

DEVELOPMENT OF A CALCIUM-BASED SORBENT
FOR HOT GAS CLEANUP

Semi-Annual Technical Progress Report

October 1, 1998 – March 31, 1999

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ABSTRACT

The preparation and testing of potential sorbents for removing H₂S and COS from hot coal gas continued. Two preparation methods received the most consideration. Both methods involve pelletizing powders in a revolving drum under moist conditions followed either by heat treatment or steam curing to harden the pellets, depending on the particle bonding mechanism. One method was used to pelletize mixtures of calcium carbonate and either alumina or a calcium aluminate cement in a single step. Another method was used to pelletize powdered limestone in an initial step followed by the application of a coating consisting of both limestone and a hydraulic cement in a second step. By employing this method, an especially promising material was produced consisting of a limestone core surrounded by a shell consisting initially of 80 wt.% limestone and 20% wt.% calcium aluminate cement. The best material exhibited both an acceptable crushing strength and adsorption capacity for H₂S.

TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY	1
INTRODUCTION	1
RESULTS AND DISCUSSION	3
Single Step Pelletization of Powder Mixtures	3
Two Step Pelletization	6
Slip Casting of Composite Materials	8
CONCLUSIONS	9
REFERENCES	10

EXECUTIVE SUMMARY

The overall purpose of this project is the development of a superior calcium-based sorbent for hot gas cleanup in IGCC power generation systems. The sorbent should be capable of removing H₂S and COS from hot coal gas and should withstand repeated loading and regeneration.

After investigating several different sorbent preparation methods, attention has focused on two methods which seem most promising. Both methods involve the pelletization of powders in a revolving drum under moist conditions followed either by heat treatment or steam curing to harden the pellets, depending on the particle bonding mechanism. One method produces relatively homogeneous pellets in a single step by pelletizing a powder mixture comprised of either calcium carbonate or limestone and a bonding material such as alumina or a hydraulic cement. Another method produces pellets consisting of a limestone core surrounded by a shell composed of both limestone particles and a hydraulic cement. This method requires two pelletization steps, one step to form the core and another step to form the shell.

Both methods have been utilized to produce pellets which appear to have the necessary porosity, crushing strength, and stability to serve as high temperature sorbents in fixed beds. However, the adsorption and regeneration characteristics of the materials have not been evaluated beyond preliminary tests of adsorption. More consideration will be given to this aspect in the coming months.

INTRODUCTION

The principal goal of this project has been the development of a strong and regenerable, calcium-based sorbent capable of removing all but traces of hydrogen sulfide from hot coal gas. Several general methods of preparing sorbents have been utilized to combine lime or limestone

with a variety of other materials to produce composites which it is hoped will retain the ability of lime to adsorb and react with hydrogen sulfide at high temperature while being stronger and more durable than lime. One of the more promising methods involves pelletizing powdered limestone and cement under moist conditions in a revolving drum followed by steam curing (1-3). A less promising method involves briquetting powder mixtures by the application of high pressure followed by heat treatment to cause sintering. When this method has been applied to mixtures of various calcium compounds and either silica or alumina, the resulting composites have either proved unstable or incapable of adsorbing more than a small amount of hydrogen sulfide (1,2). Therefore, briquetting has been set aside in favor of pelletization and other methods which hold more promise.

The results reported below were largely achieved by employing the pelletization method although some results were obtained by using a slip casting method to prepare composites. Two different pelletization procedures were employed. One procedure involved pelletizing in a single step a powder mixture comprised of two components, one component being either pure calcium carbonate or limestone and the other component being either pure alumina or a calcium aluminate cement. The other procedure involved pelletizing powdered limestone in an initial step followed by the application of a coating, which consisted of a mixture of powdered limestone and cement, in a second step. The second procedure produced a pellet with a soft inner core of lime encased in a hard but porous shell. Both procedures have provided encouraging results, and their development is continuing.

RESULTS AND DISCUSSION

Single Step Pelletization of Powder Mixtures

Due to the encouraging results achieved previously by pelletizing powdered limestone and cement under moist conditions (1-3), further development of the method was undertaken, and the procedure was extended to other materials including mixtures of calcium carbonate and calcined alumina. Pure calcium carbonate powder which appeared to be finer than 200 mesh and premium reactive grade calcined alumina powder finer than 325 mesh were selected. The alumina was 99.8% pure according to the supplier, Alcoa, and bore the designation A-16. The powders were blended in various proportions and then pelletized in a revolving drum by the careful addition of moisture in the form of a fine spray. Each batch of pellets was treated for 1.0 hr in the pelletizer and then was air-dried for approximately 2 hr. The pellets were subsequently heated gradually over a 12 hr period to reach a preselected induration temperature in the range of 900 to 1100°C. After the pellets had been held at this temperature for 2.0 hr, they were cooled gradually back to room temperature over a 10 hr period. The crushing strength and porosity of the heat-treated pellets were determined, and the results are indicated in Figures 1 and 2 for 5 mm diameter, approximately spherical pellets. It can be seen that as the induration temperature was raised, the crushing strength increased gradually, and the porosity decreased. Also as the calcium carbonate content of the initial mixture rose, the crushing strength of the final product fell while the porosity of the product increased. When a sample of the product made from a mixture with 60 wt.% CaCO_3 and heat-treated at 1000°C was exposed to a gas stream containing 1.1 mole% H_2S at 880°C for 1.0 hr, it exhibited a weight gain of 4.75% which showed that the material was capable of adsorbing H_2S . Although the material appeared stable

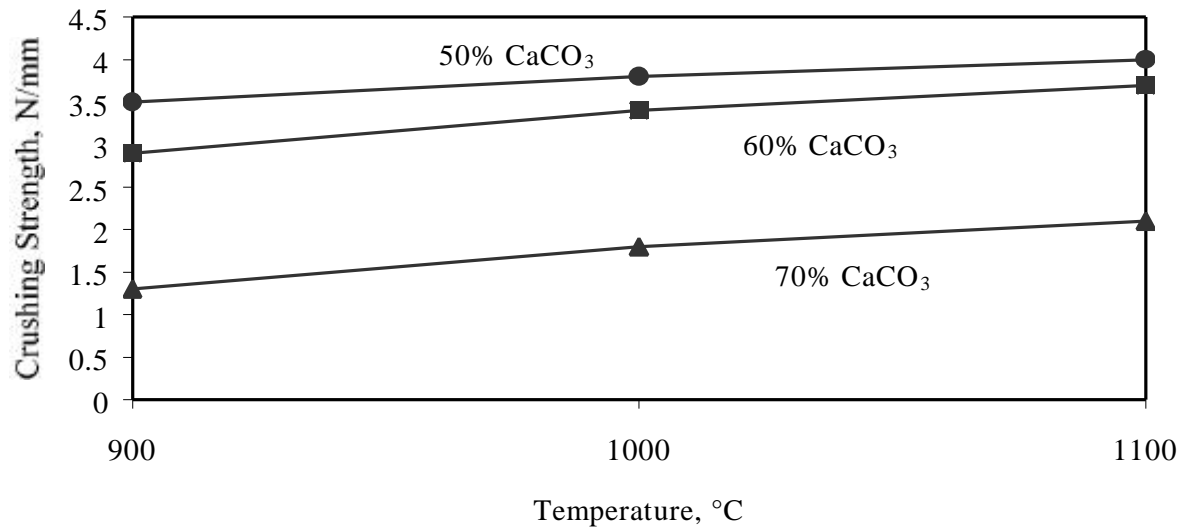


Figure 1. Crushing strength of 5 mm diameter pellets made with CaCO₃ and Al₂O₃ and subsequently calcined.

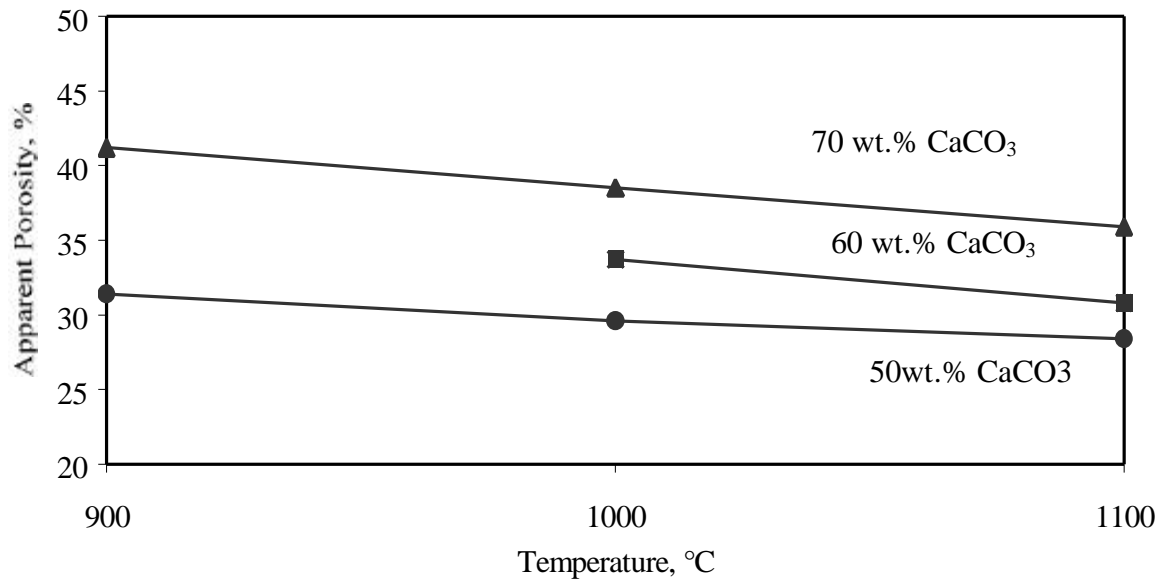


Figure 2. Apparent porosity of 5 mm diameter pellets made with CaCO₃ and Al₂O₃ and subsequently calcined.

in that it did not crack nor disintegrate, the crushing strength of the 5 mm diameter pellets was on the low side.

Additional experimentation with the pelletization method produced 8-9 mm diameter pellets which were more spherical, denser, and much stronger than the smaller pellets. The larger pellets made from a mixture with 60 wt.% CaCO_3 and heat-treated at 1000°C exhibited a crushing strength of 15.4 N/mm in contrast to 3.4 N/mm for the smaller pellets. The adsorption capacity of the larger pellets is under investigation.

The same pelletization method was also applied to mixtures of powdered limestone and CA-14 calcium aluminate cement produced by Alcoa. Since this is a hydraulic cement, the pellets had to be cured under moist conditions to achieve the necessary strength. Steam curing for three days was used for this purpose. The sample of limestone selected for initial testing came from the Ames, Iowa, quarry of Martin Marietta Co. The limestone was ground finely before blending with the cement powder. Two different mixtures were investigated. One mixture contained 50 wt.% limestone and the other contained 65 wt.%. Pellets having a diameter of 6 mm were produced. The cured but unfired pellets exhibited a crushing strength of 93.1 N/mm in the case of the material with 50 wt.% limestone and 56.7 N/mm in the case of the material with 65 wt.% limestone. After the pellets had been calcined at 1000°C for 2 hr, the crushing strength decreased to 24.4 N/mm for the first material and 14.8 N/mm for the second material. Since these values compare favorably with the best values obtained with other materials, the results are encouraging and warrant further investigation of the adsorption capacity.

Two Step Pelletization

Previous work indicated that the application of a cement coating over limestone pellets would produce a product which combines the high reactivity of lime with the strength of cement (2,3). This work was continued using limestone from the Three Rivers Quarry located near Smithland, Kentucky. Type III Portland cement (PC-III) from Holnam Inc. and CA-14 calcium aluminate cement from Alcoa were used for coating. Both of these cements are hydraulic cements which require curing under moist conditions. The two step procedure involved pelletizing the pulverized limestone in a revolving drum by the application of a fine water spray in the first step followed by the application of a cement coating in the second step using the revolving drum and similar conditions. While most of the water required for pelletization of the limestone in the first step was introduced in the first 5 min. and the material balled up rapidly, it was found that by extending the tumbling time to 60 min., the sphericity and uniformity of the pellets were improved. During this time the surface of the pellets was kept moist by spraying the pellets occasionally. After the first step was completed, the pellets were separated into various sizes by hand screening with 5, 6, and 7 mesh screens. Next a batch of uniformly sized pellets was returned to the pelletizing drum for coating with cement.

To obtain the results reported below, the limestone pellets were prepared by using -297/+210 μ m size particles. For the coating, limestone particles of the same size were premixed with cement powder, and then the mixture containing 80 wt.% limestone and 20 wt.% cement 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.

Table 1. Breaking force and adsorption capacity of limestone pellets coated with a mixture of 80% limestone and 20% cement.

Pellet coating		Pellet dia., mm	Tumbling time, min.	Force/diam., N/mm		Wt. gain, %
Cement	Thick., mm			Cured	Calcined	
PC-III	0.40	4.76	15	5.8	<1	16.0
PC-III	0.40	4.76	60	16.1	<1	9.9
PC-III	0.40	4.76	120	18.7	<1	8.3
CA-14	0.40	4.76	15	4.8	1.5	17.5
CA-14	0.40	4.76	60	7.6	2.6	14.1
CA-14	0.40	4.76	120	12.1	2.1	13.7
CA-14	0.83	5.62	120	20.7	13.6	11.4

Type III Portland cement was used for some batches and CA-14 refractory cement for other batches.

The prepared pellets were characterized by measuring the force required to crush the pellets after curing and after calcining at 1000°C and by measuring the gain in weight of the pellets exposed to a gas stream containing 1.1 mole % H₂S at 880°C for 1.0 hr. The results presented in Table 1 indicate that with either type of cement the force required to break the cured but uncalcined pellets increased with tumbling time. Also the breaking force for the uncalcined pellets was greater for pellets coated with a mixture of type III Portland cement than with a mixture of CA-14 cement. Although both types of pellets exhibited a loss in crushing strength upon heating and reaction with H₂S, the pellets coated with Portland cement exhibited the greatest loss. Also the pellets coated with a mixture of Portland cement tended to crack and fall apart during reaction with H₂S, while those coated with a mixture of CA-14 cement held up better. Furthermore, pellets coated with a mixture of CA-14 cement exhibited larger weight gains when reacted with H₂S. Finally by employing CA-14 cement in the coating and increasing

the coating thickness to 0.83 mm, pellets were produced which after 2.0 hr of tumbling and 3 days of steam-curing, were much stronger both before and after calcining than pellets made with a thinner coating. Although the pellets with the thicker coating exhibited a slightly lower adsorption capacity than those with a thinner coating, they still experienced a weight gain of 11.4% when reacted with H₂S. Therefore, both the crushing strength and adsorption capacity of these pellets appeared to be in an acceptable range for practical application. Consequently, the method of preparation warrants further development.

Slip Casting of Composite Materials

Slip casting is another widely used method for preparing composite materials. It was applied to the four different mixtures listed in Table 2. Pure materials including A-16 calcined alumina were used for preparing the mixtures. Boron oxide was added to Mixtures III and IV to stabilize $\alpha - \text{Ca}_2\text{SiO}_4$ which might form. Darvan 7 was included in all of the mixtures to serve as a particle dispersant. Each powder mixture was dispersed in an equal amount of water by weight, thoroughly mixed, and then poured into a mold placed on a plaster slab. This procedure produced a quantity of tablets that were 12.7 mm (0.50 in.) in diameter and approximately 6 mm (0.25 in.) thick. The tablets were dried for 3 days and then heated gradually to 900°C where they were held for 2 hr before cooling gradually back to room temperature. The apparent porosity and the pressure required to crush the tablets were determined subsequently and are indicated in Table 3. Both of these properties were relatively large for all of the mixtures which was a favorable indication. However, after the tablets had been exposed to a laboratory atmosphere for about a week, they began to disintegrate, so they lacked long term stability.

Table 2. Composition of various mixtures employed for slip casting.

Component	Concentration, Wt. %			
	Mixture I	Mixture II	Mixture III	Mixture IV
CaCO ₃	55	70		
Al ₂ O ₃	40	25		
Darvan	5	5		
CaCO ₃			54	72
SiO ₂			36	18
B ₂ O ₃			5	5
Darvan			5	5

Table 3. Properties of materials produced by slip casting and treatment at 900°C.

Mixture	Apparent Porosity %	Crushing Pressure	
		kPa	lb/in ²
I	37.5	447	64.9
II	42.6	370	53.6
III	40.8	419	60.9
IV	60.8	294	42.7

Slip casting appears to hold more promise for preparing tablets composed of relatively large limestone particles embedded in a matrix of hydraulic cement. Alcoa CA-14 cement seems particularly well suited for such an application and will be tested in the near future.

CONCLUSIONS

Several potential sorbents for H₂S in hot coal gas were prepared by pelletizing various powders in a revolving drum under moist conditions. Relatively homogeneous spherical pellets were prepared in a single step by pelletizing a mixture composed of calcium carbonate and either A-16 calcined alumina or CA-14 hydraulic cement. The pellets made with alumina were

hardened by heat treatment while the pellets made with cement were hardened by steam curing. In both cases the resulting pellets were reasonably strong and also stable. Therefore, the gas adsorption characteristics of the pellets will be determined in the future.

Other spherical pellets consisting of a limestone core surrounded by a shell composed of both limestone particles and a hydraulic cement were produced by a two step pelletization process and subsequent steam curing. The crushing strength and adsorption characteristics of the pellets were affected by the type of cement, tumbling time in the pelletizer, and shell thickness. The best combination of crushing strength and adsorption capacity was achieved by using CA-14 calcium aluminate cement in a relatively thick shell treated to a long tumbling time. The resulting material exhibited acceptable crushing strength and adsorption capacity and, therefore, warrants further development and evaluation.

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