

ENGINEERING A NEW MATERIAL  
FOR HOT GAS CLEANUP

Annual Technical Progress Report

July 1, 1999 – December 31, 1999

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ABSTRACT

The engineering development of a promising sorbent for desulfurizing hot coal gas was initiated and preliminary results are presented. The sorbent is calcium-based and is designed to be regenerated and reused repeatedly. It is prepared by pelletizing powdered limestone in a rotating drum pelletizer followed by the application of a coating which becomes a strong, porous shell upon further treatment. The resulting spherical pellets combine the high reactivity of lime with the strength of an inert protective shell. Preliminary work indicates that a satisfactory shell material is comprised of a mixture of ultrafine alumina powder, somewhat coarser alumina particles, and pulverized limestone which upon heating to 1373°K (1100°C) becomes a coherent solid through the mechanism of particle sintering. Several batches of core-in-shell pellets were prepared and tested with encouraging results.

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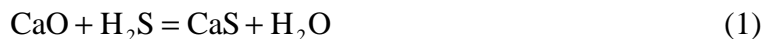
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## INTRODUCTION

This progress report presents the initial results of a new project which has as its overall purpose the engineering development of a superior, reusable calcium-based sorbent for desulfurizing hot coal gas. The project will build upon the results of a previous study which showed that a promising sorbent can be prepared by pelletizing a mixture of pulverized limestone and a calcium aluminate cement in two stages so as to produce a layered structure (1). By using a smaller concentration of cement (e.g., 20 w/w%) in the first stage and a larger concentration (e.g., 40 w/w%) in the second stage, composite pellets can be produced which have relatively weak but highly reactive cores encased in stronger but less reactive shells. The best results were achieved with a calcium aluminate refractory cement which was steam cured and then calcined at 1000°C. Pellets were produced which had a diameter of 4.76 mm and apparent porosity of 65.5%. These pellets were capable of resisting a compressive force of 11.5 N/mm before breaking and underwent an increase in weight of 7.83% when treated with a gas stream containing 1.1% H<sub>2</sub>S at 880°C for 1.0 hr. The increase in weight was believed due to the following chemical reaction:



The present project will seek to improve upon these results by considering other types of cements designed for high temperature applications and by considering pellet-coating materials which can produce a strong, porous shell through the mechanism of powder sintering. While there are a number of materials which can be sintered at high temperature to produce strong porous structures, alumina is one of the more promising since it is relatively inert under the conditions for the proposed sorbent usage.

Because of its promise, alumina was chosen as a shell material for an initial series of sorbent formulations. To develop a suitable material for the shell, two different grades of alumina powder were combined in different proportions together with varying amounts of pure calcium carbonate. The different shell formulations were molded into small tablets which were subsequently sintered and then subjected to a compression test. The strongest material was then utilized in the preparation of several batches of core-in-shell pellets which were made to study the effects of core formulation, pellet diameter and shell thickness on the overall compressive strength and adsorption capacity of the pellets. Other properties of the pellets such as pore volume and apparent porosity were also determined.

### EXECUTIVE SUMMARY

The initial results of a new project are presented. This project is directed towards the engineering development of a superior and reusable calcium-based sorbent for desulfurizing hot coal gas and builds on the results of a previous study which showed that a promising sorbent can be prepared by a two-stage pelletization method. The method produces spherical pellets with a limestone core encased in a strong but porous shell. The main goal of the present project is to improve certain properties of the sorbent such as its strength, durability, and adsorption capacity so that it can become a practical and economical material to use.

The immediate effort is aimed at improving the properties of the shell by making it out of powdered alumina followed by sintering. Initial results indicate that a relatively strong material can be made by combining ultrafine alumina powder with somewhat coarser alumina particles and pulverized limestone and then sintering the mixture at 1373°K (1100°C). It has also been found that the compressive strength of the limestone core can be improved by incorporating 10 to 20% ultrafine alumina powder in the core but with some loss in apparent adsorptive capacity. Several batches of core-in-shell pellets have been made with the sintered alumina shell and with varying amounts of alumina in the core. In some cases the compressive strength of the pellets was adequate for fixed bed applications. Also the adsorption capacity seemed adequate based on the gain in weight of the sorbent when it was exposed to a gas mixture containing 1.1% H<sub>2</sub>S at 1153°K (880°C) for 1 hr.

## EXPERIMENTAL

### Materials

Several materials were used for the preparation of different sorbent formulations. One of the principal materials 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. According to the suppliers, the Iowa limestone contained over 99%  $\text{CaCO}_3$ , whereas the Kentucky limestone typically contained 92.8%  $\text{CaCO}_3$ , 5.9%  $\text{MgCO}_3$ , and 1.1%  $\text{SiO}_2$  after drying. Reagent grade  $\text{CaCO}_3$  was also used in certain shell formulations. The shell formulations were largely a mixture of A-16 SG alumina powder and T-64 tabular alumina particles. The first material had a median particle diameter of 0.88  $\mu\text{m}$  and the second a median particle diameter of 8.65  $\mu\text{m}$ . Both materials were supplied by Alcoa.

### Methods

To investigate the properties of various shell formulations, A-16 SG alumina powder and T-64 tabular alumina were combined in various proportions and then mixed with water to form a very 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. The tablets were subsequently tested to determine the force required to break a tablet when a single sample was placed on edge 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 tablets selected at random from each batch of tablets.



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 in the drum. Limestone particles in the 44 to 297  $\mu\text{m}$  size range were used. While the drum was turned 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 optimum shell formulation which consisted of 48% T-64 tabular alumina, 32% A-16 SG alumina, and 20% limestone (-297/+44  $\mu\text{m}$ ). While the drum speed was kept constant, a measured amount of the coating material was added gradually as the pellets were sprayed with a 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.

The compressive strength of the spherical pellets was determined by measuring the force required to break a pellet when a single sample 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 adsorption characteristics of the pellets was determined by measuring the gain weight of a

sample when it was exposed to a stream of gas containing 1.1% H<sub>2</sub>S at 880°C for 1.0 hr.

Other properties of the pellets were determined by standard methods.

## RESULTS AND DISCUSSION

### Shell Formulations

To study the effect of composition on the breaking strength of the pellet shell material, 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 crushing force for a given composition. It can be seen that the strength of the material was a maximum when the material contained about 60% T-64 alumina or, in other words, when the ratio of T-64 alumina to A-16 SG alumina was 3:2.

Several additional batches of tablets were prepared to study the effect of adding either pure calcium carbonate or Iowa limestone to the 3:2 mixture of T-64 alumina and A-16 SG alumina. The tablets were prepared and tested as described above, and the results are

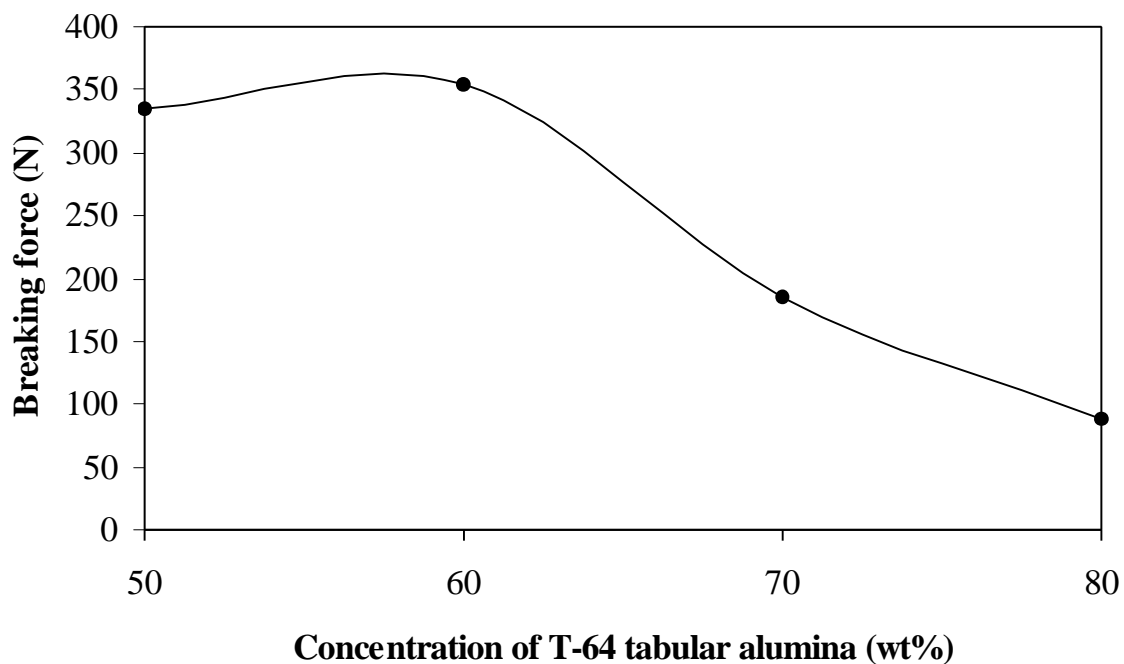


Figure 1. Effect of composition on compressive strength of tablets made with a mixture of T-64 alumina and A-16 SG alumina powders.

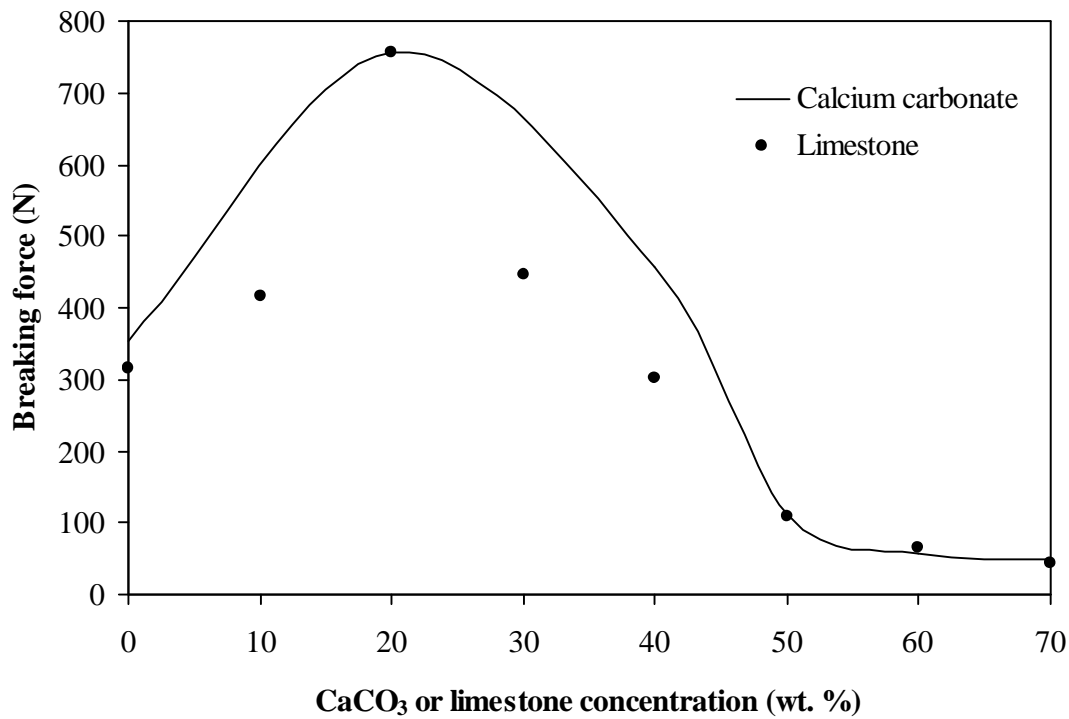


Figure 2. Effect of CaCO<sub>3</sub> or limestone concentration on compressive strength of tablets made with 3:2 ratio of T-64 alumina to A-16 SG alumina.

presented in Figure 2. The results obtained with Iowa limestone are very similar to those obtained with pure calcium carbonate. It is apparent that the crushing strength of the material is a maximum when 20%  $\text{CaCO}_3$  is incorporated in the formulation. For this formulation the crushing strength is nearly twice that of the formulation which does not contain calcium carbonate. However, when the calcium carbonate content is increased beyond the optimum level, the crushing strength decreases rapidly. The results suggest that with the optimum level of  $\text{CaCO}_3$  a calcium aluminate compound ( $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ ) probably forms upon sintering because the ratio of  $\text{CaO}$  to  $\text{Al}_2\text{O}_3$  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. However, when excess calcium carbonate is incorporated in the formulation, free  $\text{CaO}$  could be present in the calcined product which serves to weaken the material.

Remarkably, when Kentucky limestone was substituted for pure  $\text{CaCO}_3$  in the optimum formulation, the crushing strength of the material was nearly double that of the material made with pure  $\text{CaCO}_3$ . Therefore, the higher level of impurities in the Kentucky limestone seems to have a profound effect on the crushing strength which was due most likely to enhanced reaction or sintering kinetics.

#### Core-in-Shell Sorbent Pellets

To investigate the effect of incorporating various amounts of A-16 SG alumina in the core and the effects of pellet diameter and shell thickness on the properties of the sorbent, several 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.

The nominal diameter of the finished core or pellet was determined by comparing the core or pellet to a standard screen opening.

The effects of incorporating some A-16 SG alumina in the pellet core and varying the shell thickness are indicated by the results presented in Table 1. In each case the ratio of the breaking force to the pellet diameter is reported, and the reported value is an average for two or more batches of pellets and for several pellets within each batch. The reported adsorption capacity is based on several pellets within a single batch for each case. The 95% confidence limits for the mean adsorption capacity and breaking force are also indicated. For both sizes of pellets, the crushing strength was improved by having 10% A-16 SG in the core, but increasing the alumina content of the core to 20% produced mixed results. It is clear that the adsorption capacity of the pellets increased as the limestone content of the core formulation increased. On the other hand, neither the crushing strength nor the adsorption capacity of the pellets was affected by a small difference in shell thickness. In the end only sorbents B and D appeared to have sufficient strength for fixed-bed applications since it has been suggested that the minimum breaking force for such applications is 8.9 N/mm (2). Because the adsorption capacity of sorbent B was greater than that of sorbent D, sorbent B was chosen for further study.

Four additional batches of pellets were produced having the same formulation as sorbent B except that in one case Kentucky limestone was substituted for Iowa limestone. In other words, all of the pellet cores were made with 10% A-16 SG alumina and 90% limestone, and all of the pellet shells were made with the optimum composition. The finished pellets were subjected to a more detailed characterization than was employed with

Table 1. Adsorption capacity and crushing strength of core-in-shell sorbents made with Iowa limestone.

Sorbent	Core limestone conc., wt. %	Nominal diameter, mm		Shell thick., mm	Ave. breaking force, N/mm	Adsorption <sup>a</sup> cap., wt. %
		Core	Pellet			
A	80	3.35	3.96	0.30	7.57 ± 1.35	6.99 ± 0.24
B	90	3.35	3.96	0.30	8.94 ± 1.39	7.20 ± 0.94
C	100	3.35	3.96	0.30	3.39 ± 0.79	12.26 ± 2.33
D	80	3.96	4.76	0.40	9.64 ± 1.76	4.80 ± 2.10
E	90	3.96	4.76	0.40	4.03 ± 0.33	8.14 ± 1.44
F	100	3.96	4.76	0.40	3.15 ± 0.74	12.80 ± 1.06

<sup>a</sup>Gain in weight of sorbent exposed to 1.1% H<sub>2</sub>S at 880°C for 1 hr.

previous batches of pellets. The results presented in Table 2 show that the overall pellet diameter and shell thickness varied somewhat among batches. The pellet dimensions were determined more accurately than before by measuring the overall diameter and shell thickness of a number of pellets with a hand held caliper and averaging the results.

The fractional shell volume was calculated by using the following equation:

$$V(\%) = \left(1 - \frac{d^3}{D^3}\right) 100 \quad (2)$$

where  $d$  is the core diameter and  $D$  is the overall pellet diameter. The ratio of pellet breaking force to pellet diameter is reported as well as the pellet breaking pressure, which is the ratio of the breaking force to the pellet cross-sectional area. The breaking force was adequate in all cases for most applications, and it increased with shell thickness. The breaking force did not vary significantly between the Iowa and Kentucky limestones. However, the Kentucky limestone had a greater adsorption capacity as indicated by its gain in weight when exposed to  $H_2S$ . While the last two sorbents were stronger than the first two, their adsorption capacity was lower. These effects were due in all likelihood to the greater shell thickness of the last two materials.

Several core-in-shell pellets were cross-sectioned and examined with a scanning electron microscope both before and after calcination at  $1100^\circ C$  for 2 hr. In both cases 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. After calcination the texture of the shell material was much finer

Table 2. Specific characteristics of various core-in-shell sorbents

Sorbent	G	H	I	J
Source of Limestone	Iowa	Kentucky	Iowa	Iowa
Pellet diameter (mm)	4.20 ± 0.06	4.23 ± 0.13	5.88 ± 0.12	4.80 ± 0.20
Shell thickness (mm)	0.40 ± 0.04	0.42 ± 0.05	0.55 ± 0.05	0.78 ± 0.03
Fractional shell volume (%)	47 ± 3	48 ± 3	46 ± 3	69 ± 2
Compressive strength (N/mm)	8.94 ± 1.39	8.57 ± 1.79	10.82 ± 1.17	16.44 ± 0.48
Compressive pressure (kPa)	2877 ± 447	2758 ± 575	3485 ± 376	5293 ± 155
Apparent density (g/cm <sup>3</sup> )	3.40 ± 0.05	3.30 ± 0.03	3.35 ± 0.25	3.46 ± 0.04
Pore volume (cm <sup>3</sup> /g)	0.294 ± 0.004	0.303 ± 0.003	0.300 ± 0.022	0.289 ± 0.003
Apparent porosity (%)	52.7 ± 3.8	38.4 ± 4.8	40.2 ± 3.0	43.8 ± 0.0
Adsorption capacity (%) <sup>a</sup>	7.20 ± 0.94	11.34 ± 2.02	3.47 ± 0.60	4.83 ± 0.46

<sup>a</sup>Gain in weight of sorbent exposed to 1.1% H<sub>2</sub>S at 880°C for 1 hr.



due to the particle sintering which had taken place. In both cases the texture of the core material was relatively fine. A number of holes or voids could be seen in both the core and shell both before and after calcination.

### CONCLUSIONS

The initial results of this project are highly encouraging because they have demonstrated the feasibility of using a sinterable powder for making the protective shell of a pelletized sorbent for hot gas desulfurization. Although it had been shown previously that a core-in-shell sorbent could be made by encasing a limestone pellet in a shell made largely of hydraulic cement, the latest work has shown that a strong, porous protective shell can be made by coating a limestone pellet with particles of alumina followed by high temperature treatment to sinter the particles. It has been found advantageous to combine ultrafine alumina particles which are highly sinterable with somewhat coarser and more stable alumina particles for this purpose. Also it has proved advantageous to incorporate some limestone particles in the coating mixture. Furthermore, the overall compressive strength of a core-in-shell pellet can be improved by incorporating 10-20% alumina in the form of ultrafine particles in the limestone core. However, this tends to reduce the adsorption capacity of the material.

### REFERENCES

1. T. D. Wheelock, L. K. Doraiswamy, K. Constant, T. Akiti, and J. Zhu, "Development of a Calcium-Based Sorbent for Hot Gas Cleanup," Semi-annual Technical Progress Report, April 1, 1999 – September 30, 1999, Chemical Engineering Department, Materials Science and Engineering Department, and Center for Sustainable Environmental Technologies, Iowa State University, Ames, Iowa.

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