MASTER

IS-T- 880

Fluidization characteristics of power-plant fly ashes and
fly ash-charcoal mixtures

by

Chuc Tu Nguyen

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MS Thesis submitted to Iowa State University

Ames Laboratory, DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: March 1980

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-eng-82

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

eb

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5265 Port Royal Road
Springfield, VA 22161

Fluidization characteristics of power-plant fly ashes and
fly ash-charcoal mixtures

by

Chuc Tu Nguyen

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE

Major: Chemical Engineering

Approved:

In Charge of Major Work

For the Major Department

For the Graduate School

Iowa State University
Ames, Iowa

1979

TABLE OF CONTENTS

	Page
ABSTRACT	iv
INTRODUCTION	1
OBJECTIVES OF THE INVESTIGATION	5
LITERATURE REVIEW	6
Classification of Powders	6
Fluidization of Free-Flowing Powders	8
Pressure drop characteristics	9
Bed expansion characteristics	13
Mixing and Segregation in Gas-Fluidized Beds	15
Fluidization Characteristics of Segregating Fluidized Beds	17
Fluidization of Cohesive Powders	20
EXPERIMENTAL INVESTIGATION	24
Fluidization Apparatus and Accessories	24
Materials	29
C-1 Illinois fly ash	31
Tennessee fly ash	35
Kentucky fly ash	36
Darold-Tabor (Commanche) fly ash	37
Kentucky charcoal	41
Star coal	41
Chlorinated Kentucky fly ash	42
EXPERIMENTAL METHODS AND PROCEDURES	46
Charcoal and Coal Pulverization and Subsequent Grading	46
Chlorination of Kentucky Fly Ash and Charcoal Mixtures	47
Particle Density Determination	47

	Page
Particle Size Determination	48
Fluidization Procedure	49
EXPERIMENTAL RESULTS AND OBSERVATION	51
Fluidization of Nonmagnetic Fractions of Fly Ashes	51
Nonmagnetic C-1 Illinois fly ash	51
Nonmagnetic Tennessee, Kentucky and Darold-Tabor fly ashes	53
Fluidization of Fly Ash and Charcoal Mixtures	55
The effect of charcoal size	56
The effect of the "aspect ratio"	62
Fluidization of a Fly Ash and Coal Mixture	71
Fluidization of the Chlorinated Kentucky Ash	76
DISCUSSION	77
CONCLUSIONS	87
SUGGESTIONS FOR FUTURE WORK	89
LITERATURE CITED	92
ACKNOWLEDGMENTS	96

ABSTRACT

As a part of the continuing research on aluminum recovery from fly ash by HiChlor process, a plexiglass fluidization column system was constructed for measurement of fluidization parameters for power-plant fly ashes and fly ash-charcoal mixtures. Several bituminous and subbituminous coal fly ashes were tested and large differences in fluidization characteristics were observed. Fly ashes which were mechanically collected fluidized uniformly at low gas flow rates. Most fly ashes which were electrostatically precipitated exhibited channeling tendency and did not fluidize uniformly.

Fluidization characteristics of electrostatically collected ashes improve when the finely divided charcoal powder is added to the mixture. Up to 30 weight percent of larger-sized charcoal is added according to the stoichiometrical requirement of the HiChlor process. The fluidization of the mixture was aided initially by a mechanical stirrer. Once the fluidization had succeeded, the beds were ready to fluidize without the assistance of a mechanical action. Smooth fluidization and large bed expansion were usually observed. The effects of charcoal size and aspect ratio on fluidization characteristics of the mixtures were also investigated. Scanning electron micrographs of samples of fly ash-charcoal mixtures give some evidences of inter-

particulate forces between small fly ashes and larger charcoal particles. Fluidization characteristics of a fly ash-coal mixture were tested. The mixture fluidized only after being oven-dried for a few days.

INTRODUCTION

When pulverized coal particles are burned to generate electricity in power plants, residues of burned coal are left in the furnace gas stream in the form of suspended, finely divided particles. These particles are known as fly ash and are collected as a fine powder. With the anticipation that coal will be a major energy resource to oil in the future, the production of coal ash could easily reach 70 million tons a year by 1980 (1). In recent years, there has been an increasing number of attempts made to utilize coal ash in highway and soil improvement projects, though the aggregate quantity of ash utilized barely exceeds 10 percent of total ash generated in the United States (1). The remaining ash must be disposed directly into landfills, ponds or abandoned mines. Present day ash disposal practices are causing numerous environmental problems. Recent investigations by environmental groups have identified coal ash as a possible radioactive material (2) and as a source of heavy metal leachates to the local environments (3). These findings imply that direct landfill disposal of coal ash could lead to serious environmental damage and could pose a potential health hazard. Consequently, the best answer to the disposal problem is to find attractive alternative large scale utilizations of coal ash.

Fly ash is known to contain appreciable amounts of commercially important metals such as aluminum and iron. A typical fly ash contains about 21 percent alumina, (Al_2O_3), and 17 percent iron oxide, (Fe_2O_3), the balance primarily silica, (SiO_2) (4). The concentration of alumina in fly ash compares well with that found in several bauxite ores (5). With a successful large scale utilization of fly ash as a resource for commercial metals, the problem of ash disposal would be alleviated and the economic potential of the recovery of valuable metals is evident.

Research aimed at large scale utilization of fly ash has developed two feasible processes to extract metals from fly ash. In one process, a mixture of fly ash, limestone and soda ash is sintered and the aluminum extracted from clinker using a dilute sodium carbonate solution (6). A second method involves high temperature chlorination of fly ash in the presence of a reducing agent. At 900 degrees Celsius and in the presence of carbon powder as a reducing agent, the chlorination of fly ash is very rapid and up to 80 percent of aluminum can be recovered in the form of gaseous aluminum chlorides (4). The overall reactions of the major components of fly ash can be expressed by the following equations:

The important chlorination products (metal chlorides) are volatile at reaction temperature and flow in the gas stream to a product separation and purification stage. Research is in progress to access the purification of volatile chlorides by such methods as selective condensation, fused salt adsorption or selective crystallization to produce an acceptable level of product purity (7).

Once the feasible recovery of metals from fly ash by chlorination has been demonstrated, the next question is how to design the chlorination process for large scale operation with the least operational cost. One proposal is to chlorinate the fly ash in a continuous fluidized bed reactor. A continuous operation cuts down labor cost and operation time as compared to batch operation. A fluidized bed reactor offers an attractive continuous chlorination process for fly ash, as the reacting chlorine gas can also serve as the fluidizing gas for the fly ash particles. Since carbon particles are added in the chlorination reaction to serve as a reducing agent, the good mixing characteristics of a fluidized bed appear to favor this type of solid-gas-solid reaction. Additionally, the high reaction temperature makes the good heat transfer characteristics of a fluidized bed

reactor attractive. In summary, a fluidized bed reactor is well-suited for a possible continuous chlorination of fly ash. One fact which remains to be investigated before chlorination can be carried out in a fluidized bed is whether a cohesive fly ash can be satisfactorily fluidized.

OBJECTIVES OF THE INVESTIGATION

The primary purpose of this investigation is to examine the feasibility of fluidizing power plant fly ashes and to obtain pertinent design information for the eventual study of the chlorination of fly ash in a fluidized bed reactor.

As the presence of carbon as a reducing agent is essential to the chlorination process, direct experimental observations should be made to determine fluidization characteristics of fly ash-charcoal mixtures at a 10 to 3: ash to charcoal weight ratio.

The fluidization experiments will employ compressed, dried air at room temperature as a fluidizing gas. The fluidization parameters to be determined should include bed pressure drop and bed expansion at a range of fluidizing velocities.

LITERATURE REVIEW

There is a great deal of published information on gas-fluidized systems. The following review describes the fluidization characteristics of free-flowing gas fluidized systems. This 'normal' system will subsequently be used as a basis of comparison for the experimental observations of a fly ash-air fluidized bed.

Classification of Powders

Fluidization of a bed of particles occurs when the upward flow of a gas through a bed keeps the particles in suspension and moving freely in close proximity with one another. Some particles systems or powders can not be kept in suspension or fluidized by the upward flow of gas alone. From the standpoint of the fluidizability, particulate solids may be classified into two general categories: free-flowing and nonfree-flowing or cohesive powder. The major difference between a free flowing and a cohesive powder is that for free-flowing materials the particles can slip easily over one another when under a stress, whilst for cohesive powders there is more frictional resistance to flow and in some cases this resistance is strong enough to prevent movement. Thus, a free-flowing powder is normally fluidized without any difficulty, whilst the fluidization of cohesive powders is

normally difficult and can require the modification of either the flow properties of the powder or of the fluidization equipment (8, 9).

Flowability of powder depends on particle size, shape (10) and inter-particle forces (11). The inter-particle forces that cause poor fluidization characteristics are generally the result of very small particle sizes, strong electrostatic charges, or the presence of moisture in the bed. With decreasing particle size, it becomes increasingly difficult to initially fluidize the powder bed, although once initiated, it may fluidize well at very high velocity (12). Powders of size below about 40 microns are generally cohesive (13), whereas those above 100 microns are generally free-flowing. Geldart (11) suggested particle size and density as criteria to classify various powders into four groups having different gas-fluidization behaviors. Group A materials are free-flowing powders and have a small particle size and/or a low particle density (less than about 1.4 g/cm^3). Beds of powders in this group expand considerably before bubbling starts as gas velocity is increased. Gross solid circulation occurs even when only a few bubbles are present, producing rapid mixing. Group B materials are also free-flowing and have the mean size range of 40 to 500 microns and a particle density range between 1.4 and 4.0 g/cm^3 . In contrast to group A, bed expansion is small and

bubblings starts at or only slightly above the onset of fluidization. There is little or no particle circulation in the absence of bubbles. Group C materials are cohesive powders. "Normal" fluidization of such powders is extremely difficult. Fluidization can only be made possible by the use of mechanical stirrers or vibrators to break up stable channels. Group D materials are free-flowing but large in size, usually in the order of 500 to 2,000 microns. One particular characteristic of this group is that the velocity of gas in the dense phase exceeds the rising velocity of the bubbles so that gas flows into the base of the bubble and out of the top. Solids mixing is relatively poor and the bed is easy to become spouted bed.

Fluidization of Free-Flowing Powders

Many of the commercial applications of fluidization as well as the research and theoretical developments have involved free-flowing or nearly free-flowing solids which are readily fluidized and therefore may be called "well-behaved" or "ideal" powders (group B materials). The typical fluidization characteristics of the beds of these particles can be best described by the pressure drop versus superficial gas velocity diagrams.

Pressure drop characteristics

The pressure drop of a fluidizing gas flowing through a bed of particles at different velocities is useful as an indication of the state and the quality of fluidization (12).

As a small flow of gas is initiated, the pressure drop through a packed bed of particles increases linearly with gas velocity. The mass of particles behaves like a fixed, porous bed. If the gas velocity is increased sufficiently, a point will eventually be reached where particles are suspended and separated enough to move freely, and the bed is said in "incipient" fluidization and the bed expands to give a larger bed voidage. The bed continues to expand with further increases in gas velocity, but the pressure drop remains practically unchanged and theoretically equals the weight of the bed per unit of bed cross-sectional area. If bubbles do not appear, the bed is said to be in the state of nonbubbling or particulate fluidization, and typically group A materials would behave in this way at low gas velocities. If bubbles are present, the bed is termed a bubbling or aggregate bed and typically group B materials or group A powders at high velocities would fluidize in this way. A typical pressure drop versus gas velocity diagram of a well-fluidized bed is depicted in Figure 1.

If the gas flow continues to increase the bubble

Figure 1. Pressure drop versus gas velocity for a bed of uniformly sized sand particles. u_{mf} is minimum fluidization velocity (14)

frequency and subsequently the bubble size increase as a result of bubble coalescence. A point may be reached where the bubble diameter approaches the diameter of the retaining vessel. This point marks the onset of slugging (15, 16). Several forms of slugging bed behavior have been observed. An axi-symmetric slugging is commonly seen in beds of fine powder of low density (16). A square-nosed, solids slugs are also observed in beds of small diameter containing large particles of high density (17). This latter type of slugging bed is characterized by successive regions of dense and dilute phase separated by horizontal interfaces through which

particles rain continuously, whilst in the axi-symmetric slugging bed the particles tend to flow around the outside of the large bubbles. For systems having small ratios of bed height to bed diameter, slugging may not occur. At high gas velocities, these systems may suffer a very rapid loss of particles by entrainment without ever reaching a slugging state. When slugging occurs, large and significant pressure drop fluctuations are usually observed as a result of large bubbles bursting the bed surface as shown in Figure 2.

Figure 2. Pressure drop diagram of slugging beds (14)

Another gas-fluidized bed characteristic which is undesirable is channeling or "rat-holing". Channeling is the phenomenon observed when a disproportionally large amount of the fluidizing gas follows one or several preferential paths

through a bed (18). Channeling usually occurs in beds of very fine or cohesive particles. Channeling could also be a result of a poor gas distribution which gives an inadequate uniform gas distribution (14). Leva et al. (18) investigating the channeling tendency of sand, iron and Fischer-Tropsch catalyst and coal concluded that the shape and moisture content of the solids also affect channeling. A pressure drop versus velocity diagram can be useful as an indication of a channeling bed. Such a channeling bed is shown in Figure 3, noting the abnormally low pressure drop for most of velocity range (14).

Figure 3. Pressure drop diagram of channeling beds (14)

Bed expansion characteristics

Another macroscopic property of a gas fluidized bed is bed expansion. A smooth and large bed expansion is considered a good fluidization characteristic from the point of view of chemical reaction, because a large bed expansion indicates a good gas-solid contact.

For gas-fluidized systems, the upper surface of the bed is usually uneven and oscillating at bubbling velocities. Bed height fluctuation is the result of bubbles escaping at the bed surface (19). The amplitude of fluctuation increases with an increase in gas velocity and a decrease in bed diameter as depicted in Figure 4.

Figure 4. Bed expansion for a bed of well-fluidized particles (L_{mf} is bed height at incipient fluidization, d_f is bed diameter) (14)

However, in a fluidization regime which is free of bubbles (particulate fluidization), Richardson and Davis (20) observed that bed expansion of 55-micron catalyst has a straight line relationship with superficial gas velocities between minimum fluidizing and minimum bubbling velocities. Minimum fluidizing velocity is the velocity at which the bed starts to fluidize and minimum bubbling velocity is the velocity at which a gas bubble appears. Increases in gas velocity cause further bed expansion mostly because of increasing of bubble hold-up. Eventually, bed expansion levels off as bubbles coalesce and attain maximum size. In addition, Richardson and Davies (20) observed that a gas bubble injected into a nonbubbling fluidized bed grew at the expense of gas in the interstitial phase. As a consequence, the bed contracted. The contraction is a complex function of bubble frequency, bubble size, the fluidizing gas rate, and the bed height (20).

In a similar investigation of the division of fluidizing gas between bubble and interstitial phases, but with powders containing 28 percent fines (less than 45 microns), Rowe et al. (21, 22) observed that fine powder expanded erratically at gas velocities in excess of minimum fluidizing velocity, and became fully fluidized only when higher gas velocity was reached. Beyond this critical velocity, the bed expanded uniformly with increasing flow rate. Between the two velocities, an erratic

bed expansion was attributed to bed channeling. Once channeling was eliminated, and the bed expanded at high velocities, the large bed expansion was more than that which could be accounted for bubble hold-up alone. Rowe et al. suggested that the increase in interstitial voidage contributed markedly to the expansion of a bed of fine powder. In fact, the interstitial voidage increased with fine content (21).

Mixing and Segregation in Gas-Fluidized Beds

Rowe et al. (23) conducted pioneering studies of the mechanisms of solids movement in gas-fluidized beds. They observed that in freely bubbling fluidized beds, bubbles provide a very effective means of transportation for the solids and could account almost entirely for the high rates of particle circulation which have been noted in gas-fluidized beds. As bubbles rise through a bed, they gather nearby particles in their wakes and carry those particles upward. The other particles which are not caught in the paths of the bubbles must move downward elsewhere. The net result is an effective vertical mixing of solids in gas fluidized beds. The mixing can be very fast and some particle systems were reported to perfectly mix within a few minutes (24).

However, if a gas fluidized bed contains particles differing in size or in density, segregation due to particle size and density differences may occur. When such systems are

fluidized, a dynamic mixing-segregating equilibrium is set up which is mainly a function of the density and size of the particles and of the gas flow rate (25). Rowe et al. (25) made a systematic study of segregation in fluidized beds. Six binary mixtures of spherical material differing in particle size, density and minimum fluidizing velocity were investigated. Narrowly sieved groups of four free-flowing materials (steel, copper shots, ballotinni and polysterene beads) comprising a wide particle density range ($1.65\text{--}8.86\text{ g/cm}^3$) were employed. They found that differences in particle density readily lead to segregation with the denser material forming a relatively pure bottom layer. Some dense material invariably appears more or less uniformly throughout the upper part of the bed and this proportion increases with gas flow rate. If the density ratio is about 1.2 or less, the mixing can be improved appreciably by increasing the gas velocity, and near perfect mixing is often possible by this means (24). At larger density differences, no mixing occurs because the terminal falling velocity of light material would be exceeded before dense material can fluidize.

Different sized particles of the same density will also segregate when fluidized, with larger ones settling to the bottom. However, the effect of size difference is slight; almost perfect mixing can be achieved even when the mass

ratio of the particles is as high as 300 (24). When both density and size differences are involved, the degree of mixing is a complex function of density and size ratio, and gas velocity. In general, less dense and smaller particles follow the wakes of the bubbles to the top; larger and denser particles descend in the bed by falling through bubbles. The denser and smaller particles also descend by interparticle percolation but only in regions distributed by passing bubbles. Finally, less dense particles were never found to sink even if they were larger in size; eventually they would float on a fluidized bed of denser material (25).

Fluidization Characteristics of Segregating Fluidized Beds

Because the degree of mixing (or segregation) depends very much on gas velocity, the segregation-prone bed assumes various segregated or stratified structures at different gas velocities. The fluidization characteristics of the segregating fluidized bed are expected to be different from those of monocomponent fluidized beds, and they depend on the experimental measurement techniques (26). For example, the pressure drop versus gas flow rate relationship with increasing superficial velocity (ascending curve) will generally be different from that obtained on subsequently reducing the gas flow rate from the well-mixed condition.

This is due to the segregation that can occur once the bed becomes fluidized. The difference between the increasing and decreasing pressure drop curves is an indication of segregation of the fluidized bed (27). Chiba et al. (26) investigated fluidization characteristics of binary mixtures of free-flowing materials at three levels of mixing: complete mixing, complete segregation and partial mixing. For completely mixed beds which were obtained by selecting particles almost identical in size and density, the fluidization characteristics are similar to those of homogeneous fluidized beds. For completely segregated beds in which segregation into two distinct layer occurs, the pressure drop diagram shows two sharp breaks at two gas velocities corresponding to minimum fluidizing velocities of two components as depicted in Figure 5(a).

The two defluidization procedures (fast and slow decreasing of the gas velocity) gave the same value of u_g . A shift in the slopes of pressure drop curve corresponds to the segregation of the bed when two separate layers of particles are formed and an upper layer remains fluidized. This characteristic is also obvious in examining the bed expansion where step increases in bed expansion were noted as shown in Figure 5(b).

For partially mixing beds, similar but less intense

Figure 5(a). Pressure drop characteristics of a completely segregating bed (26) (u_p = minimum fluidizing velocity of dense particles, u_F = minimum fluidizing velocity of light particles, u_s = apparent minimum fluidizing velocity of a mixture)

Figure 5(b). Bed expansion characteristic of a completely segregating bed (26) (H_s is the static bed height, u_F and u_p are minimum fluidizing velocities of light and dense particles, respectively)

characteristic bed expansion phenomena occur. The pressure drop diagram is more dependent on the procedures of defluidization. The apparent minimum fluidization velocity is not the same in both defluidization procedures as shown in Figure 6.

Figure 6. Pressure drop characteristic of a partially mixed bed (26)

Fluidization of Cohesive Powders

Cohesive powders can not be fluidized by ordinary means. When beds of these solids were aerated, channels formed through the beds and the particles balled up (13). The cohesiveness depends on particle size and shape. Particles

with a needle, platelike or modular shape also tend to be cohesive (10).

Various techniques have been developed to fluidize cohesive powders. Reed and Fenske (28) found that carbon powder having an average size of 4.3 microns was difficult to fluidize by gas flow alone. By using a specially designed mechanical agitator, they were able to disperse the gas, causing the bed to expand and become very fluid even at the low gas flow rate of 0.3 cm/sec. Fluidization of other cohesive powders was also successful in a mechanically stirred gas fluidized beds (9, 29). A similar technique employing a horizontal rotating nozzle in place of a common gas distributor also fluidizes cohesive powders successfully (30).

Vibration of fluidized beds has achieved effects similar to those produced by stirring. Morse (31) showed that low frequency, high intensity sonic energy inputs promote the fluidization of nonfluent, cohesive powders. Under the influence of sonic energy, the channels were destroyed and very smooth fluidization was obtained. Similar results were also obtained when the glass column was vibrated transversely by clamping a 60 cycle vibrator to the side of the column (31). The actions of the added vibrational energy are to break up the stable channels and to reduce the friction between particles, thus promoting the fluidization of cohesive powders.

Another technique which can be applied to improve the

fluidization of cohesive powders was reported by Jolley and Stanton (32). They found that while attempts to fluidize the nonfluid coal particles, (90.4 percent less than 74 microns), in beds up to 10 inches in depth and 2 inch diameter tube resulted in the formation of blow holes and very poor fluidization, excellent fluidization was obtained in beds up to 40 inch or more in depth using the same diameter tube. Fried (33) also investigated the effect of bed height to bed diameter ratio on fluidization of flour and found that fluidization of pure flour is not possible. Anti-caking agents must be added to the flour to obtain satisfactory fluidization and the amount of anti-caking agent needed to induce fluidization decreased as the bed height to diameter ratios increased.

Finally, the fluidization of cohesive powders can be achieved by another method. This method involves the modification of the flow properties of the cohesive powder. Trawinski (34) discovered that the addition of fine sized particles to the bed of coarse particles greatly facilitates fluidization. Rowe et al. (24) also observed that small amounts of added fines considerably enhances the onset of fluidization of coarse particles. Fried (33) employed sub-micron powders to achieve fluidization of cohesive flour. Although most successful fluidizations were obtained by the addition of fines to a bed of relatively coarse but cohesive powder, it

was also believed that fluidization of nonfree-flowing fine powders could be facilitated by the addition of slightly coarser particles (18).

EXPERIMENTAL INVESTIGATION

The experimental plan used in this work consisted of the following steps:

1. Construction of the fluidization column and set-up of auxiliary equipment.
2. Selection and preparation of various fly ashes for the fluidization experiments.
3. Determination of the physical properties such as density, size and size distribution of the materials under investigation.
4. Performance and observation of the fluidization experiments; measurement of fluidization properties where possible.

Fluidization Apparatus and Accessories

A flow sheet of the equipment used to determine the fluidization characteristics of the materials under investigation is shown in Figure 7. The equipment consisted of:

1. A pressure regulator to reduce the pressure of compressed air from 80 psig to 15 psig.
2. An air filter to filter out any contaminants such as oil and dust from the compressed air.
3. A pressure gauge to monitor the line pressure.

Figure 7. Schematic of fly ash fluidization system

4. Three rotameters of different capacities, fitted with needle valves. The capacities of the rotameters were chosen to cover the range of flow rates yielding superficial velocities from 0.01 to 10 cm/sec in a 3.75 inch inside-diameter tube. The rotameters were calibrated by a gas wet-test meter (manufactured by Precision Scientific Company, Chicago, U.S.A.) at 25°C and one atmosphere.
5. An anhydrous CaSO_4 drying tube to absorb moisture from the compressed air.
6. Two water-filled, glass, U-tube manometers used to measure the pressure drop across the bed and the distributor.
7. A network of copper tubing and fittings to connect the whole flow system together. Much time was spent ensuring an air-tight system. A final test for air leaks was done by pressurizing the entire system to 15 psig and then observing to see if the pressure changed with time.
8. A fluidization column shown separately in Figure 8. The fluidization column consisted of a plexiglass column to contain the bed of materials and the column was fitted with a porous disc at the base to act as an air distributor. The porous gas distributor employed in this work was a half inch thick

Figure 8. Fly ash fluidization column

Alundum porous disc (mixture P2120), manufactured by the Norton Company, Ceramics Division.

Preliminary experiments showed the pressure drop across the Alundum distributor to be about 40 percent of that across the fluidized bed of fly ash. In cases where a higher resistance to gas flow was needed to ensure uniform gas distribution, provision was made to use a one-inch thick, or a finer pore grade of, porous distributor.

After the fluidization column was set up with rubber gaskets in place, an attempt was made to check the uniformity of air distribution within the column. Using ballotini as free-flowing particles, it was observed that the air flow was greater around the inside wall edge than in the center region of the column. A closer inspection of the rubber gaskets revealed that they were not effectively sealing off the air bypass inside the air chamber. To remedy this situation, a high vacuum grease, manufactured by Dow Corning was used to seal the gaps at the gasketed joints. The flow still initiated around the inside wall at very low flow rates, but air movement was also observed simultaneously in the center region of the column. This was considered satisfactory in terms of uniform air distribution.

The 3.75 inch inside diameter, 1/8-inch thick plexiglass column was installed to serve as a container for the bed of particles. There were three separate column sections of the

same diameter which could be fastened together tightly and easily by nuts, bolts and rubber-O-rings. The bottom two sections were both 8-inch high to allow easy loading or unloading of the fluidized materials. The longest column section was 3 feet high and was needed for deep bed fluidization experiments and to serve as a transport disengagement section to keep particle entrainment at a minimum (14,35) Taps were located intermittently along the column sections to serve either as pressure taps or as sampling taps. When they were used as pressure taps, fiberglass plugs were used to prevent particles from entering the manometer lines. Attached on the top of the fluidization column was a plexiglass cover plate which had a centrally cut vent. Connected at the vent hole was a 2 inch diameter plexiglass tube packed with glass wool to serve as a filter to retain entrained particles. A photograph of the entire fluidization system is shown in Figure 9.

Materials

Four coal power plant fly ashes were investigated. Three of them have high iron-content and had to be magnetically separated into two fractions: magnetic and nonmagnetic. It was the nonmagnetic fraction whose fluidization characteristics were investigated in this work. For fly ashes

Figure 9. Fluidization system with all three column sections in place

which are low in iron content, magnetic separation is not necessary. In addition to the low-iron fly ashes, charcoal and coal required as sources of reducing carbon in the HiChlor chlorination process of aluminum recovery were also used in the fluidization in combination with fly ashes. The following is a listing and detailed description of the materials used.

C-1 Illinois fly ash

Plain C-1 fly ash was collected by mechanical precipitators at the Lakeside Power Plant, Milwaukee, Wisconsin while coal from western Kentucky and southern Illinois were being burned. This fly ash has a high iron content and had to be magnetically separated. The chemical compositions of total ash, magnetic and nonmagnetic fractions are shown in Table 1.

The nonmagnetic fraction is grayish in color, having a density of approximately 2.0 g/cm^3 . The particles have sizes ranging from 1 to 200 microns and an average volume to surface diameter of about 21 microns. Ninety volume percent of the nonmagnetic ash is larger than 10 microns and 10 percent is larger than 100 microns. A scanning electron micrograph of a sample of the nonmagnetic ash is provided in Figure 10.

Table 1. Composition of C-1 fly ash and two magnetically separated fractions
(37)

Constituent	Chemical composition, Weight, Percent		
	Whole fly ash	Magnetics	Nonmagnetics
SiO ₂	40.99	12.32	47.99
Al ₂ O ₃	17.87	6.75	20.61
Fe ₂ O ₃	18.62	76.87	6.10
CaO	4.73	1.49	5.53
MgO	0.68	0.26	0.78
Na ₂ O	0.32	0.10	0.37
K ₂ O	1.60	0.43	1.88
TiO ₂	0.73	0.32	0.83
SO ₃	1.77	0.75	1.97
C	8.02	1.10	8.16
L.O.D. ^a	-	-	-
L.O.I. ^b	10.19	0.68	10.80
Wt. percent	-	-	78.5

^aL.O.D. is loss on drying.

^bL.O.I. is loss on ignition to 800°C.

Figure 10. A scanning electron micrograph of the non-magnetic fraction of C-1 fly ash (X = 400)

Figure 11. A scanning electron micrograph of the non-magnetic fraction of the Tennessee fly ash (X = 500)

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

Tennessee fly ash

Tennessee fly ash was collected by electrostatic precipitators at Kingston Power Station, Tennessee and was residue of Tennessee and Kentucky coal. The chemical composition of total ash and magnetic and nonmagnetic fractions is presented in Table 2. The nonmagnetic fraction is grayish in

Table 2. Composition of Tennessee fly ash and two magnetically separated fractions (36)

Constituent	Chemical composition, Weight percent		
	Whole fly ash	Magnetics	Nonmagnetics
SiO ₂	49.95	13.80	52.06
Al ₂ O ₃	27.17	8.20	28.29
Fe ₂ O ₃	10.28	74.50	6.98
CaO	1.48	0.60	1.57
MgO	0.96	0.29	0.97
TiO ₂	1.24	0.59	1.37
Na ₂ O	0.30	0.07	0.32
K ₂ O	3.14	0.36	3.21
P ₂ O ₅	0.67	0.37	0.62
SO ₃	0.37	0.56	0.49
C	3.08	0.33	3.11
L.O.D.	0.09	0.03	0.10
L.O.I.	3.38	-	3.67
Wt. percent	4.16	95.09	

color and less free-flowing than the C-1 ash fraction. It has a density of 2.3 g/cm^3 . The sizes of Tennessee fly ash particles range from 1 to 50 microns with a mean volume to surface diameter of about 6 microns. Ninety volume percent is larger than 4 microns and only 10 percent is larger than 30 microns. A scanning electron micrograph of a sample of nonmagnetic Tennessee fly ash is shown in Figure 11. Most of the particles are spherical and some particles are believed to be fused together.

Kentucky fly ash

Kentucky fly ash was precipitated electrostatically from Louisville Power Station, Kentucky, while burning western Kentucky coal. The chemical composition of total ash, magnetic and nonmagnetic fractions is provided in Table 3. The nonmagnetic fraction is light brown in color, tends to resist flow when it is closely packed and has an apparent particle density of 2.5 g/cm^3 . The particle sizes range from 1 to 50 microns with a mean diameter of about 6 microns. Ninety percent by volume of the nonmagnetic ash is larger than 3 microns, but only 10 volume percent is larger than 25 microns. The scanning electron micrograph in Figure 12 shows some spherical particles to be present.

Table 3. Composition of Kentucky fly ash and two magnetically separated fractions (36)

Constituent	Chemical composition, Weight percent		
	Whole fly ash	Magnetics	Nonmagnetics
SiO ₂	43.75	20.00	51.50
Al ₂ O ₃	17.00	8.25	18.90
Fe ₂ O ₃	21.75	65.90	13.60
CaO	4.22	1.74	6.46
MgO	0.74	0.39	0.80
TiO ₂	0.40	0.46	0.83
Na ₂ O	0.25	0.09	0.22
K ₂ O	2.12	0.75	2.59
P ₂ O ₅	0.20	0.13	0.15
SO ₃	2.28	0.81	2.60
C	1.92	0.36	1.49
L.O.D.	0.20	0.10	0.23
L.O.I.	0.85	-	0.97
Wt. percent	-	13.40	81.96

Darold-Tabor (Commanche) fly ash

This fly ash is subbituminous and was electrostatically collected at Commanche Power Station, Pueblo, Colorado, while burning Wyoming coal. It has a low iron content but is high in calcium content. The chemical composition is shown in Table 4.

Table 4. Composition of Darold-Tabor (or Comanche) fly ash (36)

Constituent	Chemical composition, Weight percent
SiO ₂	30.18
Al ₂ O ₃	19.71
Fe ₂ O ₃	5.38
CaO	28.79
MgO	4.47
Na ₂ O	1.66
K ₂ O	0.32
TiO ₂	1.51
SO ₃	2.18
C	-
L.O.D.	-
L.O.I.	0.71

This fly ash exhibited very strong agglomerative tendencies and was much more cohesive than the Tennessee and Kentucky fly ashes. The particle density is about 2.6 g/cm³ and the size distribution is similar to those of the Tennessee and Kentucky fly ashes. Ninety volume percent of the ash is larger than 3 microns and 10 percent is larger than 32 microns. The average diameter is about 6 microns. A scanning electron micrograph of the Darold-Tabor fly ash is shown in Figure 13.

Figure 12. A scanning electron micrograph of the non-magnetic fraction of the Kentucky fly ash (X = 1000)

Figure 13. A scanning electron micrograph of the non-magnetic fraction of the Darold-Tabor fly ash (X = 500)

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

Kentucky charcoal

The Kentucky charcoal which was available in granular size was pulverized and separated into different size fractions. The sizes and size distributions of various charcoal size fractions identified by particle diameter in microns are listed in Table 5. Charcoal particle densities (1.6 g/cm^3) for the various size fractions are the same within experimental error.

Table 5. Sizes and size distributions of the various charcoal fractions

	Average particle diameter, microns	Fifty volume %, larger than, microns	Upper limit of particle size, microns
Charcoal 45-53	11	21.0	53
Charcoal 63-74	13	31.0	74
Charcoal 74-105	18	52.0	105
Charcoal 105-149	73	110.0	149

Star coal

This coal was selected for fluidization experiments because of its relatively low ash and sulfur contents. It was obtained from Star mine, Monroe County, Iowa and was also pulverized to the desired sizes. The Star coal has about 1.0 percent organic sulfur and was more difficult to size than the charcoal particularly at the small particle

sizes. At sizes below 53 microns, it was observed that coal particles balled up and refused through the shaking sieves. The Star coal fraction obtained between 63 and 74 micron sieves when the pulverized coal was sieved for one hour in a Ro-tap shaker had a size ranging from 2 to 75 microns with an average diameter of about 28 microns. Ninety volume percent was larger than 54 microns. The particle density is about 1.3 g/cm^3 .

Chlorinated Kentucky fly ash

A mixture of Kentucky fly ash and charcoal was chlorinated following the chlorination procedure (HiChlor process) developed at Ames Lab, Iowa State University (4). The surface of the chlorinated fly ash appears to be flaked and roughened by the reaction with chlorine gas. The particles appear very porous and agglomerated as seen in Figure 14. Size analysis showed that the particle size of this chlorinated ash ranged from 2 to 50 microns with a mean diameter of about 5 microns. Ninety volume percent was larger than 5 microns and 10 percent larger than 88 microns. The apparent density, which was determined by a displacement method, varied considerably with a mean value being $2.5 \pm 0.2 \text{ g/cm}^3$. The variation in density was possibly due to the different porosity of the size fractions and the extent of water penetration into these pores. The chemical composition of Kentucky ash before and after chlorination is shown in Table 6.

Figure 14. A scanning electron micrograph of partially chlorinated Kentucky fly ash particles; charcoal as the reductant

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

(X = 1000)

(X = 3000)

Table 6. Composition of nonmagnetic fly ash before and after chlorination

Component	Weight percent before chlorination	Weight percent after chlorination	Percent removed
Al_2O_3	18.9	5.38	51.4
Fe_2O_3	13.6	5.58	73.2
SiO_2	51.8	44.3	44.2
TiO_2	0.83	0.14	88.7
CaO	6.46	9.90	0
L.O.I. ^a	0.97	28.5	
L.O.D. ^b	0.27	6.5	

^aL.O.I. is loss on ignition.

^bL.O.D. is loss in drying.

EXPERIMENTAL METHODS AND PROCEDURES

The description of the experimental techniques employed to determine the properties of the experimental materials and how they were prepared is given below.

Charcoal and Coal Pulverization and
Subsequent Grading

Charcoal and coal were pulverized in the high speed pulverizer (Mikro-Samplmill, Division of the Slick Corp., Summit, New Jersey). About 300 grams of granular-sized charcoal (or coal) were fed into the pulverizer. The particles were crushed between the high speed rotating blades and a stainless steel screen inside the pulverizer. The particle size could be reduced smaller than 45 microns if the screen had small enough apertures.

The pulverized charcoal (or coal) was then placed on the top of the stack of sieves. The sieves used were U.S. standard sieves and had sieve apertures ranging from 45 to 149 microns (equivalent to 320 and 100 mesh in Tyler standard sieves, respectively). The sieves were shaken horizontally and tapped vertically in a Ro-tap sieve shaker, (W. S. Tyler Company), for one-half hour in the case of charcoal sieving and for one hour in the case of coal sieving. The coal was more difficult to screen than the charcoal. The sieving of the pulverized charcoal produced large amounts of sub-45

micron material, while the coal gave only a very small amount of material less than 53 microns.

Chlorination of Kentucky Fly Ash and Charcoal Mixtures

The changing physical properties (density, shape and nature of particle surface) of the chlorinated ash can be expected to affect the fluidization characteristics of the bed quite significantly as reaction proceeded. For this reason, the fluidization characteristics of the partially chlorinated ash in particular were also investigated.

The Kentucky fly ash and charcoal were mixed in a fluidized bed and chlorinated using the HiChlor process. Ash samples from 10 chlorination experiments were mixed homogeneously and analyzed by atomic absorption from technique (37) to determine the extent of chlorination.

Particle Density Determination

The densities of the materials used were determined by applying a gravitational-displacement technique. Distilled water was used as the displacement medium. In a typical density measurement, about 2 grams of the material were weighed in a tared density bottle. A small amount of water was added with 3 drops of wetting agent (Type IB, Coulter dispersant, Coulter Electronics, Inc.). The resulting slurry

was then ultrasonically shaken for 3 minutes. The density bottle was then completely filled with distilled water and weighed. The specific gravity was then calculated from the equation:

$$\text{Specific gravity} = \frac{W_2 - W_1}{(W_4 - W_1) - (W_3 - W_2)} = \frac{\text{Weight of solid sample}}{\text{Weight of water representing volume of solid sample}}$$

W_1 = weight of dry bottle

W_2 = weight of bottle + solid sample

W_3 = weight of bottle + solid sample + full water

W_4 = weight of bottle + full water

Particle Size Determination

The size and size distribution of the materials used were determined by using a Model TA Coulter Counter (Coulter Electronics, Inc., Hialeah, Florida). The general instrument operating procedure was followed as described in the instruction manual. The conducting solution used was a 2 percent (by weight) sodium chloride solution. Background noise was accounted for in the calculation of the particle size distribution. The average surface particle diameter was computed from the cumulative volume percent according to the following equation.

$$\text{Average diameter} = \frac{1}{\sum_i \frac{x_i}{d_{pi}}}$$

where x_i is i volume fraction having an average particle diameter dp_i .

Fluidization Procedure

In a typical run, the material to be tested was charged in the column to a desired height according to a specified height to diameter (L/D) ratio. If the material fluidized readily, the air flow was increased rapidly to a "well-fluidized" velocity and maintained in the fluidized state for about two minutes. The air flow was then stopped, the bed allowed to contract and the final bed height measured as the packed bed height. The air velocity was then increased from zero in several increments until vigorous fluidization was observed and then decreased in the same way to zero. At each velocity, the bed pressure drop and the bed height (expansion) were recorded after waiting 3 to 5 minutes to reach a steady state. The maximum velocity actually attained in any run was usually limited by high entrainment or by turbulence in the bed.

If the material being tested did not readily fluidize, an electric stirrer was used to assist the initial bed fluidization. The electric stirrer would be placed in operation with the stirrer blades positioned about 1 centimeter above the air distributor and the flow of air initiated.

The bed would then usually fluidize and expand considerably. The stirred bed fluidization would be maintained for 5 to 15 minutes at which time the stirrer would be removed. Fluidization of the bed would then be continued without the stirrer in place for an additional few minutes. After this treatment, the bed usually fluidized readily on subsequent occasion. The bed height and bed pressure drop would be recorded at various air velocities as before.

EXPERIMENTAL RESULTS AND OBSERVATION

Fluidization of Nonmagnetic Fractions
of Fly AshesNonmagnetic C-1 Illinois fly ash

The C-1 fly ash fluidized rather easily with smooth bed expansion at velocities above 0.1 cm/sec. Figure 15 shows how the pressure drop across the bed varied with velocity. The bed was motionless for velocities up to about 0.09 cm/sec. A little beyond this velocity, the pressure drop decreased sharply as the first movement of particles was observed. The sharp decrease of pressure drop indicated a local fluidization within a small section of a bed. Increasing the flow rate caused the bed to begin to expand and fluidize across the entire cross section. The pressure drop increased again up to a maximum. Solids motion was downward along the wall at full fluidization. This implies that particle motion was upward in the center region of the bed. Air bubbles several millimeters in diameter were visible. Upon decreasing the flow rate, the pressure drop followed a lower (descending) curve. This is probably an indication of de-mixing of the bed, although the removal of fine ash particles by entrainment could also give a lower pressure drop curve. Increasing the flow rate a second time after vigorously fluidizing the bed for 2 minutes caused the first (ascending) curve to be reproduced. This fact indicates that the effect

Figure 15. Variation in bed pressure drop with air velocity for C-1 fly ash

of fine ash being lost by entrainment on the pressure drop characteristic is insignificant for C-1 fly ash in the velocity range investigated.

The pressure drop characteristics of the bed of C-1 fly ash at a height to bed diameter (L/D) ratio of 2 was similar to that of an $L/D = 1$. The minimum fluidizing velocities for both cases were about the same at 0.1 cm/sec.

Bed expansion for C-1 ash is shown as a function of velocity in Figure 16. A bed expansion of up to 65 percent was observed for C-1 ash. In general, the percent bed expansion increased linearly with velocity and fell off only at high velocities. In defluidization of the bed (decreasing the velocity), the bed contracted rapidly with a slight reduction in the air velocity.

Nonmagnetic Tennessee, Kentucky and Darold-Tabor fly ashes

Attempts to fluidize nonmagnetic fractions of Tennessee, Kentucky and Darold fly ash were also made at an aspect ratio, L/D , of about 1. In contrast of the C-1 fly ash, the fluidization of these fly ashes was not successful. The bed did not fluidize at all. Several channels developed through the bed where the high velocity air broke the bed surface with an intermittent stream of ash particles which resulted in excessive particle entrainment.

With the assistance of an electric stirrer, the bed

Figure 16. Variation in percent bed expansion with air velocity for C-1 fly ash

expanded about 40 percent. However, when the electric stirrer was removed, the bed defluidized or fluidized non-uniformly. Little or almost no particle motion was observed. The bed pressure drop measurements were not consistent.

In deeper bed fluidization experiments (at an aspect ratio, L/D , of 5), fluidization and bed expansion seemed better. However, only the upper part of the bed fluidized to some degree. Particles in the lower part of the bed did not move, at least in the region close to the column wall. More often, the lower part developed stable cracks through which most of the air flowed. At some critical bed heights, the channels broke up into bubbles which caused the upper part of the deep bed to fluidize.

Fluidization of Fly Ash and Charcoal Mixtures

The fluidization of a mixture of fly ash and charcoal was investigated for two main reasons. One reason is that the chlorination of fly ash by the HiChlor process, the addition of carbon powder is required to increase the rate and completeness of reaction. Secondly, the addition of slightly coarser particles to a bed of plain fly ash will facilitate fluidization of the resulting mixture. The aim was to find out if the carbon particles influenced the fluidization characteristics of cohesive fly ashes.

c The effect of charcoal size

Most of the fluidization experiments for the mixture of fly ash and charcoal were carried out with nonmagnetic fraction of Kentucky ash. For the mixture fluidization experiments, charcoal and nonmagnetic Kentucky ash were weighed in the proportion 3 parts to 10, according to the stoichiometrical requirements of the HiChlor process. Two layers of charcoal and Kentucky ash were mixed and fluidized initially with the aid of an electric stirrer for about 5 to 15 minutes as described in the "experimental procedures" section. All mixtures of Kentucky ash and various sized charcoal particles fluidized without stirring after such a pre-treatment.

Figures 16, 17, 18 and 19 were evidence of the good fluidization of the mixtures of charcoal and Kentucky fly ash and show the effect of charcoal size on fluidization characteristics at an aspect ratio, L/D , of 2. All charcoal-ash mixtures fluidized well at higher air flow rates. Minimum fluidizing velocities could not be determined with any degree of certainty, but they were probably within the range of 0.05 to 0.4 cm/sec. The difficulty in determining the minimum fluidizing velocity was due to the lack of the normal fixed bed region in a pressure drop versus velocity plot. Upon initiating the air flow, the whole bed usually rose upward

Figure 16. Pressure drop through bed of nonmagnetic fraction of Kentucky fly ash and charcoal mixture as a function of gas velocity at bed height two times bed diameter ($L/D = 2$), charcoal mean size, 11 microns

Figure 17. Pressure drop through bed of nonmagnetic fraction of Kentucky fly ash and charcoal mixture as a function of gas velocity at bed height two times bed diameter, charcoal mean size, 13 microns

Figure 18. Pressure drop through bed of nonmagnetic fraction of Kentucky fly ash and charcoal mixture as a function of gas velocity at bed height two times bed diameter, charcoal mean size, 18 microns

Figure 19. Pressure drop through bed of nonmagnetic fraction of Kentucky fly ash and charcoal mixture as a function of gas velocity at bed height two times bed diameter, charcoal mean size, 73 microns

like a piston. When a bed collapsed, several small regions fluidized locally at very low flow rates. Therefore, a fixed bed region could not be obtained in the fluidization of these mixtures.

Upon decreasing the air velocity, all mixtures usually exhibited rapid defluidization and substantial lowering of pressure drop in the velocity range of 1.6 down to 0.6 cm/sec. At velocities of about 0.5 cm/sec, large increase in pressure drop occur and simultaneously a large bed expansion and a small bubbling, uniform fluidization were observed. This phenomenon was most obvious in Figures 16, 18 and 19. Charcoal size fraction 63-74 seemed to have the smallest gap between the ascending and descending curves, while a mixture of the smallest charcoal size showed the widest gap.

Particle motion was downward along the wall at intermediate velocities (between 0.4 and 1.4 cm/sec). At low velocities (usually lower than 0.3 cm/sec) some stagnant bed regions close to the column wall and the distributor surface were observed. At high air velocities, when air bubbles of several millimeters in diameter were seen close to the column wall, the stagnant regions were broken and rapid particle motion was observed.

The effect of the "aspect ratio"

A series of experiments using mixtures of Kentucky ash and charcoal were made at various static bed heights. Figures 20, 21 and 22 show the effect of varying the aspect ratio from 1 to 5. All of the beds fluidized well at air velocities larger than 0.4 cm/sec. A comparison of Figures 20, 21 and 22 suggests that a deeper bed, up to an aspect ratio of 5, did not significantly affect size segregation. On decreasing the air velocity, the familiar return to smooth and uniform fluidization from unstable, large bubbled fluidization was also observed. The motion of the particles was not much different when a deep and a shallow bed were compared except that the stagnant region which existed at low air velocities in all experiments seemed to extend higher in a deeper bed. The percentage bed expansion seemed a little larger in a deep bed than in a shallow bed as shown in Figures 23, 24 and 25.

Fluidization of mixtures of charcoal (45-53 micron fraction), with Tennessee and with C-1 Illinois fly ash were also investigated at an aspect ratio of 1. Figures 26 and 27 show the plots of bed pressure drop versus air velocity for Tennessee and C-1 Illinois and respectively. The Tennessee mixture behaved similarly to the Kentucky mixture. The C-1 mixture shows good fluidization and mixing. The corresponding

Figure 20. Pressure drop through a bed of nonmagnetic fraction of Kentucky fly ash and charcoal mixture as a function of gas velocity (bed height equal bed diameter)

Figure 21. Pressure drop through a bed of nonmagnetic fraction of Kentucky fly ash and charcoal as a function of gas velocity (bed height is two times bed diameter)

Figure 22. Pressure drop through a bed of nonmagnetic fraction of Kentucky fly ash and charcoal as a function of gas velocity (bed height is five times bed diameter)

Figure 23. Percent expansion of a bed of charcoal-nonmagnetic Kentucky ash-charcoal mixture as a function of gas velocity (bed height equal bed diameter)

Figure 24. Percent expansion of a bed of charcoal-nonmagnetic Kentucky ash-charcoal mixture as a function of gas velocity (bed height is two times bed diameter)

Figure 25. Percent expansion of a bed of charcoal-non-magnetic Kentucky ash-charcoal mixture as a function of gas velocity (bed height is five times bed diameter)

Figure 26. Pressure drop through a bed of nonmagnetic fraction of Tennessee fly ash and charcoal mixture as a function of gas velocity

Figure 27. Pressure drop through a bed of nonmagnetic fraction of C-1 fly ash and charcoal mixture as a function of gas velocity

bed expansion characteristics of Tennessee and C-1 Illinois ash are shown in Figures 28 and 29, respectively. Up to 70 and 80 maximum percent expansion were obtained for Tennessee and C-1 Illinois ash, respectively.

Fluidization of a Fly Ash and Coal Mixture

Coal can be the least expensive carbon source to serve as a reducing agent in the chlorination of fly ash. Thus, it was proposed that the fluidization characteristics of coal and fly ash mixture be investigated.

Star coal 63-74 and nonmagnetic Kentucky fly ash were weighed on a 10 to 3 (ash to coal) ratio. Attempts to mix and fluidize two layers of coal and ash by air alone failed. The use of an electric stirrer to assist mixing and fluidization of the bed did not improve the fluidization. Finally, the mixture was oven-dried at 105°C for a few days. The dried mixture of Star coal and Kentucky ash fluidized readily and rather smoothly at high air velocities. Figures 30 and 31 show the results of pressure drop and bed expansion of the coal-Kentucky ash mixture. The general bed performance was similar to the charcoal mixture.

Figure 28. Percent expansion of a bed of nonmagnetic Tennessee-charcoal mixture as a function of gas velocity

Figure 29. Percent expansion of a bed of nonmagnetic C-1 fly ash-charcoal mixture as a function of gas velocity

Figure 30. Pressure drop through a bed of nonmagnetic Kentucky ash and dried coal mixture as a function of gas velocity

Figure 31. Percent expansion of a bed of nonmagnetic Kentucky ash and dried coal mixture as a function of gas velocity

Fluidization of the Chlorinated Kentucky Ash

Fluidization characteristics of the chlorinated Kentucky ash were also investigated at an aspect ratio of 2. The bed of chlorinated Kentucky ash fluidized readily and did not require the assistance of the mechanical stirrer. The fixed bed region was clearly established. The minimum fluidizing velocity was about 0.1 cm/sec. The percent bed expansion up to 60 percent was observed.

DISCUSSION

With the exception of C-1 fly ash, all of the ashes tested fluidized with some difficulty. Air channels readily developed in shallow beds, while in deeper beds only partial fluidization existed in some upper regions of the bed of Tennessee, Kentucky and Darold-Tabor ashes.

C-1 fly ash collected by mechanical precipitators has an average particle size of 21 microns and a wide size distribution (from 1 to 200 microns). While the other fly ashes that exhibited channeling tendency when fluidized were collected by electrostatic precipitators. These ashes have similar particle size distribution and almost the same average particle size of about 6 microns. Their largest particle sizes are considerably smaller than that of C-1 fly ash and their size distributions are narrow in the small size fraction as compared with C-1 fly ash. These facts could explain the different fluidization characteristics between C-1 fly ash and the other ashes. It would be advantageous to utilize only mechanically collected ashes (such as C-1 fly ash) in the fluidized bed HiChlor process because of their good fluidization characteristics. However, the fact that more and more fly ashes being collected by the electrostatic precipitators would make the idea unattractive.

It was discovered that the fluidization properties of

cohesive fly ash improve considerably when finely pulverized charcoal powder was added to the mixture. Up to 30 percent by weight of charcoal was present in the mixture. The observed fluidization characteristics of the mixture closely matched the fluidization behavior of group A powder in Geldart's classification (11). That is they expanded considerably before air bubbles were visible and solid mixing was quite fast. It was usual to achieve a maximum of 70 to 80 percent bed expansion. At velocities nearer the onset of fluidization, the bed characteristics were inconsistent. This is understandable as at the transition point between the fixed and the fluidized states, nonuniformity in the bed structure was expected and this resulted in fixed and fluidized regions co-existing within the bed. In addition, at low air velocities, it was possible that small and light particles began to fluidize before the large and heavy particles. At these velocities, the bed structure was changed and rearranged itself in such a way that an equilibrium bed segregation was eventually established. When the air velocity was increased, more and more particles fluidized until the whole bed was in the fluidized state. At the same time, the smallest and lightest particles were elutriated from the bed and were collected at the filter.

Most of the mixtures exhibited turbulent fluidization

with large bubbles escaping from the surface at velocities of about 2 to 4 cm/sec. A slight increase in bed pressure drop was noted at these higher velocities as seen in Figures 19 and 30. This is probably normal for an easily-fluidized system as described in the literature (Figure 1). The initiation of large scale entrainment probably began at air velocities of about 4 cm/sec for the mixtures of Kentucky ash and charcoal. S. Weiss (7) had calculated the material balances for a chlorination reaction of C-1 ash. Using this material balance data, a required chlorine flow rate was estimated about 4 cm/sec which is of the same order of the air fluidizing flow rate required for good fluidization.

The defluidization procedure (decreasing the air velocity) employed in this work had the effect of maximizing the segregation of the bed (29). Upon defluidizing from the highest velocity, the bed usually showed an immediate and rapid decrease in pressure drop for mixtures of Kentucky ash, but this was not so for mixtures of C-1 fly ash and Tennessee fly ash (compare Figures 18, 26 and 27). This segregation pattern of mixtures of Kentucky ash can be traced to the larger amount of magnetic particles present in the Kentucky ash than in the C-1 and Tennessee fly ashes. The density of a magnetic particle is usually three times as much as that of nonmagnetic particles (37). And Rowe et al. (27) showed

that large difference in particle density readily causes segregation.

Concerning the possible segregation between charcoal particles (density equal 1.6 g/cm^3) and fly ashes (density about $2.0\text{--}2.6 \text{ g/cm}^3$), little data was available, except that a rapid, visual color blend of the black charcoal powder and the lighter fly ash was attained. The lower density charcoal particles were compensated by their larger average particle size when mixing with fly ash. It is believed at high enough flow rates, such as 3 cm/sec , the mixing of different size and density charcoal and fly ash can be completed. At these high velocities, solids circulation was observed very fast. Even in a deep bed of L/D equal 5, the solids were believed well-mixed.

The phenomenon of a sudden increase in the pressure drop at velocities of 0.6 cm/sec when the air velocity was decreasing was usually observed as seen in Figures 16, 18 and 19. This occurred at the same time that the bed changed from turbulent bubbling fluidization to smooth, uniform fluidization. This implied that in the re-structuring of the fluidized bed, a few large and turbulent bubbles were replaced by a uniform distribution of numerous tiny bubbles. The result was more air flowing interstitially and the bed pressure drop returned to the high values.

Good fluidization of mixtures of charcoal and cohesive fly ashes was achieved only after mechanically stirring the fluidized mixtures for about 5 to 15 minutes. The reason why this pre-treatment is required is not clear. It is possible that the presence of the 30 percent by weight of coarser charcoal powder in the mixture simply raised the mean particle size of the mixture to an acceptable level for fluidization. The action of the mechanical stirring was probably to initially mix the charcoal particles into the mass of cohesive fly ash and then to break down preferential gas channeling. It is interesting to note that once the onset of fluidization of the mixtures was established, the removal of the mechanical stirrer did not affect the fluidization. Beds which were fluidized many times were always ready to fluidize without the further assistance of a stirrer.

It is also possible that after an initial fluidization, fine particles were lost by elutriation and the bed was easier to fluidize a second time. To check this possibility, the size analysis of two mixtures of Tennessee and Kentucky ashes with charcoal were carried out before and after fluidization of the mixtures. The results were shown in Figures 32 and 33 for Tennessee and Kentucky ashes, respectively. These results showed that the fine particle loss was not significant for both fly ashes in the experimental conditions used in this work and that the loss of fine particles was not,

Figure 32. Size distribution of a mixture of Tennessee ash and charcoal, before and after one fluidization

Figure 33. Size distribution of a mixture of Kentucky ash and charcoal, before and after one fluidization

therefore, the explanation of the problem.

In order to investigate the nature of the action of the charcoal particles in the mixtures, several electron-microscope photographs of samples of the mixtures were taken. Figures 34 and 35 showed that some fly ash particles adhered to the larger charcoal particles. There are also some indications of fly ash agglomeration.

Figure 34. A scanning electron micrograph of a sample of
a mixture of charcoal and Tennessee ash
(X = 500)

Figure 35. A scanning electron micrograph of a sample of
a mixture of charcoal and Kentucky ash
(X = 500)

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

CONCLUSIONS

The fluidization characteristics of several of the most common power plant fly ashes were experimentally investigated and large differences in their fluidization characteristics were observed. Conclusions derived from the results were:

1. The fluidization of a larger particle size, mechanically collected fly ashes was simple and the resulting bed had the characteristics of a well-fluidized system.
2. Most fly ashes which were collected by electrostatic precipitation had a smaller particle size and did not fluidize normally.
3. The fluidization characteristics of those small particle size, cohesive fly ashes were considerably improved when 30 percent by weight of charcoal powder was added to the mixture.
4. The particle size of the charcoal powder which could be used to achieve a satisfactory fluidization performance for the mixture ranged from 10 microns to 149 microns. The charcoal particle size distribution need not be narrow to yield good fluidization characteristics.

5. A bed depth of up to five times the bed diameter can be fluidized without any serious particle segregation, provided that an air superficial velocity of about 2 to 4 cm/sec is maintained.
6. The fluidization of dried coal and cohesive fly ash was similar to that of charcoal-ash mixtures.
7. The chlorinated fly ash can be fluidized easily.
8. A low percentage of high-density magnetic fly ash improves the fluidization characteristics of the mixture.

SUGGESTIONS FOR FUTURE WORK

On the basis of the results obtained in this work, it is suggested that some investigations are needed to advance the development of the high temperature chlorination (HiChlor) process. Future work is suggested below:

1. To investigate the entrainment and elutriation of the ashes at various fluidization conditions. The results obtained can be used to design a particle collector for a continuous HiChlor process. Additionally, chlorinated ash particles are aerodynamically lighter than unchlorinated particles and the difference between the two ashes can provide an effective means of preferentially removing the chlorinated ash.
2. To investigate the chlorination of fly ash in a fluidized bed reactor. Some practical information needed includes the fluidization behaviors of fly ash at high temperature, the fluidization characteristics of fly ash using chlorine as a fluidizing gas and the kinetics of ash chlorination in a fluidized bed reactor compared to that in a packed bed.

At high temperatures, the fluidized particles may stick together to form an agglomerating bed.

In this case the fluidization characteristics could be considerably different from those of the low temperature operation (38).

The use of chlorine gas in place of air is not expected to be a problem, but the fluidization parameters would quantitatively be different. In general, the fluidization velocity decreases with the increase in gas density and viscosity. The change in gas viscosity has a greater effect on the fluidization properties of fine powders than the change in gas density

The kinetics study is needed to establish the optimum chlorine utilization and maximum alumina recovery for a minimum reaction time.

3. To investigate the residence time distribution of different sized fly ash particles. The residence data are needed to evaluate the continuous chlorination process.
4. To investigate the continuous feeding and discharge of fly ash to develop a continuous operation.
5. To investigate the possibility of applying fast-fluidization technology in the HiChlor process. Fast fluidization is a technique for bringing gas at high velocity into intimate contact with a fine-

solid, in an entrained dense suspension characterized by extreme-turbulence (40). The fast bed possesses all the qualities of a normal bubbling fluidized bed. In addition, the fast fluidized bed permits high processing capacities which allows to use small-diameter reactors to be used. Such a system handles cohesive solids better than a bubbling fluidized bed, especially at high temperature and the fast bed operation might approach a plug flow condition giving, perhaps, a higher reaction conversion.

LITERATURE CITED

1. J. H. Faber. U.S. overview of ash production and utilization. Proceedings of Fourth Int. Ash Utilization Symposium, St. Louis, Mo., March 24, 25, 1976. Available from: The National Tech. Infor. Service, U.S. Dept. of Commerce, Springfield, Va.; 1976.
2. M. Eisenbud and H. G. Petrow. Radioactivity in the atmospheric effluents of power-plants that used fossil fuels. Science 144:288; April 1965.
3. T. L. Theis et al. Field investigations of trace metals in ground water from fly ash disposal. Proc. Ind. Waste Conf. 32:332-334; 1977.
4. H. Watjano, G. Burnet, and M. Murtha. Recovery of alumina from fly ash by high-temperature chlorination. Third Kentucky Coal Refuse Disposal and Utilization Seminar, University of Kentucky, Lexington, Ky., May 11, 12, 1977.
5. A. K. Mehrotra, P. R. Bishnor and W. Y. Svercek. Metal recovery from coal ash via chlorination, a thermodynamic study. Can. J. Chem. Eng. 57:225; April, 1979.
6. K. S. Chou, G. Burnet and M. Murtha. The lime-sinter process for production of alumina from fly ash. Proceedings Fourth Int. Ash Utilization Symposium, St. Louis, Mo., March 24, 25, 1976.
7. S. Weiss. Quarterly Report - Ames Lab, DOe. Chemical Engineering Group III. June 1, 1978 to August 31, 1978.
8. T. D. Wheelock. Literature on fluidized bed systems relevant to wheat flour modification. Dept. of Chem. Engrg., Iowa State University, Ames; 1966.
9. N. A. Kozulin and A. F. Kulyamin. Mixing of powdered materials in a fluidized bed. Int. Chem. Eng. 5(1): 157, 1965.
10. J. C. Halow, Chairman. Fluidized bed applications. Fluidization and Fluid-Particle Systems. AIChE. Symp. Ser. No. 141, 70; 1974.

11. D. Geldart. Types of gas fluidization. Powder Tech. 7:285; 1973.
12. J. F. Richardson. Incipient fluidization and particulate systems. J. F. Davison and D. Harrison, eds. Fluidization. New York: Academic Press; 1971; Chapter 2.
13. G. L. Matheson, W. A. Herbst and P. H. Holt. Characteristics of fluid-solid systems. Ind. Eng. Chem. 41: 1099; 1949.
14. D. Kuinii and O. Levenspiel. Fluidization Engineering, Chapter 3. New York: John Wiley and Sons, Inc.; 1959; pp. 64-102.
15. S. Hovmand and J. F. Davidson. Pilot plant and laboratory scale fluidized reactors at high gas velocities; the relevance of slug flow. J. F. Davidson and D. Harrison, eds. Fluidization. New York: Academic Press; 1971; Chapter 5.
16. P. S. B. Stewart and J. F. Davidson. Slug flow in fluidized beds. Powder Tech. 1:51; 1967.
17. D. Geldart, C. G. J. Baker. An investigation into the slugging characteristics of large particles. Powder Tech. 19:177; 1978.
18. M. Leva et al. Fluidization of solids. U.S. Bur. Mines Bull. 504:57, 1951.
19. H. Littman and R. C. Lirag, Jr. Statistical study of the pressure fluctuations in a fluidized bed. Fluidization: Fundamental Studies, Solid-Fluid Reactions and Applications. AIChE Symp. Ser. No. 116, 67:11; 1971.
20. J. F. Richardson and L. Davies. Gas interchange between bubbles and the continuous phase in a fluidized bed. Trans. Inst. of Chem. Eng. 44:T293; 1966.
21. D. N. Rowe, L. Santoro and J. E. Yates. The division of gas between bubble and interstitial phases in fluidized beds of fine powders. Chem. Eng. Sci. 33:133; 1978.
22. P. N. Rowe and C. X. R. Yacono. The bubbling behavior of fine powders when fluidized. Chem. Eng. Sci. 31: 1179; 1976.

23. P. N. Rowe et al. The mechanisms of solids mixing in fluidized beds. Trans. Inst. Chem. Engrs. 43: 7271; 1965.
24. P. N. Rowe, A. W. Nienow and A. J. Agbim. A preliminary quantitative study of particle segregation in gas fluidized beds - binary systems of near spherical particles. Trans. Inst. Chem. Engrs. 50:324; 1972.
25. P. N. Rowe, A. W. Nienow and A. J. Agbim. The mechanisms by which particles segregate in gas fluidized beds. Binary systems of near spherical particles. Trans. Instr. Engrs. 50:310; 1972.
26. S. Chiba, T. Chiba, A. W. Nienow and H. Kobayashi. The minimum fluidization velocity, bed expansion and pressure-drop profile of binary particle mixtures. Powder Tech. 22:255; 1979.
27. N. Harnby. Private communication. Present address, Dept. of Chem. Eng., University of Bradford, Bradford, Yorks (Gt. Britain).
28. T. M. Reed and M. R. Fenske. Effects of agitation on gas fluidization of solids. Ind. Eng. Chem. 47: 275; 1955.
29. R. H. Nielson. Particle mixing and circulation in gas-fluidized beds of flour and starch. Doctor's Dissertation, Iowa State University, Ames, Iowa.
30. J. Novosad and E. Kostelkova. Incipient fluidization of cohesive powders by horizontal rotating nozzle in fluidization. Proceedings of the Second Engineering Foundation Conference, Trinity College, Cambridge, England, 2-6, April 1978, p. 87.
31. R. D. Morse. Sonic energy in granular solid fluidization. Ind. Eng. Chem. 47:1176; 1955.
32. L. J. Jolley and J. E. Stanton. Fluidization in beds of coals and cokes particles: Some effects of size of particles and viscosity, density and velocity of gas. J. Appl. Chem. 2, S62 (Supplement issue); 1952.

33. E. M. Fried. Performance characteristic of a fluidized bed of wheat flour. Unpublished M.S. thesis, Iowa State University, Ames, Iowa.
34. H. Trawinski. Fluidization studies. Chem. Eng. Sci. 2, No. 4:201; 1963.
35. M. Leva and C. Y. Wen. Elutriation. J. F. Davidson and D. Harrison, eds. Fluidization. New York: Academic Press; 1971; Chapter 14.
36. M. Murtha. Unpublished work. Ames Laboratory, Department of Chem. Eng., Iowa State University, Ames, Iowa.
37. P. L. Boar and L. K. Ingram. The comprehensive analysis of coal ash and silicate rocks by atomic-absorption spectrophotometry by a fusion technique. Analyst 95: 124; Feb. 1970.
38. C. Y. Wen and S. Dutta. Research needs for the analysis, design and scale up of fluidized beds. Fluidization theories and applications. AIChE Symp. Ser. No. 161, 73:1; 1977.
39. D. Geldart and A. R. Abrahamsen. Homogeneous fluidization of fine powders, using various gases and pressures. Powder Tech. 19:133; 1971.
40. J. Yerushalmi and A. M. Squires. The phenomenon of fast fluidization. Fluidization theories and applications. AIChE Symp., Ser. No. 161, 73:44; 1977.

ACKNOWLEDGMENTS

I would like to express my appreciation and gratitude to Professor G. Burnet and Professor N. Harnby for the guidance and helpful commentary offered during the enjoyable course of this investigation.

I wish to thank Professor T. Wheelock for the use of the Alundum porous discs; without his authorization, the investigation would be unnecessarily delayed.

Special thanks are due to M. Murtha, Associate Engineer, Ames Lab, for his experience and counseling. The assistance offered by M. Peterson for Coulter Counter size analysis and J. Amenson for SEM photography is also appreciated.

The financial support under contract with USDOE, Ames Lab through the Department of Chemical Engineering, Iowa State University is also gratefully acknowledged.