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**SORBATE CHARACTERISTICS OF FLY ASH
QUARTERLY PROGRESS REPORT**

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ABSTRACT

This second quarterly report deals with evaluation of the fly ash sorbate characteristics for removal of organics in ash pond effluent as measured by Chemical Oxygen Demand (COD) and Arsenic.

The Mössbauer spectra is being interpreted to identify the form of the iron compounds present in the fly ashes resulting from the different combustion conditions encountered in the three different types of coal fired boilers used in this investigation and also in the coal burned in these boilers.

The results indicate that boiler conditions which produce fly ashes with sorbate characteristics that favor the removal of cations also favor the removal of the anion arsenic. The effectiveness of the fly ashes for removal of COD could not be determined because the ash pond effluents used were found to contain chloride concentration levels that interfered with the COD determination.

Interpretation of the Mössbauer spectra revealed that the chemical state of the iron in both the coal and the resulting fly ash can be used to monitor the fluid nature of the ash in the boiler. The results also indicated that the chemical state of the iron in the eastern coals used in this study can influence the fusion temperature of the ash.

INTRODUCTION

A two year investigation is being carried out to provide a design of a system for the inexpensive treatment of ash pond effluent or leachate. Twelve different coals were burned in three different types of coal fired boilers in order to determine the influence of coal composition, ash fusion temperatures, boiler additives, combustion conditions and co-firing of natural gas or oil with the coal, on the surface and bulk composition of the fly ash, bulk composition of the bottom ash as well as the leaching and sorbate characteristics of the fly ash produced. This study includes the determination of 1) SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , K_2O , Na_2O , MgO , sulfur, ash fusion temperatures Ti, Cd, Sn, Ni, Pb, Mo, Cu, Cr, As, Mn, Ba and V in the coals and their respective fly ashes and bottom ashes, 2) Mössbauer spectra of a number of coals and their fly ashes and, 3) surface analysis of the fly ashes using ESCA. All of the above analysis have been completed. However, the Mössbauer spectra obtained on the coals and respective fly ashes is still being interpreted. In addition, the leaching and sorbate characteristics of the fly ashes with regard to pH, Cd, B, Sn, Ni, Pb, Mo, Cu, Cr, As, Mn and Fe have been defined. However, the sorbate characteristics of the fly ashes with regard to the anion removal such as arsenic and organics present in ash pond effluents have yet to be determined.

A summary of the results, to date, show that Al_2O_3 , MgO , Ti, and Zn tend to concentrate in the fly ash when compared to their respective bottom ashes, whereas, Fe_2O_3 , Sn, Mo, Cu and Cr tend to concentrate in the bottom ashes when compared to their respective fly ashes. Also, the amounts of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , K_2O , Na_2O , and MgO in the fly ashes do not appear to be influenced by boiler temperatures, power levels, addition of the

additive Coaltrol M (MgO) to the flue gases and the particle size of the fly ash particles. Analysis of the fly ashes produced from the low ash fusion temperature of the same coal at different boiler temperatures indicate that Ti, Sn, Ni, Pb, Mo, Cu, Cr, Zn, Mn, V and S concentrate in the fly ashes produced at the lower boiler temperatures. Also, Ti, Cd, Sn, Ni, Pb, Mo, Cu, Cr, As, Mn, and V tend to concentrate more in the smaller fly ash particles than the larger fly ash particles. ESCA analysis reveals that the relative amounts of Si, Al and Ca on the surfaces of the fly ashes decrease in the same order as their respective amounts present in the bulk of the fly ashes. However, the amount of sulfur present on the surface of the fly ashes, which appears to be partially due to the addition of the sulfur bearing additive LPA-40 to the fly ash particles, is significantly greater than that present in the bulk of the fly ash particles. Other factors responsible for this accumulation of sulfur on the surface of the fly ash particles have yet to be identified.

Leaching studies of the fly ashes produced from the same coal, but at different boiler temperatures, reveal that the amounts of Cd, B, Sn, Ni, Pb, Mo, Cu, Cr, Zn, Mn and Fe present in the leachate is influenced by the amounts of these trace elements in the fly ash and decreases in pH of the leachate. Decreases in the pH of leachate were observed to follow increases in the sulfur content in these fly ashes. However, no correlation was observed when comparisons are made between the pH and the amounts of the above elements in the leachate and the amounts of sulfur and the above trace elements present in fly ashes produced from different coals. The other factors, besides the sulfur and trace element composition of the fly ash, which influence the pH of the leachate and its composition have yet to be identified.

In general however, high boiler temperatures and decreases in the ash fusion temperatures tend to decrease the leaching characteristics of the fly ashes. Apparently, the fusion of the ash during the combustion process may encapsulate the above trace elements in a fused matrix which minimizes their leaching.

These findings also hold for the sorbate characteristics of the fly ashes. Low ash fusion temperatures or low excess air boiler conditions, co-firing the coal with oil or natural gas that provide temperatures adequate to melt the ash and cause fusion reactions to occur, provides favorable sorbate characteristics to the fly ash. Fly ash particles which in general leach the least amount of above trace elements exhibit the best removal of these trace elements from the ash pond effluent.

This second quarterly report is concerned with further sorbate characterization of the fly ashes for removal of arsenic and organics. Also, interpretation of the Mössbauer spectra is being carried out to determine 1) the forms of iron in the coal that may influence its ash fusion temperatures, 2) the forms of iron in the fly ashes that can be used to indicate the degree of fusion that has occurred and 3) whether the forms of iron in the fly ashes reflect the combustion conditions encountered in the boiler by the fly ash during its formation.

RESULTS

Sorbate Characterization of the Fly AShes for the Removal of Organics and Arsenic

Since the ash pond effluent collected from P.S.E. & G. Hudson generation station was used to evaluate the sorbate characteristics of the fly ashes for the removal of the trace elements described above. It

was also used in the evaluation of the fly ashes for their removal of organics as indicated by the Chemical Oxygen Demand (COD) and Arsenic.

Although, the Hudson facility uses tidal river water to transport the ash from the ash hoppers to the ash pond, it was anticipated that the facility was sufficiently upstream so that no salt water intrusion would be encountered. However, analysis of the ash pond effluent for chlorides revealed concentration levels that interfere with the COD determination. As a result, the sorbate characteristics of the fly ashes for COD removal will be evaluated in the next report period using the P.S.E. & G. Mercer generating facility ash pond effluent that utilizes fresh water to transport the ash to the ash pond.

The fly ashes produced from the twelve test coals under the boiler conditions described earlier have been evaluated for arsenic removal using the Hudson generating facility ash pond effluent. The removal of arsenic were evaluated by measuring concentration in the ash pond effluent before and after treatment with the fly ash using a carbon rod furnace with the Varian A.A. spectrophotometer (i.e. flameless atomic absorption spectroscopy).

Investigation of the fly ashes produced from the combustion of high ash fusion temperature coal under a variety of boiler conditions showed only that the Badger fly ash is capable of removing arsenic from the ash pond effluent (see Figure 1). In addition, the smaller fly ash particles (collected from the back precipitators) exhibited better removals than the larger particles (collected from the front precipitator). No removals of arsenic from the ash pond effluent were observed using the Militant, Deep Hollow and Upshur fly ashes. None of these fly ashes produced at

Fig. 1 As Absorption profile Curve for
Badger Coal
Boiler

different power outputs or the different size fly ashes collected from the front and back precipitators (which are operated in series) exhibited any arsenic removals. The concentration of arsenic in the leachate for these fly ashes, after treatment with the high ash fusion temperature fly ashes, is equal to or greater than the concentration of arsenic present in the ash pond effluent (see Figure 2, 3 and 4).

In the case of the Connemaugh and Keystone fly ashes, the fly ashes produced from the high ash fusion temperature coal burned in the Connemaugh boiler showed some removal of arsenic (see Figure 5). The fly ash produced in the Keystone boiler shows no removals of arsenic. The concentration of arsenic in the leachate treated with the Keystone fly ash is greater than that originally present in the ash pond effluent (see Figure 6).

On the other hand, all of the fly ashes produced from the low ash fusion temperature coal burned in the Mercer coal fired boiler showed removals of arsenic from the ash pond effluent. The inlet precipitator fly ashes produced by the number 11 boiler (operated at some 400°F higher than the similarly designed number 12 boiler operated in parallel) exhibited greater arsenic removals than the outlet fly ashes produced by the number 12 boiler (see Figures 7 through 11). The only exception is the Nora fly ashes. Both the Nora inlet and outlet fly ashes exhibited essentially the same removal (see Figure 12). In addition, the higher temperatures encountered in the Mercer boilers during the combustion of Wellmore Ackiss coal at maximum power output produced an inlet fly ash which exhibited better arsenic removals than the inlet fly ash produced at minimum power. The inlet fly ashes produced at full power reduced the arsenic in the ash pond effluent from 0.15 mg/l down to about 0.06 mg/l whereas the fly ash produced at minimum power reduced the arsenic to about 0.09 mg/l (see Figure 7).

Fig.3

As Absorption Profile for
Deep Hollow Coal Ash

Fig. 4 AS - Absorption profile Curve for
Upshure Coal
Boiler

Fig. 5 As Absorption Profile Curve for
Conomough Boiler

Fig. 6 As. Absorption Profile Curve for
Keystone Boiler-

Fig. 7 As Absorption profile curves for
Wellmore Ackiss

Fig. 8 As Absorption profile curve for
Mercer Blender

Fig.9 As Absorption profile curve for
Wellmore Cactus (I)

Fig. 10 AS - Absorption profile Curve for
Wellmore Cactus #2 coal
Mercer Boiler

Fig. 11 As Absorption profile curve for Ellsworth coal
Mercer Boiler

Fig. 12 As Absorption profile Curve for
Nora Coal
Mercer Boiler

The inlet fly ashes produced from the Wellmore Ackiss, Mercer Blend, and Nora coals exhibited the most significant removals of arsenic from the ash pond effluent. In general, the arsenic concentration in ash pond effluent was reduced from 0.15 mg/l down to about 0.05 mg/l (see Figures 7, 8 and 12). The inlet fly ashes produced from Wellmore Cactus I and Cactus II exhibited the next best removals of arsenic followed by the inlet fly ashes produced from the Ellsworth coal. The arsenic concentration in ash pond effluent after treatment with the Wellmore Cactus fly ashes was reduced to an average of about 0.085 mg/l (see Figures 9 and 10). The inlet Ellsworth fly ash was reduced the arsenic in the treated effluent to about 0.12 mg/l (see Figure 11).

These findings are the same as observed for the removal of Ti, Cd, Sn, Ni, Pb, Mo, Cu, Cr, An, Mn, Ba and V from the Hudson ash pond effluent. The Wellmore Ackiss, Mercer Blend, and Nora fly ashes were observed to exhibit the best sorbate characteristics for removal of the above elements as shown in the earlier progress reports. The next best removals were exhibited by the Wellmore Cactus fly ashes, followed by the Ellsworth fly ashes.

The above results indicate that the high boiler temperatures and boiler conditions that lead to melting and fusion reactions within the fly ash favor the formation of fly ash sorbate characteristics that favor the removals of not only the above cations but also the anion, arsenic.

" Mossbauer Results

The analysis of fly ash by ⁵⁷Mossbauer spectroscopy is very difficult

because of the overlap of many absorptions in the low velocity range. The iron silicate quadrupole doublets overlap strongly with the inner two absorptions of the magnetic patterns. In order to resolve this overlap a permanent magnet was used to separate the magnetic portion of the sample (Fe_3O_4). Figure 13 shows the Mössbauer pattern of the magnetic portion of the fly ash along with the Mössbauer pattern of pure α Fe_2O_3 and Fe_3O_4 . Magnetic (Fe_3O_4) is definitely present in the fly ash. However, because Fe_2O_3 should not be attracted to a magnet, it is not certain if the iron is in the form of α Fe_2O_3 or γ Fe_2O_3 in the other iron oxide present.

It can be seen in Figure 13 that an unrestrained computer fit of this data using a non-linear least square fit of Gaussian functions results in a fairly consistent position for each absorption in the coal analyzed. The quality of computer fit can be seen in Figure 14. There is an inconsistency in the Wellmore Ackiss data which is yet to be resolved. A complete computer interpretation of these results is still in progress. The interpretation of the Mossbauer data in terms of α Fe_2O_3 and Fe_3O_4 is reasonably good in terms of the centers of the Mossbauer pattern (see Table 1).

The relative heights and relative areas of the various absorptions (see Figures 14 and 15, and Table 2 and 3) can be interpreted in terms of relative composition if the recoil free fraction is assumed to be the same for both iron oxides. The iron in the magnetic fraction of the two high fusion coals, Militant and Badger, was around 80% in the form of Fe_3O_4 and around 20% in the form of Fe_2O_3 , and the iron in the magnetic fraction of the low fusion coals was around 86% in the form of Fe_3O_4 and around 14% in the form of Fe_2O_3 (see Table 4). This is consistent with the formation of Fe_3O_4 at the higher temperatures encountered in wet bottom boilers. It should be noted that there is more magnetic material separatable in the ash from the high fusion coals

FIGURE 13

FIGURE 14

FIGURE 15

WEL ACK, NORA, BADGER, MILITANT NONMAGNETIC FLY ASH

FIGURE 16

because there is less iron in the silicate lattice (see previous report) and more iron in the oxide forms for silicon. The magnetic fractions contains mainly iron, but aluminum, potassium, calcium, and titanium were also found. Work is continuing on this topic.

The fly ash sample which remains after the magnetic fraction is removed has not been completely analyzed yet. The small amount of magnetic patterns which remains causes difficulty in the computer fitting. Unrestrained computer fitting of the Mössbauer data yields a fairly consistent center for lack of the peaks (see Table 5) but it is difficult to interpret this data in terms of two doublets of equal intensity. Table 6 gives the relative heights of each peak and Table 7 gives the relative area of each peak. At this stage of the investigation it appears that there are two quadrupole doublets; one with a splitting of .94 mm/sec and an isomeric shift of .34 mm/sec and the other with a splitting of 2.38 mm/sec and an isomer shift of .65 mm/sec. The first quadrupole ($\delta = .34, \epsilon = .94$) is probably an Fe^{3+} silicate. The second quadrupole ($\delta = .65, \epsilon = 2.38$) may be a Fe^{2+} mullite).

In a previous report, it was concluded that the low fusion coals contain substantial iron in a non-pyrite form. The ash from these coals, when burned in a boiler, contains iron mainly in a silicate lattice with much less iron in the form of the oxides Fe_3O_4 and Fe_2O_3 . The role played by the initial state of the iron in the coal seems to be significant in determining the form of the iron in the final fly ash. For example, a sample of a low fusion coal, Wellmore Ackiss, and a high fusion coal, Militant, were ashed at 600°C by the ASTM Method. It can be seen in Figure 16 that the iron in the resulting ash was in a different form for each of the two samples. In the low fusion coal, Wellmore Ackiss, there was considerably more Fe_3O_4 , than in the high fusion coal. The ashes from these coals are attracted by a magnet but the separation

TABLE 1.

MAGNETIC PEAK POSITIONS (mm/sec)

<u>MILITANT</u>	<u>NORA</u>	<u>BADGER</u>	<u>WELLMORE ACKISS</u>	<u>Fe₂O₃</u>	<u>Fe₃O₄</u>
-6.56	-6.57	-6.53	-6.78	-	-6.50
-4.10	-4.09	-4.07	-4.14	-4.16	-4.07
-3.44	-3.41	-3.39	-3.44	-	-3.41
-0.84	-0.87	-0.85	-0.89	-0.78	-0.89
-0.54	-0.44	-0.51	-0.46	-	-0.47
1.43	1.46	1.46	(1.21)	-	1.50
1.63	1.66	1.67	1.61	1.74	1.76
4.72	4.70	4.69	4.73	-	4.80
5.11	5.07	5.07	5.10	5.20	-

TABLE 2.

RELATIVE PEAK HEIGHTS (MAGNETIC)

<u>AVERAGE PEAK POSITION</u>	<u>MILITANT</u>	<u>NORA</u>	<u>BADGER</u>	<u>WELLMORE ACKISS</u>
-4.10*	1.000	1.000	1.000	1.000
-3.42	0.426	0.423	0.483	0.456
-0.86	0.466	0.460	0.490	0.585
-0.49	0.384	0.430	0.426	0.451
1.45	0.467	0.512	0.435	(0.206)
1.64	0.466	0.385	0.522	(0.750)
4.71	0.818	1.024	0.867	1.119
5.09	0.487	0.348	0.531	0.330

TABLE 3.

RELATIVE AREAS (MAGNETIC)

<u>AVERAGE PEAK POSITION</u>	<u>MILITANT</u>	<u>NORA</u>	<u>BADGER</u>	<u>WELLMORE ACKISS</u>
-4.10*	1.000	1.000	1.000	1.000
-3.42	0.939	0.855	1.028	0.911
-0.86	0.405	0.343	0.382	0.428
-0.49	1.017	1.324	1.060	0.995
1.45	0.854	1.035	0.799	(0.782)
1.64	0.335	0.286	0.394	(0.782)
4.71	1.452	1.466	1.365	1.486
5.09	0.388	0.218	0.387	0.233

*Base Peak

which occurs for the fly ashes from the actual boilers was not obtained

A comparison of Mossbauer patterns of both the coal and fly ash for high and low fusion coals, along with the leaching data, suggests that iron may play a role in the fusion of the ash which results in the incapsulating of the above trace elements in a fused matrix. However, this effect is still being investigated. Once the position of each of the states of iron are determined a semi-quantative determination of each of the four form of iron, Fe_2O_3 , Fe_3O_4 and two iron silicate will be made. The distribution of iron in these states can then be correlated with the leaching data to determine the role played by the state of the iron influence on leaching.

TABLE 4.

	<u>MILITANT</u>	<u>BADGER</u>	<u>NORA</u>	<u>WELLMORE ACKISS</u>
Fe_2O_3	20%	22%	13%	14%
Fe_3O_4	80%	78%	87%	86%

TABLE 5.
NON-MAGNETIC POSITIONS (mm/sec)

<u>MILITANT</u>	<u>BADGER</u>	<u>NORA</u>	<u>WELLMORE ACKISS</u>
-0.489	-0.542	-0.505	-0.630
-0.0965	-0.095	-0.143	-0.170
0.7946	0.839	0.801	0.802
1.773	1.960	1.802	1.830

TABLE 6.
RELATIVE HEIGHTS

<u>AVERAGE POSITION</u>	<u>MILITANT</u>	<u>BADGER</u>	<u>NORA</u>	<u>WELLMORE ACKISS</u>
-0.542	23.6%	9.7%	15.2%	10.3%
-0.126	28.4	33.7	36.5	41.4
0.809	33.7	24.2	34.4	36.2
1.841	14.2	15.5	13.9	12.2

TABLE 7.
NON-MAGNETIC RELATIVE AREAS

<u>MILITANT</u>	<u>BADGER</u>	<u>NORA</u>	<u>WELLMORE ACKISS</u>
22.4	7.5	13.5	8.2
20.3	36.8	29.8	37.7
34.6	33.2	34.1	37.7
22.7	22.5	22.6	16.8