

Laboratory Techniques for Evaluating Ash Agglomeration Potential in Petroleum Coke Fired Circulating Fluidized Bed Combustors

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INTRODUCTION

Petroleum coke is a waste product which is produced in large quantities in refineries throughout the U. S. Traditionally, petroleum coke has not been a boiler fuel of choice due to its relatively high sulfur content. Its burning in conventional pulverized coal-fired boilers is not desirable unless costly flue gas desulfurization is available or the coke is blended with coal to achieve acceptable sulfur emissions. However, in a CFB the coke can be effectively utilized in an environmentally sound manner by using a sorbent material for sulfur capture.

Based on experience with heavy oil fired boilers, vanadium in the fuel can result in the formation of low-melting compounds and consequent backpass deposits. In a CFB, vanadium can cause additional concerns of agglomeration in the combustor or loop seal due to molten ash compounds. When petroleum coke is burned, vanadium will ultimately oxidize to vanadium pentoxide (V_2O_5), which has a melting point well below nominal combustor temperatures (1275°F). In addition, other constituents in the coke ash and calcium-based sorbents can react with vanadium to form complexes with low melting temperatures. This paper presents simple laboratory techniques which were developed for assessing the agglomeration potential from petroleum coke firing. The results of this work helped define CFB operating conditions and identify solid additives which minimize ash agglomeration.

EXPERIMENTAL

Several laboratory tests were utilized for evaluating the potential of ash agglomeration from petroleum coke firing. These tests included measurement of ash sinter strength, electrical resistance and "hot" angles of repose/internal friction. These tests were conducted with loop seal ash (j-valve) taken from a full scale 100 MW CFB firing 100 percent delayed petroleum coke.

Analyses of the petroleum coke ash and j-valve ash are shown in Table 1. The petroleum coke contained 0.51% ash, with V_2O_5 and NiO contents of 57.0% and 10.2%, respectively. As expected the concentration of nickel and vanadium in the j-valve ash were much lower as a result of dilution from the limestone sorbent. Ash fusion temperatures are shown in Table 2. The ash fusion temperatures were considerably lower for the pure coke ash due to its relatively high vanadium content. As expected the ash fusion temperatures were lower in an oxidizing atmosphere, since vanadium compounds in a reduced state have much higher melting points than vanadium pentoxide. Particle size analysis showed that the j-valve ash

received at the laboratory was fairly fine and had a D_{50} of about 150 microns.

Ash sintering tests were performed with the j-valve ash in order to evaluate the effect of time, temperature and atmosphere on ash particle-to-particle bonding. This test has been used extensively in the past for evaluating the backpass fouling tendencies of coal ashes in p.c.-fired boilers (1, 2). This simple test involved heating a compacted ash sample in a tube furnace under an artificial atmosphere to a desired temperature for a specified period of time. After cooling the sample was measured to determine the extent of shrinkage, then crushed with a Buehler metallurgical press to measure the compressive strength. The accuracy of this machine yielded strengths which were ± 25 psi; an average strength was obtained by crushing triplicate samples. Both shrinkage and compressive strength are parameters which give an indication of the extent of agglomeration. The effect on sintering of chemical additives containing magnesium (MgO and dolomite) was also evaluated.

In conjunction with these sintering tests, electrical resistance measurements were performed on ash compacts as a function of temperature. This test is much more sensitive than conventional ash fusion tests and has been used to determine the temperature at which trace ash components melt (3,4,5). These tests were accomplished by placing ash in a crucible (0.5 in dia x 1.0 in high) between two platinum foil electrodes and measuring the electrical resistance with a Fluke multimeter. The ash sample was heated in air at a rate of $10^\circ\text{F}/\text{min}$ to a temperature of 1800°F .

A simple test was also used to measure the angles of repose and internal friction of j-valve ash samples at temperatures up to about 1500°F . This test can provide important information related to the flow properties of ash in a CFB loop seal. In this test, about 3 lb of ash was placed in a 5 inch diameter quartz cylinder centered on ceramic insulation with a 1 inch diameter hole. A stainless steel strip was used to cover the hole and act as a slide gate to allow flow. This setup was placed on ceramic bricks in a box furnace which was then heated at a rate of about $5^\circ\text{F}/\text{min}$ in air at temperatures between 1100°F and 1500°F . After the furnace was heated to the desired temperature, the stainless steel strip was removed which then allowed the solids in the cylinder to flow. The dimensions of the ash pile and the remaining ash in the cylinder were then measured with calipers to calculate the angles of repose and internal friction (see Figure 1).

RESULTS AND DISCUSSION

Ash sintering test results are shown in Table 3 for the j-valve ash; the effect of temperature, time and atmosphere were evaluated in these tests. Heat treatment temperature was shown to have the most significant effect on the compressive strength of ash compacts sintered in a gas mixture containing 1000 ppm SO_2/air . This gaseous environment was used to simulate that present in the bed of the CFB. No measurable compressive strength was observed until the ash was heated up to 2000°F . However, the ash compacts revealed minor shrinkage when sintered at temperatures less than 2000°F , thus indicating that agglomeration was occurring.

Table 4 lists some of the possible low melting point constituents in the j-valve ash. Even

though the j-valve ash contained only 0.8% V_2O_5 , other ash and sorbent constituents can interact with vanadium to yield phases with melting points of less than 1650°F. Formation of these low melting phases was probably responsible for the shrinkage of the ash compacts below 2000°F. The development of sinter strength at 2000°F was probably due to increased liquid phase formation, coupled with a lower liquid phase viscosity. Ceramic literature has shown that the rate of agglomeration in the presence of a liquid phase is inversely proportional to the viscosity of the liquid phase (6). Ash samples heated to 2000°F appeared to have a liquid layer on the surface which actually became bonded to the alumina crucibles upon cooling. The compressive strength of the sintered ash compacts increased by a factor of three as the sintering time was increased from 2 to 18 hours (Table 3). This threefold increase in sinter strength is consistent with ceramic data which shows that the rate of ash sintering is proportional to time to the one-half power (6).

The compressive strength was found to be higher for samples sintered in the SO_2 /air atmosphere compared to those sintered in air and a 1000 ppm CO/N_2 mixture. The higher compressive strength of the sample sintered in the atmosphere containing SO_2 was probably a result of bonding from the sulfation of unreacted CaO. The lower compressive strength of the ash sintered in the reducing atmosphere may be due to more vanadium being present in a reduced state. As shown in Table 4, the melting point is much higher for vanadium trioxide and tetroxide (V_2O_3 and V_2O_4) compared to V_2O_5 .

Sintering tests were also performed with additives containing magnesium. These additives included a commercially available boiler additive (88.5% MgO) and a calcined dolomite containing about 40% MgO. Magnesium compounds have been used extensively to inhibit corrosion/deposition in gas turbines firing residual oil fuels containing vanadium. In gas turbines the magnesium reacts with vanadium in the fuel to form $Mg_3V_2O_8$ which has a much higher melting point than V_2O_5 . Sintering test results showed that the addition of 1 wt% of the boiler additive greatly reduced the compressive strength of the ash compacts. Calcined dolomite was also shown to reduce the ash sinter strength, but to a lesser degree than the boiler additive probably due to the lower concentration of magnesium in the dolomite.

Electrical resistance measurements are shown in Figure 2 for the j-valve ash as a semi-logarithmic plot of resistance versus inverse absolute temperature. As shown in this plot, there is a change in the slope of the plot at a temperature of about 1300°F. This sharp increase in the slope of the log r versus inverse absolute temperature curve has generally been attributed to trace melting on particle surfaces, which consequently allows increased electrical conduction (3). This technique is much more sensitive than conventional ash fusion tests and can detect the melting of minor ash constituents (~1%). The onset of melting in the j-valve ash appears to coincide with the melting point of vanadium pentoxide, though it could actually be due to other ash eutectics with vanadium (Ni and Ca). Resistance measurements were also performed with ash containing 1% of the boiler additive, in order to elucidate the role of vanadium on melting. As shown in Figure 2, there was no change in the slope of the log resistance versus 1/T plot, possibly indicating that the magnesium was reacting with the vanadium to form a higher melting point material.

A several inch thick deposit taken from the upper cyclone of the 100 MW coke fired CFB

was also studied in laboratory tests. The ash chemical analysis in Table 1 shows that the deposit was enriched in vanadium (3.4% vs. 0.8%). As expected the ash fusion temperatures were much lower for the deposit compared to the j-valve ash due to this enrichment. The compressive strength of this deposit (3500 psi) was much higher than the laboratory sintered ash samples; this difference was probably due its higher vanadium content and extended exposure to elevated temperatures. A piece of this highly fused deposit was ground to less than 100 mesh (149 microns) for electrical resistance measurements. As shown in Figure 2, the deposit also had a lower onset of melting than the j-valve ash (1250 vs 1300°F).

SEM photomicrographs of the inner deposit layer and middle cross-section are shown in Figure 3. The deposit appeared to have been fairly molten and contained particles on only several microns in diameter. Semi-quantitative XRD analysis showed that the deposit was relatively consistent throughout in Ca, S and V concentrations. It was likely that vanadium interacted with calcium in the sorbent to form a low melting, low viscosity phase which promoted particle-to-particle bonding. The phase diagram for the CaO and V_2O_5 system shows equimolar concentrations of V_2O_5 and CaO form a low melting eutectic at 1432°F. Even though most of the outer surface of sorbent particles would be a sulfated shell ($CaSO_4$), some portion of the surface could be CaO due to attrition. This CaO on the surface could then react with vanadium. Phase equilibria between V_2O_5 and $CaSO_4$ could not be found in the literature and is an area for future work.

The results of ash flow tests are summarized in Table 3. For the j-valve ash without additive, the angles of repose and internal friction began to increase at about 1300°F. This temperature is approximately the same temperature at which the electrical resistance measurements show trace melting within the ash. When the temperature was increased to 1400°F, the solids would not flow and remained hung-up in the cylinder. A crusted layer was observed on the top of the ash along with weak agglomeration throughout the cylinder. With 1% of the boiler additive, the ash was observed to flow freely at temperatures up to 1500°F. Apparently, the MgO in the additive increased the melting point of eutectics and prevented agglomeration.

The extent of melting in this test appeared minor, but sufficient to inhibit the flow of solids. As a result, poor fluidization zones should be avoided in a loop seal since defluidized ash could agglomerate over a period of time, even at relatively low temperatures. This problem can be compounded in a full-scale CFB due to the weight of the column of solids causing pressure sintering.

SUMMARY AND CONCLUSIONS

Even though petroleum coke is relatively low in ash, several thousand ppm of vanadium in a coke can cause concern for ash agglomeration problems in a CFB loop seal. Laboratory tests showed that two major operating parameters can have a significant effect on controlling agglomeration. First, combustor temperature has a strong effect on the formation of low melting vanadium eutectics and the rate of agglomeration. Second, defluidization of combustor ash can lead to sintering at relatively low temperatures since dense packing promotes particle-to-particle bonding. Commercial experience with petroleum coke firing has

shown that maintaining the combustor temperature below 1700°F has helped eliminate the formation of cyclone deposits. Likewise, proper fluidization in the loop seal has been shown to reduce agglomeration of settled ash over a long period of time. Magnesium-based solid additives can also be utilized as a means of controlling vanadium related ash agglomeration. Although commercially available boiler additives can reduce agglomeration in laboratory tests, they are probably not viable candidates for commercial units due to cost considerations. On the other hand dolomite as a source of vanadium should be considered, provided it has the proper size distribution to interact with vanadium.

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Table 1 Composition of Ash from 100 MW CFB

Ash Composition, wt%			
	Pet Coke Ash	J-Valve Ash	Cyclone Deposit
SiO ₂	13.8	0.3	Nil
Al ₂ O ₃	5.9	0.1	0.3
Fe ₂ O ₃	4.5	Nil	Nil
CaO	3.6	47.1	43.1
MgO	0.6	1.4	1.7
Na ₂ O	0.4	0.1	0.1
NiO	10.2	0.2	0.7
V ₂ O ₅	57.0	1.4	3.8
SO ₃	1.6	48.0	48.0
Total	97.9	98.6	97.8

Table 2 Fusion Temperatures of Ash from 100 MW CFB

Ash Fusion Temperatures, °F						
ID	Pet Coke Ash		J-Valve Ash		Cyclone Deposit	
	Reducing	Oxidizing	Reducing	Oxidizing	Reducing	Oxidizing
ST	2187	1974	2900(+)	2567	2765	2453
ST(sph)	2205	2037	2900(+)	2656	2810	2459
ST(hemi)	2213	2061	2900(+)	2798	2814	2706
FT	2220	2077	2900(+)	2800	2815	2707

Table 3 Sinter Test Results with J-Valve Ash

Temperature °F	Duration, hr	Atmosphere	Compressive Strength, Psi	Shrinkage, %
1800	2	SO ₂ /air	0	5
1900	2	SO ₂ /air	0	11
2000	2	SO ₂ /air	320	25
2000	18	SO ₂ /air	960	33
2000	2	air	200	18
2000	2	CO/N ₂	125	10
2000*	2	SO ₂ /air	125	12
2000*	18	SO ₂ /air	200	15
2000**	2	SO ₂ /air	200	22

* 1% MgO additive added

** 1% calcined dolomite added

Table 4 Possible Ash Constituents formed During Combustion of Petroleum Coke and their Melting Points

Compound		Melting Point, °F
Calcium Sulfate	CaSO ₄	2642
Nicke Oxide	NiO	3794
Sodium Sulfate	Na ₂ SO ₄	1616
Vanadium trioxide	V ₂ O ₃	3578
Vanadium tetroxide	V ₂ O ₄	3578
Vanadium Pentoxide	V ₂ O ₅	1274
Calcium Metavanadate	CaO.V ₂ O ₅	1432
Sodium metavanadate	Na ₂ O.V ₂ O ₅	1166
Nicel pyrovanadate	2NiO.V ₂ O ₅	1650
Ferric metavanadate	Fe ₂ O ₃ .V ₂ O ₅	1580

Table 5 Angles of Repose and Internal Friction for J-Valve Ash

Temperature, °F	No Additive Angle, deg.		1% MgO additive Angle, deg.	
	Repose	Internal Friction	Repose	Internal Friction
1500	- -	no solids flow - -	40	90
1400	- -	no solids flow - -	37	53
1300	37	90	35	51
1200	29	53	37	51
1100	30	51	36	51
Cold	30	48	35	50

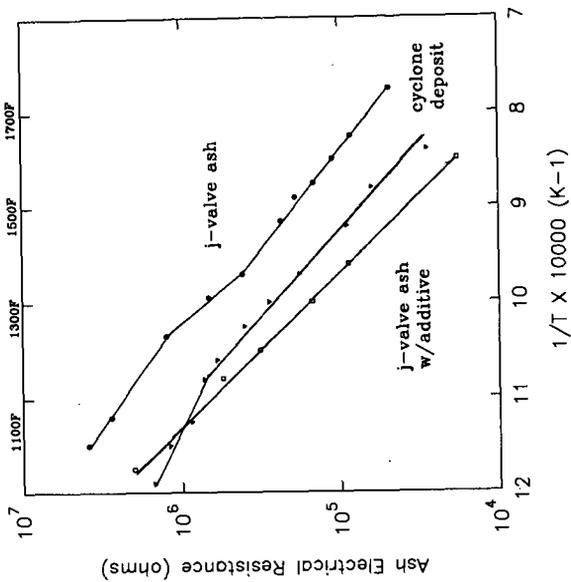


Figure 2 Ash electrical resistance measurements

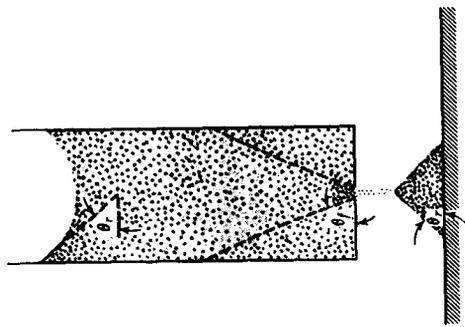
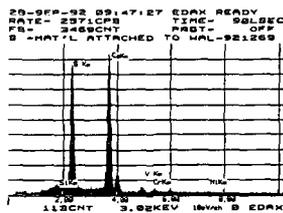
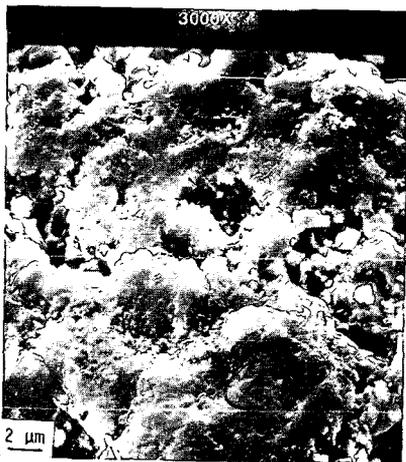
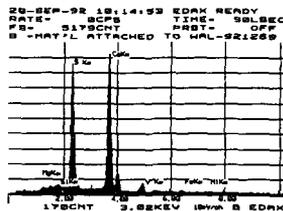
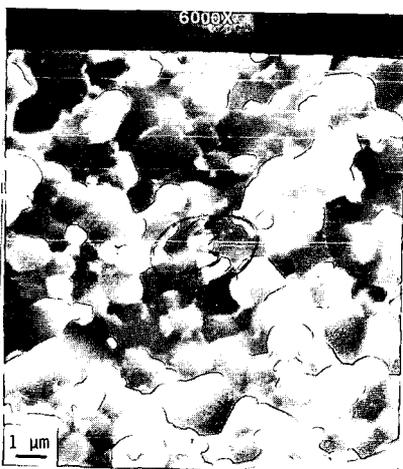


Figure 1 Angles of repose and internal friction (7)



ELEM	CPS	AT %
S K	340.407	41.442
CA K	416.483	52.584
V K	15.923	2.086
CR K	7.906	1.110
NI K	3.537	0.778
TOTAL		100.000

(a) inner layer



ELEM	CPS	AT %
MG K	4.317	0.646
SI K	14.869	1.213
S K	502.562	41.121
CA K	633.079	51.248
V K	40.092	3.367
FE K	10.808	1.238
NI K	8.267	1.166
TOTAL		100.000

(b) cross-section

Figure 3 SEM photomicrographs and EDX spectra for cyclone deposit:
 (a) inner layer and (b) cross-section