with much finer but discrete alumina and limestone particles, Figures 3a (ii) and (iv). After calcination the texture of the shell material was much finer due to the particle sintering which had taken place, Figure 3b (iii). Figures 3a (iii) and 3b (iii) show that the texture of the core material was relatively fine before and after calcination. A number of holes or voids can be seen in both the core and shell in both cases.

Figure 4 shows the decomposition of several pellets containing CaSO$_4$. Run 1 was made with a pellet representing only the core of a core-in-shell pellet, whereas, the rest of the runs were made with core-in-shell pellets. Unsurprisingly the initial decomposition rate and the amount of weight ultimately lost decreased as the shell thickness was increased. Two of the curves are labeled to show where reduction, Reaction 4, or oxidation, Reaction 6, took place. The results of Runs 6 and 7 suggest the presence of an initial induction period. A possible explanation for a slower initial rate is that, as the shell became thicker, the rate of
diffusion through the shell was slower which delayed the contact between the gas and the reactive material. The time delay could have been responsible for the slow initial rate and, hence, the change in shape of the curves. The weight loss after the first reduction cycle for the core-in-shell pellets in Figure 4 was on average 91.7 ± 1.1% of the final weight loss. This tended to confirm that Reaction 5 was responsible for the incomplete decomposition during the first cycle.

Absorption tests. Preliminary TGA runs were conducted to establish the reproducibility of absorption tests with limestone and calcium sulfate hemihydrate-based cores. The runs were conducted at a constant temperature of 880°C with 1.1% H₂S in a nitrogen atmosphere. The results are shown in Figure 5. It is evident that there was a good agreement between the replicate runs for both the limestone and calcium sulfate hemihydrate-based pellets. Furthermore, CaO derived from the different starting materials behaved similarly as all the curves overlap and are only distinguishable upon close inspection.

The next set of runs was conducted to investigate the effect of shell thickness on the absorption rate and capacity of both limestone and calcium sulfate hemihydrate-based pellets. The results are shown in Figures 6a and 6b, respectively. In both cases, as the shell thickness increased the absorption capacity decreased. Although the dimensions of the pellets tested were similar, the ultimate weight gains of the samples derived from limestone were on average higher than that of their calcium sulfate hemihydrate counterparts. On the other hand, the overall reaction rate of the calcium sulfate hemihydrate-based pellets was higher than that of the limestone derivatives. A calcium sulfate hemihydrate core started out mostly as CaSO₄·2H₂O with a molecular weight of 145 g/mol versus 100 g/mol for a limestone core.
Hence, if one gram of each compound were decomposed, the amount of CaO in the sample derived from limestone would be 72% more than that in the sample derived from calcium sulfate hemihydrate. Therefore, it is conceivable that on average the calcined limestone-based pellets were more massive than the calcium sulfate hemihydrate ones, hence, the discrepancy. From Figure 6a it is also evident that the initial rate of reaction of the pellets with different shell thickness was very similar. In contrast, the initial rate of reaction of the calcium sulfate hemihydrate-based pellets varied with shell thickness, Figure 6b. A possible explanation for this difference between the two types of pellets is that diffusion though the shell may have been the rate controlling step in the second case (Figure 6b), whereas chemical reaction may have been the rate controlling step in the first case (Figure 6a).

Figure 7 shows the results of absorption runs performed with 2% H₂S at 880°C on two different pellets having similar overall diameters but different shell thicknesses and core diameters. Sample 1 had a shell thickness of 0.61 mm and core diameter of 3.61 mm whereas Sample 2 had a shell thickness of 0.42 mm and a core diameter of 4.00 mm. The fractional core volumes were 0.42 and 0.56 respectively. It is clear from Figure 7 that the initial rates were identical for the first 15 minutes. The different core volumes seemed to be responsible for the difference in ultimate absorption capacity. It is apparent that the ultimate weight gain of the sample with the thicker shell, Sample 1, was achieved later than that of Sample 2 with the thinner shell.

From Table 1, and from Figures 6a and 6b it is evident that shell thickness and, hence, fractional shell volume has an effect on both pellet strength and absorption capacity. To further investigate these relationships, the pellet strength and weight gain were plotted against fractional shell volume for both limestone and calcium sulfate hemihydrate
formulations, Figures 8a and 8b. Both graphs show similar trends, the weight gain decreases sharply with increasing fractional shell volume while the crush strength increases sharply. For limestone-based pellets the best compromise between crush strength and absorption capacity would be achieved with a fractional shell volume of approximately 0.56. This fractional shell volume would result in a weight gain of about 8 wt. % and a crush strength of approximately 8.1 N/mm. For calcium sulfate hemihydrate-based pellets, the best compromise would be achieved with a fractional shell volume of approximately 0.44, corresponding to a weight gain of around 7.5 wt. % and crush strength of about 7.5 N/mm. It should be noted that such pellets would have crush strengths below the recommended 8.9 N/mm, for fixed bed applications.

Experiments were carried out varying the H$_2$S concentration while keeping all other parameters constant. For both limestone and calcium sulfate hemihydrate derived samples an effort was made to keep the shell thickness constant. Figures 9a and 9b show the results for the limestone and calcium sulfate hemihydrate-based pellets, respectively. The three limestone-based samples treated with 3, 2 and 1.1% H$_2$S in Figure 9a had fractional shell volumes of 0.47, 0.44 and 0.46, respectively. The corresponding calcium sulfate hemihydrate-based samples in Figure 9b have fractional shell volumes of 0.60, 0.61 and 0.61, respectively. For both formulations similar trends were observed; there was a steady increase in absorption rate as the H$_2$S concentration was increased from 1.1 to 3%. Figure 10 shows the initial rate of change in pellet weight plotted against H$_2$S concentration for both formulations. In both cases the initial rate was directly proportional to the H$_2$S concentration. This suggests an apparent reaction rate order of unity with respect to H$_2$S concentration since the reaction rate would have been directly proportional to the change in pellet weight.
Although the calcium sulfate hemihydrate-based pellets had a larger shell volume, the initial rate was higher. The higher rate could have been due to a larger surface area because it had been determined previously that surface area has an effect on the sulfidation kinetics of CaO. Unfortunately the surface area was not known.

The effect of reaction temperature between 840 and 960°C was investigated for both pellet formulations and the results are shown in Figures 11a and 11b. Again, pellets with similar dimensions and weights were used for this investigation. From Figure 11a it is apparent that for the limestone-derived sorbent the reaction rate was affected very little by loading temperature between 840 and 920°C. Although the ultimate capacity differed slightly over this temperature range, the different values were all within the expected value. Also, in all of these runs the ultimate capacity was reached after 110 minutes, an indication that all of the available lime had reacted. At 960°C, however, the initial rate and ultimate capacity were significantly lower than for the other temperatures investigated. Also, it was evident that the sample would have continued to gain weight if the time had been extended beyond 120 minutes. The calcium sulfate hemihydrate-based pellets showed a slightly different trend. The overall reaction rate and one hour weight gains were similar for runs made at 880 and 920°C, Figure 11b. However, the reaction rate and weight gain both suffered outside of this temperature range. For both formulations, sintering of the CaO may have been responsible for the drop in the rate at 960°C.

**Sorbent regeneration.** For a sorbent to be a competitive candidate for hot gas desulfurization, it should be able to withstand numerous absorption and regeneration cycles. Therefore, in this study regeneration of lime-alumina sorbents was investigated.
Samples of both limestone and calcium sulfate hemihydrate-derived cores were subjected to multi-cycle tests under similar conditions. For the absorption phase, 3% H₂S was introduced for a preset time. The flow of H₂S was discontinued after the absorption period, and the temperature was raised to a regeneration temperature of 1050°C while the sample was blanketed with nitrogen. The previously described regeneration technique was then used. The results achieved with a limestone-based core are shown in Figure 12. It is evident that the limestone-based core suffered a systematic loss in absorption capacity over 3 cycles. The weight gain after the 3rd cycle was approximately 60% that of the fresh pellet. This change was probably due to sintering.

Although gases such as H₂O and CO₂ are known to promote sintering of lime at high temperature, none of these gases were present in significant amounts. Hence, the loss in reactivity may have been due to any of the following factors: a) sintering of the CaO enhanced by the small amount of A-16SG alumina in the core, or b) sintering of the CaO alone. To establish which of the factors was responsible for the deactivation, a regeneration run was performed with a CaO pellet derived solely from reagent grade calcium carbonate. Just as with the limestone core, the pellet suffered a loss in capacity over the test; the results are not shown. This eliminated the first explanation. The absorption phase of the 7th cycle was continued to determine if and when the weight gain would reach the same level as when the fresh pellet was sulfided. The results of this experiment are shown in Figure 13. It can be seen that, during the 7th cycle a loading time of 75 minutes was required to achieve the same loading achieved during the first cycle in 10 minutes. The fact that the same weight gain was achieved is evidence that sintering most probably reduced the surface area of the CaO sample, which in turn reduced its reactivity.
When a calcium sulfate hemihydrate-based core was subjected to a similar multi-cycle test, no loss in reactivity was observed over 5 cycles, Figure 14. To confirm the results, a second pellet from a different batch was subjected to the same treatment and no deactivation was observed. Next a calcium sulfate hemihydrate-based core-in-shell pellet was subjected to a 10-cycle test. The results, which are presented in Figure 15, show that the sorbent suffered no loss in capacity over the 10 cycles.

An explanation for the difference in results obtained with limestone and calcium sulfate hemihydrate-derived pellets can be postulated. The starting materials had different molar volumes, 46 cm$^3$/mol for anhydrate CaSO$_4$ and 36.7 cm$^3$/mol for CaCO$_3$. Both samples decomposed to CaO, which had a molar volume of 16.9 cm$^3$/mol. For the calcium sulfate hemihydrate-based pellets this meant that there was at least a 63% void volume surrounding each CaO particle. The CaO particles resulting from the limestone-based pellets had approximately a 54% void volume. During regeneration, all samples form CaSO$_4$, by Reaction 6, as an intermediate. In the case of the limestone-based samples, this compound has a larger mole volume than the available void space. This expansion of the pellet may cause defects in the crystal lattice of the sample. Such defects are known to promote sintering. This phenomenon may not have occurred during the regeneration of the calcium sulfate hemihydrate-based pellets because the maximum void volume was already available.

Conclusions

The core-in-shell pelletization method of fabricating structurally enhanced sorbents for hot gas desulfurization was employed with a lime-alumina system. A suitable shell formulation was found by combining 48 wt. % coarse alumina powder with 32 wt. %
ultrafine alumina powder and 20 wt. % limestone. Core-in-shell pellets were made with cores derived from limestone or calcium sulfate hemihydrate and coated with this optimum shell composition. Initial sorbent screening led to limestone-based formulations that contained 90% limestone and 10% alumina in the core. Calcium sulfate hemihydrate-based pellets were prepared with 100% calcium sulfate hemihydrate in the core. The calcined pellet strength was found to increase exponentially with fractional shell volume.

Sulfidation tests revealed that the limestone-based pellets generally had a higher capacity but lower absorption rate than the calcium sulfate hemihydrate pellets when tested under the same conditions. For both formulations there was an exponential decrease in absorption capacity as the fractional shell volume increased. The absorption rate for calcium sulfate hemihydrate pellets proved to be more sensitive to temperatures between 840 and 960°C. However, both materials showed a significant decline in absorption rate at 960°C, which may have been due to sintering.

Repeated absorption and regeneration tests showed that the calcium sulfate hemihydrate-based sorbent was superior. While limestone-based cores showed a significant loss in reactivity upon cycling, cores derived from calcium sulfate hemihydrate showed no loss in reactivity when subjected to the same test. In addition, a calcium sulfate hemihydrate-based core-in-shell pellet showed no signs of deactivation when it was subjected to a ten-cycle sulfidation and regeneration run. Furthermore, the pellet maintained its integral structure throughout the 10 cycles.
Acknowledgement

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Nomenclature

d_c = core diameter (mm)
d = overall pellet diameter (mm)
P_a = apparent porosity (dimensionless)
V_f = fractional shell volume (dimensionless)
\rho_a = apparent density (g/cm^3)
\rho_b = bulk density (g/cm^3)

Literature Cited


(8) Gupta, R. private communication, Center for Engineering and Environmental Technology, Research Triangle Park, North Carolina., December 6, 1999.


Table 1. Characteristics of various sorbent formulations after calcination at 1100°C for 2 hr.

<table>
<thead>
<tr>
<th>Sorbent designation</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core composition</td>
<td>90% Ames limestone + 10% A-16SG Alumina</td>
<td>90% Kentucky limestone + 10% A-16SG Alumina</td>
<td>90% Ames limestone + 10% A-16SG Alumina</td>
<td>100% Calcium sulfate hemihydrate</td>
<td>100% Calcium sulfate hemihydrate</td>
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<tr>
<td>Pellet diameter (mm)</td>
<td>4.20 ± 0.06</td>
<td>4.23 ± 0.13</td>
<td>4.80 ± 0.20</td>
<td>4.54 ± 0.14</td>
<td>5.14 ± 0.17</td>
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<tr>
<td>Shell thickness (mm)</td>
<td>0.40 ± 0.04</td>
<td>0.42 ± 0.05</td>
<td>0.78 ± 0.03</td>
<td>0.62 ± 0.12</td>
<td>0.91 ± 0.15</td>
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<tr>
<td>Fractional shell volume</td>
<td>0.47 ± 0.03</td>
<td>0.48 ± 0.03</td>
<td>0.69 ± 0.02</td>
<td>0.64 ± 0.01</td>
<td>0.73 ± 0.07</td>
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<tr>
<td>Compressive strength (N/mm)</td>
<td>8.94 ± 1.39</td>
<td>8.57 ± 1.79</td>
<td>16.44 ± 0.48</td>
<td>12.10 ± 3.16</td>
<td>18.28 ± 3.09</td>
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<tr>
<td>Apparent density (g/cm³)</td>
<td>3.40 ± 0.05</td>
<td>3.30 ± 0.03</td>
<td>3.46 ± 0.04</td>
<td>3.39 ± 0.02</td>
<td>3.49 ± 0.11</td>
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<tr>
<td>Bulk density (g/cm³)</td>
<td>1.60 ± 0.09</td>
<td>2.03 ± 0.15</td>
<td>1.95 ± 0.02</td>
<td>1.48 ± 0.06</td>
<td>1.86 ± 0.03</td>
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<td>Apparent porosity (%)</td>
<td>52.7 ± 3.8</td>
<td>38.4 ± 4.8</td>
<td>43.8 ± 0.0</td>
<td>56.4 ± 2.2</td>
<td>46.7 ± 2.7</td>
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Figure 1. Effect of composition on compressive strength of calcined tablets made with a mixture of T-64 alumina and A-16 SG alumina powders.
Figure 2. Effect of limestone concentration on compressive strength of calcined tablets made with 3:2 ratio of T-64 alumina to A-16 SG alumina.
Figure 3a. Micrographs of a freshly made limestone-based pellet; i) section of an entire pellet at ×17, ii) the shell at ×110, iii) the core at ×110, and iv) the shell at ×1000.
Figure 3b. Micrographs of a fired limestone-based pellet; i) section of an entire pellet at \( \times17 \), ii) the shell at \( \times110 \), iii) the core at \( \times110 \).
Increasing shell thickness

Reduction

Oxidation

Figure 4. Decomposition of CaSO₄ in various pellets. Runs were performed at 1070°C with 30% CO – reduction cycle and 20% O₂ – oxidation cycle.
Figure 5. Replicate runs with calcium sulfate hemihydrate and limestone based cores. Absorption was performed with 1.1% $\text{H}_2\text{S}$ at 880°C.
Figure 6a. Absorption rate and capacities of limestone-based core-in-shell pellets, runs performed with 1.1% H$_2$S at 880°C.
Figure 6b. Absorption rate and capacities of various calcium sulfate hemihydrate-based core-in-shell pellets, runs were performed with 1.1% H$_2$S at 880°C.
Figure 7. Effect of shell thickness on absorption rate and ultimate capacities of limestone-based pellets, runs performed with 2.0 % H₂S at 880°C.
Figure 8a. Effect of fractional shell volume on strength and ultimate capacity of limestone-based core-in-shell pellets.
Figure 8b. Effect of fractional shell volume on absorption capacity and strength of calcium sulfate hemihydrate-based pellets.
Figure 9a. Effect of H$_2$S concentration on absorption rate of limestone-based pellets. Runs were performed at 880°C.
Figure 9b. Effect of H2S concentration on absorption rate of calcium sulfate hemihydrate-based core-in-shell pellets. Runs were performed at 880°C.
Figure 10. The effect of $\text{H}_2\text{S}$ concentration on initial reaction rate. Runs were performed at $880^\circ\text{C}$. Calcium sulfate hemihydrate-based pellets had an average shell thickness of 0.66 mm and the limestone-based pellets an average shell thickness of 0.47 mm.
Figure 11a. Effect of temperature on absorption rate of limestone-based core-in-shell pellets. Runs were conducted with 1.1% H₂S in nitrogen.
Figure 11b. Effect of temperature on absorption rate of calcium sulfate hemihydrate-based core-in-shell pellets. Runs were conducted with 1.1% H₂S in nitrogen.
Figure 12. Results achieved when a limestone-based core was subjected to a 3-cycle absorption/regeneration test.
Figure 13. Comparison of the absorption capacity achieved during the 1st and the 7th cycles of a pellet made from reagent grade calcium carbonate.
Figure 14. Results achieved when calcium sulfate hemihydrate-based core was subjected to a 5-cycle absorption/regeneration test.
Figure 15. Results achieved when calcium sulfate hemihydrate-based core-in-shell pellet was subjected to a 10-cycle absorption/regeneration test.
CHAPTER 7. AN EXTENDED SHRINKING CORE MODEL TO ACCOUNT FOR SHELL LAYER DIFFUSION CONTROL

A research note to be submitted to *Industrial and Engineering Chemistry Research*

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**Abstract**

This paper introduces an additional element into the shrinking core model to account for shell-layer diffusion control for a non-catalytic gas-solid reaction. Such a case arises when a solid material reactive to an exposed gas is encased in a porous inert material. The spherical core-in-shell pellets developed by Akiti *et al.*\(^{1-3}\) to serve as sorbents for desulfurizing hot coal gas are a good example. A model for representing this case was developed and tested. The results showed that the shell of the core-in-shell pellets investigated did not offer significant resistance. The reaction rate was found to be controlled by chemical reaction at the surface of the unreacted core.

Keywords: Shrinking core model, shell diffusion, core-in-shell pellet, desulfurization, sorbent

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Introduction

One of the simplest and most popular mechanistic models used to describe the reaction between a solid particle and a gas is the shrinking core model. The mechanism assumes that the reaction starts on the surface of the unreacted solid material. In the case where the overall pellet size remains unchanged, as the reaction proceeds an ash or product layer builds and the unreacted core shrinks. At final conversion only product remains. In another case where no ash layer forms, the unreacted core diminishes until at final conversion nothing remains. In the first case the reaction rate may be controlled by gas film diffusion, ash layer diffusion, chemical reaction at the surface of the unreacted core or by a combination of these processes. In the second case since no ash layer exists, diffusion through the ash layer is absent. Models for each of these cases have been developed and can be found in Levenspiel. Several studies have found the shrinking core model adequate to describe various gas-solid reaction systems.

In some cases the shrinking core model has proved inadequate to describe a gas-solid reaction; hence, alternative mechanistic models have been proposed. Another popular model for describing gas-solid reactions is the grain model. This model assumes that the bulk solid is comprised of many grains which act independently of each other, each of which follows the shrinking core model upon reaction. The reaction zone model is yet another model that has been developed to describe a gas-solid reaction. The mechanism suggests that the reaction front occurs within a moving zone rather than along a sharp interface. As the reaction zone thickness approaches zero, this model approaches the shrinking core model. Several investigators have utilized the reaction zone model to describe reacting systems. Yet another class of models are the pore models. Here the solid reacts in a layer around the
pore surface. Several subclasses of the pore model that have been identified include: the single pore model, the distribution pore size model and the random overlapping pore model. These models have been applied successfully to gas-solid reaction systems.\textsuperscript{12, 13}

The present note extends the original shrinking core model for another case where an additional rate-determining step, diffusion through a shell layer, is considered. This case comes about when a porous material that is inert to a reacting gas surrounds another material that reacts with the gas. If the shell has a lower diffusivity than that of the ash layer that forms and if film and surface reaction resistances are negligible, then shell diffusion will control the reaction rate. The core-in-shell pellets developed by Akiti et al.\textsuperscript{1-3} for hot coal gas desulfurization have such a configuration. Hence, these pellets were used to test the extended model.

\textbf{Model development}

In extending the shrinking core model, all the assumptions associated with the original model were adopted. In addition the following assumptions were made:

1. The size of the entire core and the size of the shell remain unchanged throughout the reaction process.

2. The shell undergoes no changes in physical properties throughout the reaction process.

3. Film and ash layer diffusion as well as chemical reaction at the surface of the unreacted core take place instantaneously.

4. The shell is inert to the reactant gas.

5. The shell is porous.
The model was developed for the general gas-solid reaction:

\[ A_{(g)} + bB_{(g)} = rR_{(g)} + sS_{(g)} \]  

(1)

Figure 1 shows the case where diffusion through the shell controls the rate of reaction. In this case the concentration gradient is in the shell as shown in the figure. For a first order reaction with shell diffusion control, the following expression can be used to describe the reaction:

\[ -\frac{dN_A}{dt} = 4\pi r^2 Q_A \]  

(2)

In Equation 2, \( N_A \) is the moles of gaseous species A, \( r \) is the radial position in the solid particle and

\[ Q_A = D_{es} \frac{dC_A}{dr} \]  

(3)

where \( D_{es} \) is the effective diffusion coefficient of the gaseous reactant in the shell layer and \( C_A \) is the concentration of gaseous species A. The substitution of Equation 3 into Equation 2 yields the following expression:

\[ -\frac{dN_A}{dt} = 4\pi r^2 D_{es} \frac{dC_A}{dr} \]  

(4)

Integrating across the shell layer from \( r = R_1 \) to \( r = R_2 \) where \( C_A \) goes from \( C_{As} \) to 0, (see Figure 1) and assuming that \( dN_A/dt \) is essentially constant the following expression is obtained:

\[ -\frac{dN_A}{dt} \left( \frac{1}{R_2} - \frac{1}{R_1} \right) = 4\pi D_{es} C_{As} \]  

(5)
To yield the complete rate expression, it is necessary to integrate Equation 5 with respect to time and the radius. In order to do so, \( N_A \) has to be expressed in terms of \( r_c \), the radius of the unreacted core. From Equation 1 it is known that,

\[
dN_B = b d N_A = \rho_B d \left( \frac{4}{3} \pi r_c^3 \right) = 4 \pi \rho_B r_c^2 dr_c
\]  

(6)

In Equation 6, \( \rho_B \) is the molar density of the reactant solid. Substituting Equation 6 into Equation 5 and integrating from \( t = 0 \) to \( t = t \) and \( r_c = R_2 \) to \( r_c = r_c \) the following expression is obtained:

\[
t = \frac{\rho_B R_2^3}{3 D_e b C_{A0}} \left( \frac{1}{R_2} - \frac{1}{R_1} \right) \left[ 1 - \left( \frac{r_c}{R_2} \right)^3 \right]
\]  

(7)

Equation 7 is the shrinking core model with diffusion through the shell layer as the rate-controlling step. For complete conversion of a single particle \( r_c \) will approach zero and the time required will be:

\[
\tau = \frac{\rho_B R_2^3}{3 D_e b C_{A0}} \left( \frac{1}{R_2} - \frac{1}{R_1} \right)
\]  

(8)

Since the fractional conversion \( X_B \) of a spherical particle is given by the following expression:

\[
X_B = 1 - \left( \frac{r_c}{R_2} \right)^3
\]  

(9)

it follows that substituting Equations 8 and 9 into Equation 7, yields the expression:

\[
\frac{t}{\tau} = X_B
\]  

(10)
Equation 10 resembles the shrinking core model with film diffusion as the controlling resistance. However, in this case $t$ depends on the effective diffusivity of the shell layer as well as the shell thickness. Therefore, when $R_1 = R_2$ Equation 8 indicates that the reaction time will be zero. Although this result is consistent with Assumption 3, this is not likely to be the case in a real situation. Shell layer diffusion is only one of the possible rate controlling resistances of the overall shrinking core mechanism. Hence, by employing the method presented by Levenspiel\textsuperscript{8,9} the effect of shell resistance can be added to the effects of other resistances that may be present during a reaction, by employing the relation,

\[ t_{\text{total}} = t_{\text{film alone}} + t_{\text{shell alone}} + t_{\text{product alone}} + t_{\text{reaction alone}} \quad (11) \]

Each individual time $t$ on the right hand side of this equation represents the time required for conversion of the particle if the corresponding resistance alone controlled the rate of reaction.

For example, let us suppose that the reaction rate between a pellet without a shell and a gas is controlled by diffusion through the ash layer. Then when a shell is placed around the pellet, the shell thickness and the magnitude of the effective shell diffusivity will determine whether the reaction rate is controlled by shell diffusion, ash layer diffusion or a combination of both resistances. For the case where the reaction rate is controlled by both shell diffusion and ash layer diffusion, it can be shown that,

\[ t = \frac{\rho_B R_2^3}{3D_{\text{ec}} bC_{\text{As}}} \left( \frac{1}{R_2} - \frac{1}{R_1} \right) X_B + \frac{\rho_B R_2^3}{6D_{\text{ec}} bC_{\text{As}}} \left[ 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \right]. \quad (12) \]

In Equation 12, $D_{\text{ec}}$ is the core ash layer effective diffusivity. In this equation when $R_2$ approaches $R_1$ the first term drops out and the pellet follows the shrinking core model with ash layer diffusion as the controlling resistance. Similarly if chemical reaction control is combined with shell diffusion control, it can be shown that,
Experimental verification

The preceding models were used to analyze the kinetic behavior of core-in-shell pellets developed by Akiti et al. The selected pellets had a lime core and an alumina-based shell. The preparation and testing procedures were reported previously by Akiti et al.

The following reaction was conducted at 880°C and 1 atm. pressure:

\[
\text{CaO(s)} + \text{H}_2\text{S(g)} = \text{CaS(s)} + \text{H}_2\text{O(g)}
\]

(14)

This reaction appeared to be first order with respect to H$_2$S concentration; hence, our models applied directly. The first step in our analysis was to determine whether film diffusion was significant and also to determine what mechanism best described the reaction of pellets that did not possess a shell layer (lime core only). For each run, a single non-calcined pellet of a known diameter was treated with 1.1% H$_2$S and 98.9% N$_2$ at a constant temperature of 880°C and 1 atm. pressure. The apparent molar solid density of a CaO calcined pellet, \( \rho_{\text{CaO}} \), was obtained by gas pycnometry and was found to be 0.059 mol/cm$^3$. The radii of three different pellets selected for reaction with H$_2$S were 1.44, 1.38 and 1.46 mm, respectively. The results of the three runs were fitted to the shrinking core model with film diffusion control only, ash layer control only, and chemical reaction control only. The results of fitting are shown in Figure 2, and they indicate that the reaction was most likely controlled by diffusion through the ash layer. It can be seen that the correlation coefficients were highest for this case.
The estimated ash layer diffusivities from the three runs were $2.2 \times 10^{-5}$, $2.0 \times 10^{-5}$ and $2.3 \times 10^{-5}$ m$^2$/s for runs 1, 2 and 3, respectively.

In the next set of experiments, core-in-shell pellets were tested against the different core-in-shell models which involved only a single rate controlling resistance. For each run a single pellet of a known diameter was treated at 880°C and 1 atm. pressure with an H$_2$S concentration which was either 1.1% or 2.0% by volume. After each run, the pellet was sliced in half to estimate the shell thickness. The results are shown in Figures 3 through 5. If gas film or shell diffusion were rate controlling, the conversion-time plots, Figure 3, would have yielded straight lines. However, it is clear that this was not the case. Assuming that film diffusion was not rate controlling and that at the beginning of the reaction when no ash layer was present, shell diffusion would control the reaction rate, the shell diffusivity could be estimated by using Equation 7. The results are shown in Table 1. It can be seen that there is very good agreement among the estimates. Also, the shell diffusivity was on average 3 times that of the core. This provides further evidence that shell diffusion was not the controlling factor. Figure 4 is a plot of the same data to test for ash layer diffusion control. It is evident that the plot did not yield a straight-line relationship. Therefore, ash layer diffusion by itself could not have been rate-controlling. Figure 5 shows the results of a test of chemical reaction as the rate-controlling step. The results of each run form a nearly perfect straight-line relationship suggesting that chemical reaction is the rate-controlling step. The average reaction rate constant determine for the different runs was found to be $0.32 \pm 0.04$ m/s.

The results show that pellets that represent the core of a core-in-shell pellet are best described by the shrinking core model with ash layer diffusion as the controlling mechanism,
whereas, for the core-in-shell pellets chemical reaction seemed to be rate controlling. A reason for this difference can be postulated. Prior to reaction, the core-in-shell pellets were calcined at 1100°C for 2 hrs. This served to sinter the shell. However, it may have also caused significant sintering of the core that in turn reduced the reactivity of the lime. This calcination step was not performed for the pellets that represented the core, hence, the lime may be more reactive posing less of a resistance.

**Conclusion**

A shrinking core model to account for diffusion through a shell layer was developed and presented. Such a case arises when a porous solid material inert to a reactant gas surrounds another solid material that does react with the same gas. Akiti *et al.* developed pellets of this type for the removal of H₂S from hot coal gas streams. For pellets that solely consisted of a reactive core, the reaction rate was limited by diffusion through the product layer. A shrinking core model with chemical reaction as the rate-controlling step best described the core-in-shell pellets used for the investigation. This indicated that the shell nor the ash layer offered significant resistance to the reaction.

**Acknowledgement**

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Nomenclature

\( b \) = stoichiometric coefficient of the reactant solid (dimensionless)

\( C_A \) = concentration of gaseous reactant (mol/cm\(^3\))

\( C_{A_b} \) = concentration of gaseous reactant \( A \) in the bulk gas (mol/cm\(^3\))

\( C_{A_s} \) = concentration of gaseous reactant \( A \) at the reaction surface (mol/cm\(^3\))

\( D_{cc} \) = core ash layer effective diffusivity (m\(^2\)/s)

\( D_{es} \) = effective shell diffusivity (m\(^2\)/s)

\( k \) = reaction rate constant (m/s)

\( N_A \) = moles of gaseous reactant \( A \) (mol)

\( N_B \) = moles of solid reactant \( B \) (mol)

\( Q_A \) = flux of material

\( r \) = radial position (m)

\( r_c \) = radius of the unreacted core (m)

\( R_1 \) = overall pellet radius (m)

\( R_2 \) = radius of solid reactant core (m)

\( t \) = time (s)

\( t_{film \ alone} \) = reaction time for the case of film diffusion control only (s)

\( t_{ash \ alone} \) = reaction time for the case of ash layer diffusion only (s)

\( t_{reaction \ alone} \) = reaction time for the case of chemical reaction control only (s)
Greek symbols

\( \rho_{\text{CaO}} = \text{density of CaO (mol/cm}^3 \text{)} \)

\( \rho_B = \text{density of solid reactant B (mol/cm}^3 \text{)} \)

\( \tau = \text{time for complete reaction for a single particle (s)} \)

Literature Cited


Table 1: Estimated values of the shell diffusivity.

<table>
<thead>
<tr>
<th>Run #</th>
<th>$\tau$ (s)</th>
<th>$R_1$ (m) $\times 10^3$</th>
<th>$R_2$ (m) $\times 10^3$</th>
<th>$D_{es}$ (m$^2$/s) $\times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1621</td>
<td>2.30</td>
<td>1.74</td>
<td>7.7</td>
</tr>
<tr>
<td>2</td>
<td>1818</td>
<td>2.42</td>
<td>1.77</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>1667</td>
<td>2.30</td>
<td>1.81</td>
<td>7.1</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td>7.18</td>
</tr>
<tr>
<td>s.d</td>
<td></td>
<td></td>
<td></td>
<td>0.38</td>
</tr>
</tbody>
</table>
Figure 1. Schematic diagram of a reacting solid particle with a gas when shell diffusion is the rate controlling resistance.
Run 1  Run 2  Run 3

\begin{align*}
\text{Run 1} & : y = 0.021x, \quad R^2 = 0.8399 \\
\text{Run 2} & : y = 0.0193x, \quad R^2 = 0.736 \\
\text{Run 3} & : y = 0.0188x, \quad R^2 = 0.6843
\end{align*}

\begin{itemize}
\item[a)] Test for film diffusion control
\item[b)] Test for ash diffusion control
\item[c)] Test for chemical reaction control
\end{itemize}

\textbf{Figure 2.} Test to determine the rate-controlling step for lime core pellets. Runs were conducted with 1.1% H$_2$S at 880°C at 1 atm.
Figure 3. Tests for film or shell layer diffusion control. The runs were performed with 1.1 and 2% H₂S in N₂ at 880°C and 1 atm.
Figure 4. Tests ash layer diffusion control. The runs were performed with 1.1 and 2% H₂S in N₂ at 880°C and 1 atm.
Figure 5. Tests for chemical reaction control. The runs were performed with 1.1 and 2% H₂S in N₂ at 880°C and 1 atm.
CHAPTER 8. CONCLUSIONS AND RECOMMENDATIONS

General Conclusions

The goal of this research was to develop a superior calcium-based sorbent for removing hydrogen sulfide from hot coal gas streams. A superior calcium-based sorbent would be one which is inexpensive and yet overcomes the friability and physical weakness of its natural counterparts such as limestone, dolomite and lime. An additional requirement was that the sorbent be regenerable and reusable over numerous cycles.

Throughout this dissertation the systematic development of such a sorbent is presented. The first two chapters provide the necessary background for the subject matter including the specific goals to be met. Chapter 3 introduces a novel core-in-shell configuration for a sorbent pellet and suggests the means for making spherical pellets. A drum pelletization method was chosen since it held the greatest promise. Chapters 4 through 6 describe results obtained during the development of several types of core-in-shell sorbents. Lime (CaO) was used as a basis for a calcium-based sorbent. The starting materials that were eventually decomposed into lime were limestone (CaCO₃) and calcium sulfate hemihydrate (CaSO₄ · 0.5H₂O). Hydraulic cements and alumina-based materials were investigated as strength enhancers and pellet coating materials. The general conclusions reached from this work are the following:

1. Results showed that there is a negative correlation between pellet strength and lime concentration.
2. Although hydraulic cements are cheap and provide enormous strength after curing, most of this strength is lost at the service temperature of the sorbent (>800°C).
(3) Pelletization time affects the overall pellet strength.

(4) The pellet strength increases with increasing shell thickness.

(5) Calcium aluminate cements provide greater high temperature strength than their calcium silicate counterparts.

(6) For the hydraulic cement-based formulations a minimum steam curing time is required to provide adequate calcined strength.

(7) The maximum H₂S absorption rate for most pellet formulations is observed at approximately 920°C.

(8) The sorbent reaction rate is directly proportional to H₂S concentration.

(9) Cement/limestone sorbent formulations revealed a marked reduction in sorbent capacity when recycled several times.

(10) Alumina-based shells are heavy, reducing the possible fractional weight gain of sorbents made with these shells considerably.

(11) Unlike limestone-based pellets, hemihydrate-based pellets showed no signs of deactivation upon recycling.

(12) The alumina/hemihydrate based pellets met the strength, regenerability and low cost requirements for a high temperature H₂S sorbent.

Chapter 7 introduces a shrinking core reaction model that accounts for shell layer diffusion control. The model along with other forms of the shrinking core model was used to analyze kinetic data obtained from core-in-shell calcium-based sorbents described in Chapter 6. The results suggested that the rate of reaction for absorption is controlled by chemical reaction, suggesting that for the selected pellets the alumina-based shell does not offer significant resistance to the reaction rate.
Recommendations for Future Work

The core-in-shell concept has by no means been fully exploited. Cheaper, lighter and stronger materials should be investigated for making the shells. Also the core-in-shell sorbents have yet to be tested with a simulated coal gas in which significant amounts of CO₂ and H₂O are present. Both gases are known to promote sintering of lime. The reason for the deactivation of the limestone-based sorbents upon regeneration should be investigated. Also the ability of the hemihydrate-based sorbent to withstand numerous cycles of loading and regeneration should be verified. In addition, the kinetic model developed here to account for shell diffusion control should be further validated and extended.
APPENDIX 1. STATISTICAL ANALYSIS OF THE TABULATED DATA IN CHAPTER 4

One-way Analysis of Variance for the Cured Strength Results in Table 1

$H_0$: The mean crush strength of the pellets made with different cements do not differ at a level of $\alpha = 0.05$.

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>$F_{0.05,2,12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>2</td>
<td>2972.6</td>
<td>1486.3</td>
<td>43.86</td>
<td>&gt; 4.75</td>
</tr>
<tr>
<td>Error</td>
<td>12</td>
<td>406.7</td>
<td>33.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>3379.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusion: We reject $H_0$ and conclude that the means do differ. So the cement type does affect the pellet strength.

We use Duncan’s multiple range test to determine which means are significantly different.

$$S_{yi} = \left(\frac{\text{MSE}}{N}\right)^{1/2} = 2.60$$

$$R_2 = r_{0.05}(2,12)S_{yi} = 3.08 \times 2.60 = 8.01$$

$$R_3 = r_{0.05}(3,12)S_{yi} = 3.23 \times 2.60 = 8.40$$
\[
\hat{Y}_{PC-IV} - \hat{Y}_{PC-I} = 52.64 - 22.40 = 30.24 > 8.40
\]
\[
\hat{Y}_{PC-IV} - \hat{Y}_{PC-III} = 52.64 - 51.87 = 0.77 < 8.01
\]
\[
\hat{Y}_{PC-IV} - \hat{Y}_{PC-III} = 51.87 - 22.40 = 29.47 > 8.01
\]

Given the data gathered, we conclude that the mean strength of pellets made from cements type III or type IV do not differ significantly.

**One-way Analysis of Variance for the Strength Results in Table 2**

H₀: The mean crush strength of the pellets coated with different cements do not differ at a level of \( \alpha = 0.05 \).

**Analysis of Variance**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>( F_{0.05,3,16} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>347.09</td>
<td>115.70</td>
<td>77.92</td>
<td>&gt; 3.24</td>
</tr>
<tr>
<td>Error</td>
<td>16</td>
<td>23.76</td>
<td>1.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>19</td>
<td>370.85</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusion: We reject H₀ and conclude that the means do differ. So the cement type used to coat the pellets does affect the pellet strength.

We use Duncan’s multiple range test to determine which means are significantly different.

\[
S_{yi} = (MSE/N)^{1/2} = 0.544
\]
\[ R_2 = r_{0.05}(2,16)S_{yi} = 3.00 \times 0.544 = 1.63 \]
\[ R_3 = r_{0.05}(3,16)S_{yi} = 3.15 \times 0.544 = 1.71 \]
\[ R_3 = r_{0.05}(3,16)S_{yi} = 3.23 \times 0.544 = 1.76 \]

\[ \hat{Y}_{L/PC-III} - \hat{Y}_{L/CA-14} = 12.783 - 10.933 = 1.85 > 1.63 \]
\[ \hat{Y}_{L/PC-III} - \hat{Y}_{L/PC-IV} = 12.783 - 9.270 = 3.513 > 1.71 \]
\[ \hat{Y}_{L/PC-III} - \hat{Y}_{L/PC-I} = 12.783 - 1.813 = 10.97 > 1.76 \]
\[ \hat{Y}_{L/CA-14} - \hat{Y}_{L/PC-IV} = 10.933 - 9.270 = 1.66 < 1.71^* \]
\[ \hat{Y}_{L/CA-14} - \hat{Y}_{L/PC-I} = 10.933 - 1.813 = 9.12 > 1.76 \]
\[ \hat{Y}_{L/PC-IV} - \hat{Y}_{L/PC-I} = 9.270 - 1.813 = 7.46 > 1.76 \]

Given the data gathered, we conclude that the mean strength of pellets coated with cement type III or CA-14 IV do not differ significantly.

**Analysis of Variance for the Strength Results of Pre-calcined Limestone Coated X% PC-III and Y(mm) Shell Thickness Pellets in Table 3**

<table>
<thead>
<tr>
<th>Factor</th>
<th>Type</th>
<th>Levels</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shell thickness</td>
<td>fixed</td>
<td>2</td>
<td>0.40 0.83</td>
</tr>
<tr>
<td>%CaCO3</td>
<td>fixed</td>
<td>5</td>
<td>20 40 60 80</td>
</tr>
</tbody>
</table>

Analysis of Variance for Strength, using Adjusted SS for Tests
Source    DF(Seq SS)    Adj SS    Adj MS    F    P
thickness 1    1.805    7.042    7.042    69.26    0.014
%CaCO3   4    119.467    119.467    29.867    293.77    0.003
Error    2    0.203    0.203    0.102
Total    7    121.475

Analysis of Variance for Adsorption, using Adjusted SS for Tests

One-way Analysis of Variance for the Strength Results of Pre-Heated Limestone Coated 20% PC-III and 80% Limestone Pellets in Table 4

H0: The mean crush strength of the pellets pelletized for different periods of time do not differ at a level of α = 0.05.

Analysis of Variance

Source    DF SS MS F F0.05,2,12
Factor    2 466.2 233.1 17.96 > 4.75
Conclusion: We reject $H_0$ and conclude that the means do differ. So the pelletization time does affect pellet strength.

We use Duncan’s multiple range test to determine which means are significantly different.

$$S_{yi} = (\text{MSE}/N)^{1/2} = 1.61$$

$$R_2 = r_{0.05(2,12)}S_{yi} = 3.08 \times 1.61 = 4.97$$

$$R_3 = r_{0.05(3,12)}S_{yi} = 3.23 \times 1.61 = 5.21$$

$$\hat{Y}_{120\text{min}} - \hat{Y}_{60\text{min}} = 18.697 - 16.134 = 2.563 < 4.97$$

$$\hat{Y}_{120\text{min}} - \hat{Y}_{15\text{min}} = 18.697 - 5.80 = 12.897 < 5.21$$

$$\hat{Y}_{60\text{min}} - \hat{Y}_{15\text{min}} = 16.134 - 5.80 = 10.334 > 4.97$$

Given the data gathered, we conclude that the mean strength of pellets pelletized for 60 minutes or 120 minutes do not differ significantly.
One-way Analysis of Variance for the Adsorption Results of Pre-heated Limestone Coated 20% PC-III and 80% Limestone Pellets in Table 4

H₀: The mean one-hour adsorption capacity of the pellets pelletized for different periods of time do not differ at a level of α = 0.05.

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>F₀.₀₅,₂,₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>2</td>
<td>89.49</td>
<td>44.75</td>
<td>19.09</td>
<td>&gt; 5.79</td>
</tr>
<tr>
<td>Error</td>
<td>5</td>
<td>11.72</td>
<td>2.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>7</td>
<td>101.21</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusion: We reject H₀ and conclude that the means do differ. So the pelletization time does affect the adsorption capacity.

We use Duncan's multiple range test to determine which means are significantly different.

\[ S_{yi} = (\text{MSE}/N)^{1/2} = 0.883 \]

\[ R_2 = r_{0.05(2,5)}S_{yi} = 3.64 * 0.883 = 3.21 \]

\[ R_3 = r_{0.05(3,5)}S_{yi} = 3.74 * 0.883 = 3.02 \]

\[ \hat{Y}_{15\text{min}} - \hat{Y}_{60\text{min}} = 16.033 - 9.853 = 6.18 > 3.02 \]

\[ \hat{Y}_{15\text{min}} - \hat{Y}_{120\text{min}} = 16.033 - 8.310 = 7.723 > 3.21 \]
\[ \hat{Y}_{60\text{min}} - \hat{Y}_{120\text{min}} = 9.853 - 8.310 = 1.543 < 3.21^* \]

Given the data gathered, we conclude that the mean adsorption capacity of pellets pelletized for 60 or 120 minutes do not differ significantly.

**One-way Analysis of Variance for the Strength Results of Pre-heated Limestone Coated 20\% CA-14 and 80\% Limestone Pellets in Table 4**

\( H_0 : \) The mean crush strength of the pellets pelletized for different periods of time do not differ at a level of \( \alpha = 0.05 \).

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>( F_{0.05,2,12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>2</td>
<td>135.88</td>
<td>67.94</td>
<td>25.22 &gt; 4.75</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>12</td>
<td>32.32</td>
<td>2.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>168.20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusion: We reject \( H_0 \) and conclude that the means do differ. So the pelletization time does affect pellet strength.

We use Duncan’s multiple range test to determine which means are significantly different.

\[ S_{yi} = (\text{MSE}/N)^{1/2} = 0.733 \]

\[ R_2 = r_{0.05(2,12)}S_{yi} = 3.08*0.733 = 2.26 \]
\[ R_3 = r_{0.05}(3,12)S_y = 3.23 \times 0.733 = 2.37 \]

\[ \hat{Y}_{120\text{min}} - \hat{Y}_{60\text{min}} = 12.10 - 7.64 = 4.47 > 2.37 \]
\[ \hat{Y}_{120\text{min}} - \hat{Y}_{15\text{min}} = 12.10 - 4.79 = 7.31 > 2.26 \]
\[ \hat{Y}_{60\text{min}} - \hat{Y}_{15\text{min}} = 7.64 - 4.79 = 2.85 > 2.26 \]

Given the data gathered, we conclude that, for the pelletization times investigated, all pre-heated mean strengths of the pellets differ.

**One-way Analysis of Variance for the Strength Results of Heat-treated Limestone Coated 20% CA-14 and 80% Limestone Pellets in Table 4**

\( H_0 : \) The mean crush strength of the pellets pelletized for different periods of time do not differ at a level of \( \alpha = 0.05 \).

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>( F_{0.05,2,12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>2</td>
<td>3.095</td>
<td>1.547</td>
<td>11.93 &gt; 4.75</td>
<td></td>
</tr>
<tr>
<td>Error</td>
<td>12</td>
<td>1.556</td>
<td>0.130</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>4.651</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusion: We reject \( H_0 \) and conclude that the means do differ. So the pelletization time does affect pellet strength.

We use Duncan's multiple range test to determine which means are significantly different.
\[ S_{yi} = (\text{MSE}/N)^{1/2} = 0.16 \]

\[ R_2 = r_{0.05}(2,12)S_{yi} = 3.08 \times 0.16 = 0.493 \]

\[ R_3 = r_{0.05}(3,12)S_{yi} = 3.23 \times 0.16 = 0.517 \]

\[ \hat{Y}_{60\text{min}} - \hat{Y}_{120\text{min}} = 2.5758 - 2.0707 = 0.505 \approx 0.493^* \]

\[ \hat{Y}_{60\text{min}} - \hat{Y}_{15\text{min}} = 2.5758 - 1.4646 = 1.111 > 0.517 \]

\[ \hat{Y}_{120\text{min}} - \hat{Y}_{15\text{min}} = 2.0707 - 1.4646 = 0.606 > 0.493 \]

Given the data gathered, we conclude that the mean strength of the heat-treated pellets pelletized for 60 or 120 minutes do not differ significantly.

One-way Analysis of Variance for the Adsorption Results of Pre-heated Limestone Coated 20% PC-III and 80% Limestone Pellets in Table 4

H\(_0\) : The mean one-hour adsorption capacity of the pellets pelletized for different periods of time do not differ at a level of \(\alpha = 0.05\).

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>(F_{0.05,2,9})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>2</td>
<td>35.43</td>
<td>17.72</td>
<td>16.39</td>
<td>&gt; 4.26</td>
</tr>
<tr>
<td>Error</td>
<td>9</td>
<td>9.73</td>
<td>1.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>45.16</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conclusion: We reject $H_0$ and conclude that the means do differ. So the pelletization time does affect the adsorption capacity.

We use Duncan’s multiple range test to determine which means are significantly different.

\[ S_{yi} = \left( \frac{MSE}{N} \right)^{1/2} = 0.520 \]

\[ R_2 = r_{0.05}(2,9)S_{yi} = 3.20 \times 0.520 = 1.664 \]

\[ R_3 = r_{0.05}(3,9)S_{yi} = 3.34 \times 0.520 = 1.737 \]

\[ \hat{Y}_{15\text{min}} - \hat{Y}_{60\text{min}} = 17.502 - 14.055 = 3.447 > 1.664 \]
\[ \hat{Y}_{15\text{min}} - \hat{Y}_{120\text{min}} = 17.502 - 13.688 = 3.814 > 1.737 \]
\[ \hat{Y}_{60\text{min}} - \hat{Y}_{120\text{min}} = 14.055 - 13.688 = 0.367 < 1.664^* \]

Given the data gathered, we conclude that the mean adsorption capacity of pellets pelletized for 60 or 120 minutes do not differ significantly.
One-way Analysis of Variance for Curing time Versus Calcined Strength

$H_0$: The mean crush strength of the pellets cured for different time periods do not differ at a level of $\alpha = 0.05$.

Analysis of Variance

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>$F_{0.05,7,32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>7</td>
<td>36928658</td>
<td>5275523</td>
<td>73.90</td>
<td>$&gt; 2.33$</td>
</tr>
<tr>
<td>Error</td>
<td>32</td>
<td>2284271</td>
<td>71383</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>39</td>
<td>39212929</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusion: We reject $H_0$ and conclude that the means do differ. So the curing time does affect the pellet strength.

We use Duncan’s multiple range test to determine which means are significantly different.

$$S_{yi} = (\text{MSE}/N)^{1/2} = 119.5$$

$$R_2 = r_{0.05(2,32)}S_{yi} = 2.89 \times 119.5 = 345.4$$

$$R_3 = r_{0.05(3,32)}S_{yi} = 3.04 \times 119.5 = 363.3$$

$$R_4 = r_{0.05(4,32)}S_{yi} = 3.12 \times 119.5 = 372.8$$
\[ R_5 = r_{0.05}(5, 32)S_{yi} = 3.20 \times 119.5 = 382.4 \]
\[ R_6 = r_{0.05}(6, 32)S_{yi} = 3.25 \times 119.5 = 388.4 \]
\[ R_7 = r_{0.05}(7, 32)S_{yi} = 3.29 \times 119.5 = 393.2 \]
\[ R_8 = r_{0.05}(8, 32)S_{yi} = 3.32 \times 119.5 = 396.7 \]

Y8-Y7  159.9460922  <  345.4*
Y8-Y6  542.2529967  >  363.3
Y8-Y5  1160.208958  >  372.8
Y8-Y4  1517.161838  >  382.4
Y8-Y3  1970.473714  >  388.4
Y8-Y2  2408.695388  >  393.2
Y8-Y1  2737.895973  >  396.7

Y7-Y6  382.3069045  >  345.4
Y7-Y5  1000.262866  >  363.3
Y7-Y4  1357.215746  >  372.8
Y7-Y3  1810.527622  >  382.4
Y7-Y2  2248.749296  >  388.4
Y7-Y1  2577.949881  >  393.2

Y6-Y5  617.9559612  >  345.4
Y6-Y4  974.9088416  >  363.3
Y6-Y3  1428.220717  >  372.8
Given the data gathered, we conclude that the mean strength of pellets cured for 24 hours are not significantly different from those cured for 72 hours and pellets cured for 0.25 hours are not significantly different from those not cured at all.
ANOVA - General Linear Model Method for Experimental Results in Table 1

Cured data

Factor  Type  Levels  Values

%CA-14  fixed  3  20  40  60
thickness fixed  2  0.40  0.83

Analysis of Variance for strength, using Adjusted SS for Tests

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>F_{0.05,df,24}</th>
</tr>
</thead>
<tbody>
<tr>
<td>%CA-14</td>
<td>2</td>
<td>258626</td>
<td>258626</td>
<td>129313</td>
<td>147.74</td>
<td>&gt; 3.40</td>
</tr>
<tr>
<td>thickness</td>
<td>1</td>
<td>19866</td>
<td>19866</td>
<td>19866</td>
<td>22.70</td>
<td>&gt; 4.26</td>
</tr>
<tr>
<td>%CA-14*thickness</td>
<td>2</td>
<td>7200</td>
<td>7200</td>
<td>3600</td>
<td>4.11</td>
<td>&gt; 3.40</td>
</tr>
<tr>
<td>Error</td>
<td>24</td>
<td>21006</td>
<td>21006</td>
<td>875</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>29</td>
<td>306699</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Unusual Observations for strength

<table>
<thead>
<tr>
<th>Obs</th>
<th>strength</th>
<th>Fit</th>
<th>StDev</th>
<th>Fit Residual</th>
<th>St Resid</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>128.000</td>
<td>188.200</td>
<td>13.231</td>
<td>-60.200</td>
<td>-2.27R</td>
</tr>
</tbody>
</table>

R denotes an observation with a large standardized residual.
Residual and normal probability plot for the cured data in Table 1

Calcined data

<table>
<thead>
<tr>
<th>Factor</th>
<th>Type</th>
<th>Levels</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>%CA-14</td>
<td>fixed</td>
<td>3</td>
<td>20 40 60</td>
</tr>
<tr>
<td>thickness</td>
<td>fixed</td>
<td>2</td>
<td>0.40 0.83</td>
</tr>
</tbody>
</table>
Analysis of Variance for strength, using Adjusted SS for Tests

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>( F_{0.05, df, 24} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>%CA-14</td>
<td>2</td>
<td>42507.3</td>
<td>42507.3</td>
<td>21253.6</td>
<td>69.24</td>
<td>&gt; 3.40</td>
</tr>
<tr>
<td>thickness</td>
<td>1</td>
<td>1320.0</td>
<td>1320.0</td>
<td>1320.0</td>
<td>4.30</td>
<td>&gt; 4.26</td>
</tr>
<tr>
<td>%CA-14*thickness</td>
<td>2</td>
<td>312.9</td>
<td>312.9</td>
<td>156.4</td>
<td>0.51</td>
<td>&lt; 3.40</td>
</tr>
<tr>
<td>Error</td>
<td>24</td>
<td>7366.8</td>
<td>7366.8</td>
<td>306.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>29</td>
<td>51507.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Unusual Observations for strength

<table>
<thead>
<tr>
<th>Obs</th>
<th>strength</th>
<th>Fit</th>
<th>StDev Fit</th>
<th>Residual</th>
<th>St Resid</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>140.000</td>
<td>74.200</td>
<td>7.835</td>
<td>65.800</td>
<td>4.20R</td>
</tr>
<tr>
<td>10</td>
<td>38.000</td>
<td>74.200</td>
<td>7.835</td>
<td>-36.200</td>
<td>-2.31R</td>
</tr>
</tbody>
</table>

R denotes an observation with a large standardized residual.

Residual and normal probability plot for the calcined data in Table 1
Normal Probability Plot of the Residuals
(response is strength)

Adsortion data

Factor     Type Levels Values
%CA-14     fixed  3 20 40 60
thickness   fixed  2 0.40 0.83

Analysis of Variance for capacity, using Adjusted SS for Tests

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Seq SS</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
<th>$F_{0.05,df,12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>%CA-14</td>
<td>2</td>
<td>136.660</td>
<td>136.660</td>
<td>68.330</td>
<td>134.00</td>
<td>&gt; 3.89</td>
</tr>
<tr>
<td>thickness</td>
<td>1</td>
<td>1.428</td>
<td>1.428</td>
<td>1.428</td>
<td>2.80</td>
<td>&lt; 4.75</td>
</tr>
<tr>
<td>Error</td>
<td>12</td>
<td>6.119</td>
<td>6.119</td>
<td>0.510</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>17</td>
<td>158.422</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Unusual Observations for capacity

<table>
<thead>
<tr>
<th>Obs</th>
<th>capacity</th>
<th>Fit</th>
<th>StDev</th>
<th>Fit Residual</th>
<th>St Resid</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>12.2000</td>
<td>10.4967</td>
<td>0.4123</td>
<td>1.7033</td>
<td>2.92R</td>
</tr>
<tr>
<td>9</td>
<td>9.1900</td>
<td>10.4967</td>
<td>0.4123</td>
<td>-1.3067</td>
<td>-2.24R</td>
</tr>
</tbody>
</table>

R denotes an observation with a large standardized residual.

Residual and normal probability plot for the absorption data in Table 1
APPENDIX 3. SAMPLE CALCULATIONS FOR RESULTS IN CHAPTER 7

Sample calculation for the determination of $D_{es}$

$\tau$ was estimated using the method shown in the figure below:

\[ \tau = 1560 \text{ s} \]
\[ \rho_{CaO} = 0.059 \text{ mol/cm}^3 \]
\[ C_{H_2S} = 1.16 \times 10^{-7} \text{ mol/cm}^3 \]
\[ R_1 = 0.00221 \text{ m} \]
\[ R_2 = 0.00179 \text{ m} \]

And,

\[ D_{es} = \frac{\rho_{CaO} R_2^3}{3 \tau C_{H_2S}} \left( \frac{1}{R_2} - \frac{1}{R_1} \right) \]
\[
D_{ec} = \frac{0.059 \cdot (0.00179)^3}{3 \cdot 1560 \cdot (1.16 \times 10^{-7} (\frac{1}{0.00179} - \frac{1}{0.00221}) \text{ mol cm}^3 \text{ m}^{-3}} \text{ cm}^3 \text{ s mol m} = 6.6 \times 10^{-3} \text{ m}^2 \text{ s}^{-1}
\]

**Estimation of** \(X_{CaO}\)

It was assumed that the final weight gain corresponded to 100% conversion so the intermediate fractional conversion could be calculated using the following equation:

\[
X_{CaO} = \frac{W_t - W_i}{F_{CaO} \cdot W \left( \frac{M_{CaS} - M_{CaO}}{M_{CaO}} \right)}
\]

where the fractional amount of CaO is,

\(F_{CaO} = 0.963\) (lime core pellets)

\(F_{CaO} = \Delta W / [(M_{CaS} / M_{CaO} - 1) \times W_i]\) (core-in-shell pellets)

\(W_i = \) initial pellet weight

\(W_t = \) weight of pellet at time t

\(\Delta W = \) total weight change

\(M_{CaO} = \) molecular weight of CaO

\(M_{CaS} = \) molecular weight of CaS
REFERENCES


Yoo, H. J.; Steinberg, M. Calcium Silicate Cement Sorbent for H$_2$S Removal and Improved Gasification Process, Final Report DOE/CH00016-1494; 1983.


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