A GRANULATION/SINTERING METHOD FOR THE CODISPOSAL OF SOLID RESIDUES FROM COAL CONVERSION PROCESSES

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ABSTRACT

A stabilization process for coal cleaning and coal combustion-related wastes has been developed that uses the energy derived from the fuel contained in the coal cleaning waste. The wastes are pulverized, when necessary, formed into granules in a rotary pan agglomerator, and then fired to a sintering temperature. The resulting readily disposable product consists of rock-hard granules that are highly resistant to environmental degradation. The green (nondried and nonfired) granules satisfy durability tests that measure the capability to be handled and stored. The sintered granules meet requirements of the standard ASTM and EP leaching tests and a freeze-thaw cycle test. The strength of the sintered granules compares favorably with the strength of natural aggregates. The process has been applied to coal cleaning refuse alone and to refuse/fly ash and refuse/FGD sludge mixtures.

INTRODUCTION

Disposal of coal cleaning and of coal combustion wastes looms as a significant problem for many coal producers and utilities. This has stimulated research on environmentally acceptable alternatives to current disposal practices. About 35% of the nearly 700 million tons of coal consumed by utilities each year receives some cleaning before it is burned (1). Most of the cleaning is performed on eastern and midwestern bituminous coals, resulting in an annual production of coal cleaning wastes in excess of 100 million tons (2). The waste piles are a source of severe air, stream, and ground water pollution (3).

Other environmentally troublesome solid wastes result from coal combustion and are proving to be even more difficult to deal with. For every three tons of coal cleaning refuse, about one ton of ash and one ton of flue gas desulfurization (FGD) solids result from combustion of the clean coal produced. Besides contributing to pollution, the waste disposal sites required mar the landscape and consume large amounts of land area.

The principle combustion-related solid waste today is fly ash from the burning of pulverized coal. In spite of vigorous research and marketing efforts, uses have been found for only about one-fifth of nearly 50 million tons of fly ash produced each year (4). Disposal is the only practical option available today for wet or dry FGD wastes. More than 150 U.S. utility installations generating wet scrubber sludge are operating, under construction or planned, with a total capacity of over 70,000 MWe (5). About 25 million tons (dry basis) of sludge or 50 million tons of wet vacuum filter cake are now generated annually and, as new systems come online, this amount will increase significantly.

A potentially beneficial approach to the disposal of the above wastes could be pretreatment in the form of stabilization or fixation. The research work reported herein deals with development of a stabilization by sintering process for the above wastes that uses the energy derived from fuel contained in the coal cleaning refuse itself. The process calls for pulverizing the wastes when necessary, forming them into granules in a rotary pan agglomerator, and then firing the granules to a sintering temperature. The resulting, readily disposable product consists of rock-hard granules that are highly resistant to environmental degradation. A flowsheet for the process is shown in Figure 1.

Stabilization results are reported for coal cleaning refuse alone and for refuse/fly ash and refuse/sludge mixtures. The amount of carbon in the granules is critical to their behavior during combustion/sintering. Other investigators (6,7) have found that a carbon content of 5-10$\%_w$ is sufficient to achieve the desired level of sintering. If the carbon content is too high, the granules overheat upon combustion of the fuel present and soften, forming a slag. Blending fly ash or FGD sludge with the refuse provides the necessary reduction in carbon content per unit weight of granules and an effective means for disposing of these wastes.

DESCRIPTION OF WASTES USED

Analyses of the coal cleaning and coal combustion wastes used are given in Table 1. The coal cleaning refuse was collected at the Peabody Coal Company River King coal preparation plant in Freeburg, Illinois. The waste was derived from Illinois No.6 coal which is high volatile C, bituminous, medium heating value (24,400 kJ/kg; 10,500 Btu/lb, as received) and medium sulfur (4.5$\%_w$). The coal is cleaned of unwanted clay, pyrite, and other impurities by jigging at a rate of up to 800 tons/hr. The major minerals present in the raw refuse are illite, kaolinite, quartz, calcite, and iron pyrite.

Table 1. Analyses of Coal Cleaning and Coal Combustion Wastes

Item	Weight Percent or Value		
	Cleaning Refuse[a]	Fly Ash[b]	FGD Sludge[b]
Constituent			
Al_2O_3	15.1%	19.8%	3.4%
CaO	5.7%	24.9%	33.7%
SiO_2	43.8%	34.4%	15.6%
Fe_2O_3	13.5%	5.1%	6.1%
MgO	n.a.[c]	4.0%	0.6%
Na_2O	n.a.	2.1%	0.2%
K_2O	n.a.	0.3%	n.a.
TiO_2	n.a.	1.5%	n.a.
P_2O_5	n.a.	1.8%	n.a.
C	13.9%	n.a.	n.a.
S (inorganic)	6.0%	n.a.	n.a.
S (total)	7.3%	0.7%	5.4%
H_2O	4.5%	-	-
LOI	24.3%	0.2%	n.a.
Value			
Heating value (gross)	6055 kJ/kg (2610 Btu/lb)		

[a] Air dried from an as-received moisture content of 20$\%_w$.
[b] Reported on a dry basis. The sludge contained 26.5$\%_w$ total C reported as CO_2.
[c] n.a. denotes not analyzed for.

The as-received refuse contained lumps as large as 8 cm in diameter and had to be ground to a size suitable for granule formation. The refuse was ground using two passes through a Holmes hammer mill equipped first with a screen with 3/16 in. circular holes and then a screen with 1/16 in. circular holes. The weighted average diameter of the product was about 330 microns; $95\%_w$ was retained on a 325 mesh screen.

The fly ash used was obtained from the Ottumwa power station of Iowa Southern Utilities in Ottumwa, Iowa and was from combustion of a subbituminous coal mined near Gillette, Wyoming. The particle size of the ash was such that about $20\%_w$ was retained on a 325 mesh screen. The FGD sludge came from the LaCygne station of the Kansas City Power and Light Company near Kansas City, Missouri. The plant was burning Missouri subbituminous coal and using a wet limestone scrubber that produced a non-oxidized sludge. The limestone was ground to about 70 microns prior to slurrying and the crystals of sulfur-containing compounds formed ranged from 5-200 microns. The S was present $78\%_w$ as $CaSO_3 \cdot \frac{1}{2}H_2O$ and $22\%_w$ as $CaSO_4 \cdot 2H_2O$; $78\%_w$ of the Ca was present as $CaCO_3$.

PREPARATION OF GREEN GRANULES

Granules as formed in the pan agglomerator are referred to as green granules. The parameters controlling green granule formation are the particle size of the wastes, amount of water added as a binder, residence time of the granules in the agglomerator (feed rate), and the angle of inclination and rpm of the agglomerator.

The pan agglomerator (Agglomiser, 36 cm pan, 1/8 hp, Mars Mineral Corp.) was equipped with a vibratory feeder (Syntron, Model FTOC, FMC Corp.). The water to serve as the binding agent was added using an automatic spray system or a manually operated spray bottle. The refuse/ash and refuse/sludge mixtures were prepared by blending the solids in a ball mill before they were added to the agglomerator.

A batch method of operation for small scale testing was developed that gave granules of predictable and reproducible properties. Depending upon the conditions used, each run lasted for 30-80 minutes and consumed about 1500 grams of feed. Granules were removed from the pan during the run as they reached the desired product size of about 12 mm diameter.

Large quantities of green granules (10-12 kg) were subsequently prepared for sintering and testing for resistance to leaching and freeze-thaw degradation. The pan agglomerator was operated continuously at a set of conditions previously determined from the small-scale batch tests.

The green granules formed had to be sufficiently durable to withstand the vibration, attrition, compression, and similar forces that would be encountered in a commercial sintering facility. Durability was measured using the ASTM B440-49 Drop Shatter Test (modified) and a drops-to-fracture test (8). Satisfactory granules would show $95\%_w$ intact or better for the drop shatter test and 15 drops or better for the drops-to-fracture test.

In determining the optimum conditions for green granule formation, the total moisture content in the pan was varied from $15\text{-}22\%_w$, the pan angle from 45-55°, and the feedrate from 15-60 g/min. Lower moisture contents resulted in poor particle adhesion and granules that developed breakage planes easily. Higher moisture contents resulted in caking in the pan.

Steeper pan angles resulted in greater granule compaction but a reduced residence time. A pan speed of 19 rpm was found to provide the rolling and cascading action required to promote continuous granule growth. The best granules were obtained at lower feed rates where uniform granule growth occurred and the longer residence time resulted in greater granule compaction.

The best refuse only granules as determined by durability testing were obtained in the 18-20$\%_w$ moisture range using a pan angle of 45°. Refuse/fly ash granules showed lower durability and required less moisture as the ash content was increased. Very satisfactory granules containing 25$\%_w$ ash were obtained at feed rates of 15-30 g/min, a pan angle of 50°, and a moisture content of 17-18$\%_w$, wet basis.

Granule durability for refuse/sludge mixtures decreased as the sludge content increased. Depending upon the amount of sludge present, the optimum moisture content varied from 15-22$\%_w$. The best results were obtained with a pan angle of 50° and a feedrate of about 50 g/min.

The amount of refuse in a refuse/ash mixture was determined by carrying out a standard loss on ignition (LOI) test. The ash present had already been ignited when it was formed in the furnace so that the total LOI could be attributed to the refuse present. The amount of sludge in a mixture was determined by analyzing for Ca by xray fluorescence. Knowing the ratio of Ca in the sludge to that in the refuse, it was then possible to calculate the composition of the blend.

COMBUSTION/SINTERING OF THE GREEN GRANULES

To cause sintering to occur, the granules were heated in the presence of air causing the coal in the refuse to burn, thus raising the temperature of the granules to the desired sintering temperature. The green granules used had been produced using the conditions previously found to give optimum granule durability.

The effect on sintered granule properties of different time-temperature treatments was determined using small scale boat tests carried out using an electrically heated laboratory tube furnace (I.D. 3.4 cm). Five to ten granules that had been previously dried in a 100°C oven were placed in an alumina boat which was then inserted into the tube furnace preheated to the test temperature. A carefully measured flow of air (10 L/min at 1 atm. and 20°C) was then introduced into one end of the furnace tube.

Granules were sintered at temperatures ranging from 900-1200°C for 1 hour to approximate the conditions in a traveling grate furnace. The amount of sintering that had taken place was determined by subjecting the cooled sintered granules to an unconfined compressive strength test using an Instron machine. The best of the small scale test results determined the operating conditions for the production of environmental test quantities of sintered granules in a large tube furnace.

Figure 2 gives the force-at-fracture for the sintered refuse only granules as a function of sintering temperature. The granules sintered at 1200°C were very weak due to early slagging on the surface and incomplete sintering inside. Insufficient sintering overall took place at temperatures below about 1075°C. The strongest granules were produced at about 1100°C.

Similar small scale sintering tests were conducted on granules made from refuse/fly ash and from refuse/sludge mixtures. The highest force at fracture (105 lb) for refuse/subbituminous coal fly ash was obtained for a 3:1 refuse/ash mixture sintered at 1000°C. Refuse/sludge mixtures in a ratio of 4:1 gave satisfactory strength (85-90 lb) at 1050°C and at 1075°C. At 1100°C, granules of both mixtures developed a vitreous melt or slag on the surface that resulted in an undersintered core and low granule strength.

The large-scale boat tests were carried out using a large horizontal, electrically heated tube furnace and a boat (4 cm x 4 cm x 15 cm) custom made from a ceramic brick. The walls of the boat were about 8 mm thick and contained frequent holes about 6 mm in diameter to allow for passage of air and combustion gases. The boat could accommodate up to 180 g of granules.

Using the best of the conditions from the small-scale boat tests, dried green granules were placed in the large boat and introduced into the furnace which had been preheated to 600°C. The flow of combustion air was then started and the furnace temperature controls reset to 1050°C for the duration of the run. A thermocouple placed in the bed of granules indicated that the bed would reach 1050°C in about 45 minutes and a peak temperature of about 1100°C after about 60 minutes. Total residence times of 90 minutes and 120 minutes were investigated.

The individual sintered granules from the large boat tests were either red-brown or black-brown in about a 1:1 ratio. The black-brown granules were found towards the bottom of the bed where the temperature was the highest and the supply of oxygen was limited. These conditions would be similar to those encountered in the granule bed in a traveling grate furnace. The black-brown granules were significantly stronger with the strength influenced by residence time. The black color is thought to result from the presence of Fe_3O_4 and of hersynite, $FeAl_2O_4$, a spinel group that would add to granule strength. The red-brown granules were found at the top of the bed where oxygen was readily available and Fe_2O_3 would form.

For a total residence time of 90 minutes, the refuse only black-brown granules gave a force at fracture of about 120 lb, the 3:1 refuse/subbituminous coal fly ash granules 100 lb, and the 4:1 refuse sludge granules 150 lb. The compounds in the sludge facilitate sintering and increase strength.

EVALUATION OF SINTERED GRANULES

In order to be environmentally disposable, the sintered granules must be very strong, able to resist cycles of freezing and thawing, and essentially nonleachable. The latter two characteristics were measured using a standard freeze-thaw resistance test (9), shake Extraction with Water Test, ASTM D3987-81 (10), and EP Toxicity Test (11).

The concentrations of elements in the leachates from the refuse/sludge granules as determined by mass spectroscopy along with the permissible levels established by RCRA regulations (12) are given in Table 2. The results for all elements are well below the current RCRA standards. Similar satisfactory results were obtained for leachates from the sintered refuse only and refuse/fly ash granules.

The results from the freeze-thaw cycle tests were most encouraging for all three types of sintered granules. The weight loss by degradation was less than $0.5\%_w$. Natural aggregate such as crushed rock will commonly show a degradation in the range of $5\text{-}10\%_w$ (13). None of the sintered granules should offer a problem when disposed of where leaching and/or freezing weather occur.

Table 2. Leachate analysis of sintered refuse/FGD sludge granules

Element	RCRA**	Concentration of metals in leachate, ppm (mg/L)* 10% FGD ASTM	10% FGD EP	20% FGD ASTM	20% FGD EP	30% FGD ASTM	30% FGD EP	Green Granules ASTM	Green Granules EP
Al	-	.68	5.33	.51	3.74	.54	7.72	-	.55
As	5	-	-	-	.03	-	.07	-	-
Ba	100	.16	.05	.22	.05	.16	.08	-	.09
Cd	1	-	-	-	-	-	-	.024	.109
Ca	-	587	303	558	287	626	545	533	2131
Cr	5	-	-	-	-	.05	-	-	-
Fe	-	-	4	-	1.5	-	2.3	-	.1
Pb	5	-	-	.005	-	-	-	-	-
Hg	.02	.0065	.0041	.0071	.0007	.0048	.0031	.008	.0096
Se	1	.007	.009	-	-	.015	-	.34	.072
Si	-	10	23	8	18	9	42	5	4
Ag	5	-	-	-	-	-	-	-	-

* Concentrations not shown were below detection limits.
** RCRA (EPA) limits are 100 times drinking water standards.

EVOLUTION OF SULFUR DURING SINTERING

Combustion/sintering of the green granules results in release of about three-fourths of the S present as SO_2 in the off gases. A microreactor system illustrated in Figures 3 and 4 has been built to obtain a more fundamental understanding of S evolution and the reactions taking place.

The microreactor is made of stainless steel and is equipped with a combustion air distributor and a removable mount for a single granule. This arrangement ensures uniform contact between the combustion air and the granule, and control of the sintering taking place. By analysis of the off gases and the granule, the effects of sintering conditions and of granule composition, diameter, and particle size on the pattern of S evolution can be determined.

Preliminary tests have shown that a surge of SO_2 consisting of about two-thirds of the S present in the granules is released in about the first one-third of the combustion process. The SO_2 concentration in the off gases during this time would be expected to be relatively high because of the limited amount of combustion air required and the recycle of combustion air from windboxes to hoods along the traveling grate furnace. A SO_2 content of 3-5$\%_v$ appears to be readily attainable. If it proves to be unattractive to thus process all of the off gases, the more dilute fraction could be recycled to the power station FGD system. Recovery of S from the off gases as S or H_2SO_4 would serve the dual purpose of controlling S emissions and generating a valuable byproduct. Sulfur recovery from waste gas streams is a well proven and well established technology (14).

CONCLUSIONS

The combustion/sintering of granules of coal cleaning refuse or of refuse mixed with fly ash or FGD sludge has been shown to yield a strong and highly vitrified product. Durable green granules were prepared in a pan agglomerator using water as the binder. A laboratory, bench scale procedure was developed to approximate the combustion/sintering that occurs in a commercial traveling grate furnace. Most of the energy required for the sintering can be derived from the fuel inherently present in the refuse. All three types of sintered granules were found to be environmentally compatible as measured using standard ASTM and EP leaching tests and a freeze-thaw cycle test. The byproduct recovery of S from the combustion/sintering off gases looks promising based on laboratory microreactor studies.

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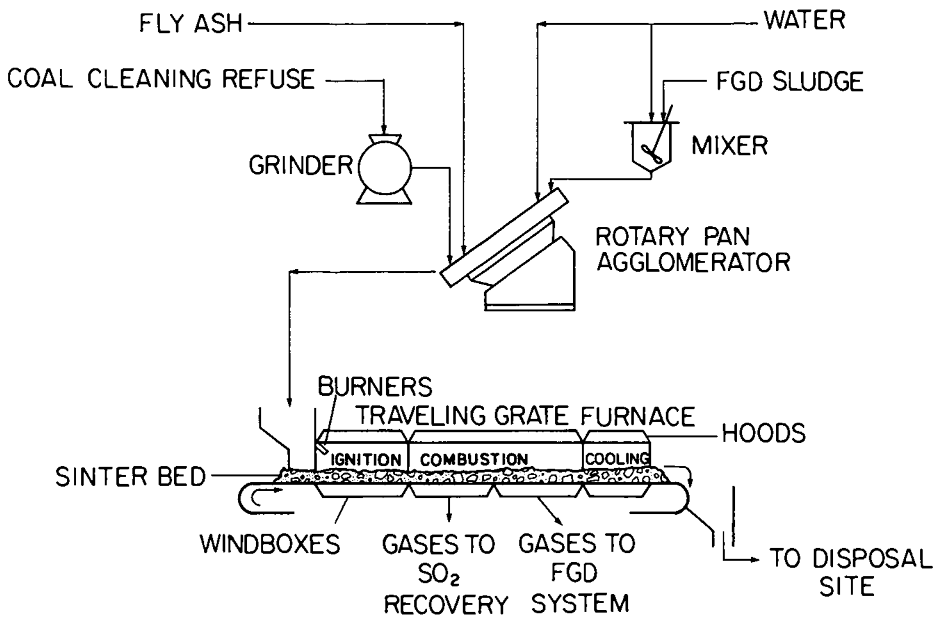

Fig. 1 Schematic flowsheet for the granulation/sintering waste stabilization process.

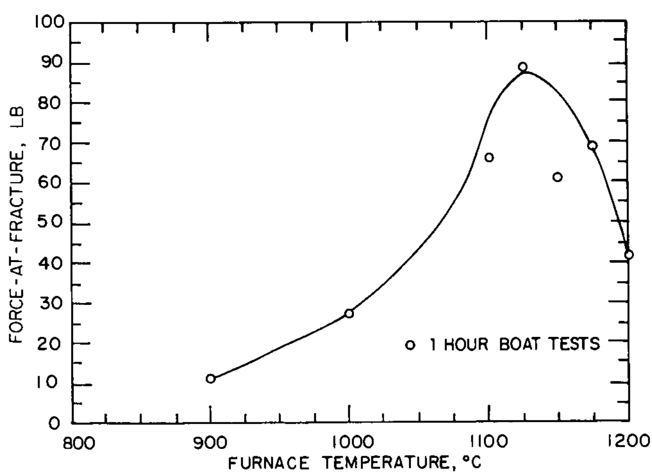

Fig. 2 Force-at-fracture for sintered refuse only granules as a function of small-tube furnace temperature.

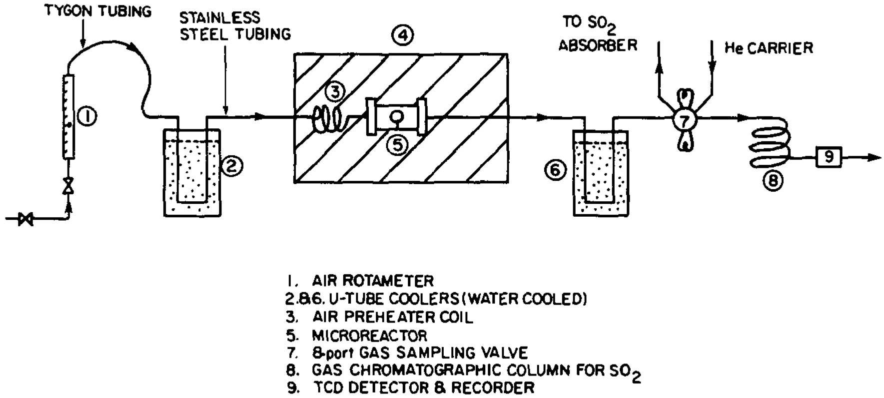

Fig. 3 Schematic flowsheet for the system to measure SO_2 evolution.

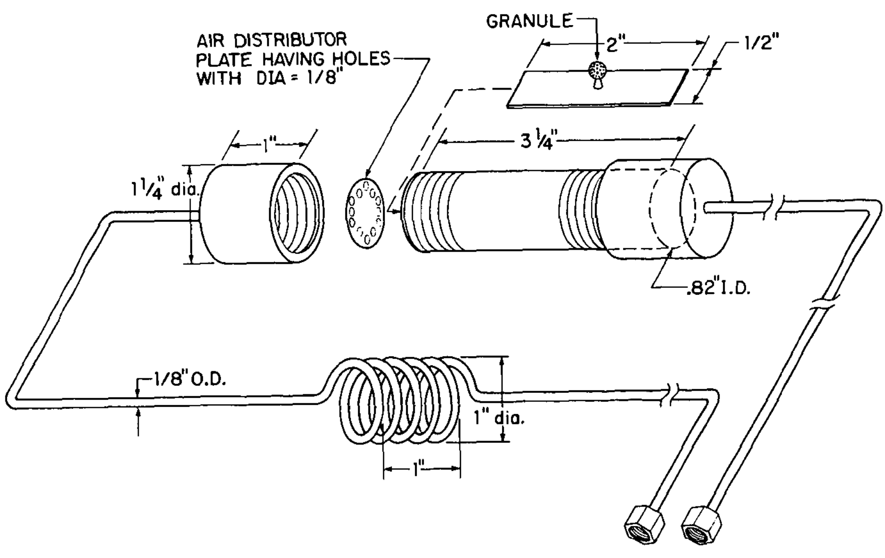

Fig. 4 Microreactor for the combustion/sintering of single granules.