

## FOULING IN A 160 MWe FBC BOILER FIRING COAL AND PETROLEUM COKE

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### ABSTRACT

The 160 MW<sub>e</sub> FBC boiler owned and operated by TVA, has recently been co-fired with coal and petroleum coke (up to 50%). However, it has suffered fouling problems. On examination of the deposits it became clear that, only in a few cases, could the fouling be partially attributed to alkali metals, and even in those cases the primarily limestone-derived materials were almost quantitatively sulphated to a level which was sufficient to cause agglomeration by itself. In other cases, it appeared that the fouling mechanism was carbonation of the free lime component of the deposit followed by sulphation. Finally, there were a few deposits, which were less sulphated than bed materials and fly ash, but where agglomeration appeared to have occurred by a conversion of the free lime in the deposits to Ca(OH)<sub>2</sub>, followed by carbonation.

### INTRODUCTION

Petroleum coke is a fuel of very high heating value, which is becoming increasingly available on the energy market in North America [1]. However, as fuel-grade petroleum coke contains significant amounts of sulphur in the ash, it must be burned in such a way as to minimize SO<sub>2</sub> emissions. One method is to burn it in a fluidized bed boiler (FBC) to take advantage of the ability of FBCs to capture SO<sub>2</sub> in situ, using limestone. Owing to petroleum coke's high heating value (typically 32-34 MJ/kg), co-firing with fuels such as coal or biomass is an option.

To take advantage of this relatively cheap fuel, the Tennessee Valley Authority (TVA) examined the co-firing of petroleum coke in their existing 160 MW<sub>e</sub> CFBC boiler. However, in order to avoid re-permitting the unit, it was decided to keep the amounts of coke fired at or below 50%. A number of operational challenges had first to be resolved [2,3]. Despite their satisfactory resolution, a new problem, significant fouling in several regions of the boiler, was discovered.

Initially, it was supposed that the fouling was due either to V, which can be present at relatively high levels in petroleum coke ash, and/or to the alkali metal content of the coals used for co-firing. However, it appeared that fouling occurred over a wide temperature range, and consequently it was felt that there was, almost certainly, a number of fouling mechanisms. Hence, it was decided to carry out a detailed series of analyses to identify the most probable mechanisms for fouling and, in particular, to determine whether the V in the petroleum coke, or Na, K and Cl in the coal played a part.

### EXPERIMENTAL

Five deposit samples were initially supplied by TVA (see Table 1), along with two coals, Warrior and Freeman, and one petroleum coke, Pine Bend, analyses of which are supplied in Table 2. These are the fuels used during the period preceding the collection of the deposits on shutdown of the boiler. The TVA limestone used for sulphur capture was 91.5% CaCO<sub>3</sub>, with the bulk of the balance comprised of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

Subsequently, a number of other deposits were obtained from lower temperature regions of the boiler. These included samples from the water wall tubes, and a deposit from the multiclones, which are known to operate at about 370°C. These deposits were also examined using the same techniques described below.

The major components were analyzed by X-ray fluorescence (XRF), sulphur by Leco analysis and infrared determination, and sulphate determinations using wet chemistry. Elemental carbon was determined by Leco analysis and infrared absorption, while direct determination of carbonate content was by coulometry. All trace analyses were carried out by induced coupled plasma spectrometry, and as the total CaO content was considered a parameter of special importance, this was also checked by neutron activation, as was the V concentration.

In addition to the above, the total alkalinity (TA), and free lime (FL) were determined by wet chemical methods [4]. Some samples were subjected to phase analysis (i.e., density separation and analysis by X-ray diffraction) using special methods developed by the authors [5]. In this

way it was possible to build a complete description of the samples in terms of their constituent components. These analyses, together with those for the bed ash (BA) and fly ash (FA), are presented, along with the Ni and V data from the minor constituents, in Table 3. For comparison it should be noted that the Ni levels in the two coals are about 17 and 25 ppm, while the Ni and V levels in the Pine Bend coke are 306 and 870 ppm respectively.

## RESULTS

Data from the various analyses can be used to develop the phase analysis for the deposits and this appears in Table 4. The difference (SUM-100%) in this Table is due to  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and other calcium compounds (OCC) formed by reaction with the  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ , e.g., larnite and calcium ferrite, whose presence was confirmed by XRD.

Table 5 gives the composition of a number of samples from lower-temperature regions of the boiler. Finally, Table 6 gives the composition of two samples taken from very-low-temperature regions of the boiler (i.e.,  $< 400^\circ\text{C}$ ). Unlike all other deposits examined, these were not highly sulphated. On examination with Thermogravimetric Analysis (TGA), it was shown that these deposits had substantial amounts of  $\text{Ca}(\text{OH})_2$ .

## DISCUSSION

The samples have been analyzed to determine the main constituent phases. As seen in Table 4, they are mainly (80%+) composed of Ca-based compounds. What is remarkable about these samples is that, with the exception of sample AD, all CaO in the deposits has been converted to  $\text{CaSO}_4$ . This is analogous to deposits, examined by the authors, from a Korean CFBC boiler firing 100% petroleum coke, which were almost entirely composed of  $\text{CaSO}_4$  from the sorbent, with little or no CaO [6]. For comparison, it should be noted that the bed and fly ash are about 35 and 26% converted to  $\text{CaSO}_4$ , and contain 31 and 39% CaO respectively. Only in three cases are there significant amounts of carbonates; i.e., samples AD, NW and NNW, collected near access doors, presumably below  $800^\circ\text{C}$ , since  $\text{CaCO}_3$  is unstable above that temperature under atmospheric FBC conditions. In the case of sample AD, the combination of  $\text{CaSO}_4$  and  $\text{CaCO}_3$  is probably sufficient to agglomerate the deposits, as they contain relatively low concentrations of alkali metals or V (see Table 3). It has also been shown in separate laboratory studies that carbonation is an even more effective method of agglomerating limestone-derived FBC materials than sulphation [7].

In samples NW and NNW, the conversion to  $\text{CaSO}_4$  is well over 60%. This has been shown to be sufficient to agglomerate the TVA bed material by itself, when exposed to sulphating conditions in a laboratory oven [8]. It also corresponds to a situation in which limestone-derived particles must expand to allow the additional conversion, because the total pore volume produced by calcination is exceeded by this degree of sulphation [9]. A possible contribution by Na and K to the agglomeration on tubes TT and TB cannot be ruled out, but the levels of alkali metals are quite moderate compared with agglomerates formed when firing biomass, for example [10].

In the case of the samples described in Table 5, although these are more highly converted to  $\text{CaSO}_4$  (varying from 45 to 66%), the presence of extremely elevated  $\text{CaCO}_3$  levels is most likely the cause of the agglomeration, presumably initiated by carbonate formation with subsequent sulphation [6].

Some samples, although only slightly sulphated, were also agglomerated (see Table 6). In those samples, carbonation was clearly extremely high, and the agglomeration could be attributed to it. However, in the case of the multiclones, which were known to operate at about  $370^\circ\text{C}$ , it was initially difficult to explain the agglomeration, as our previous work had shown that carbonation effectively ceases below about  $400^\circ\text{C}$  [11]. On more careful examination it was found that significant amounts of  $\text{Ca}(\text{OH})_2$  were present in the samples, and in those from the multiclones, no CaO at all. Given that previous work showed carbonation was relatively fast down to ambient conditions if FBC ashes are first converted to  $\text{Ca}(\text{OH})_2$  (which is stable at FBC conditions up to about  $450^\circ\text{C}$ ), it appears the free lime in the deposits is first converted to the hydroxide and then agglomerated by carbonation formation.

## CONCLUSIONS

A number of deposit samples have been examined from the TVA boiler, co-firing coal and petroleum coke. All the deposits examined are primarily limestone derived, and those from higher-temperature areas of the boiler are almost quantitatively sulphated. This high degree of sulphation is sufficient to cause agglomeration, although Na and K are present in concentrations of a few percent, which may contribute to agglomeration. At boiler temperatures below  $800^\circ\text{C}$ ,

deposits are found which, although more highly sulphated than the bed materials or fly ash, are also strongly carbonated; here the most probable cause of agglomeration is fast carbonation, followed by a slower sulphation process. Finally, some agglomerates have been found which are formed below 450°C, substantiated by the fact that any free lime in them is present as  $\text{Ca}(\text{OH})_2$ , which is unstable at FBC conditions above that temperature. These samples are less sulphated than the bed material and fly ash, but are strongly carbonated. Here agglomeration is attributed to a two-step process, which involves conversion of the free lime in the sample to hydroxide followed by carbonation. To the authors' knowledge, this is the first instance of this type of agglomeration being reported in a FBC.

## REFERENCES

1. Anthony, E.J., "Fluidized Bed Combustion of Alternate Solid Fuels; Status, Successes and Problems of the Technology", *Progress in Energy and Combustion Science*, **21**, 239-268, 1995.
2. Anthony, E.J., Carson, R., Anderson, K.D. and Lau, I., "Petroleum Coke and Coal Start Up Testing", *Journal of Energy Resources Technology*, **119**, 96-102, 1997.
3. Anderson, K.D., Manaker, A.M., and Stephens, E.A., "Operating Experience of the Tennessee Valley Authority's 160-MW Atmospheric Fluidized Bed Combustion Demonstration Unit, Proceedings of the 14<sup>th</sup> International Conference on Fluidized Bed Combustion, ASME, ed. F.D.S. Preto, Vancouver, B.C., May 11-14, 1997.
4. Anthony, E.J., Iribarne, A.P. and Iribarne, J.V. "Report on Analysis of FBC Ash Deposits from the Tennessee Valley Authority 160 MW<sub>e</sub> FBC Boiler", Division Report ERL 96-01(IR), November, 1995.
5. Iribarne, A.P., Iribarne, J.V., Anthony, E.J. and Blondin, J., "The Phase Analysis of Coal Combustion Ashes", *Journal of Energy Resource Technology*, **116**, No. 4., 278-286, 1994.
6. Anthony, E.J., Iribarne, A.P., and Iribarne, J.V., "A New Mechanism for FBC Agglomeration and Fouling in a 100 Percent Firing of Petroleum Coke", *Journal of Energy Resources Technology*, **119**, 55-61, 1997.
7. Skrifvars, B.J., Hupa, M. and Anthony, E.J., Mechanism of Bed Material Agglomeration in the Cyclone and Return Leg of a Petroleum Coke Fired Circulating Fluidized Bed Boiler", Proceedings of the 14<sup>th</sup> International Conference on FBC, ASME, ed. Preto, F.D.S., pp. 819-843, Vancouver, B.C., May 11-14, 1997.
8. Anthony, E.J., Jia, L., Preto, F. and Iribarne, J.V. "Agglomeration and Fouling in Petroleum Coke Fired Boilers", Proceedings of the 14<sup>th</sup> International Conference on FBC, ASME, ed. F.D.S. Preto, pp. 839-846, Vancouver, B.C., May 11-14, 1997.
9. Couturier, M.F., "Sulphur Dioxide Removal in Fluidized Bed Combustion, PhD Thesis, Queen's University, Ontario, 1986.
10. Miles, T.R., Miles, T.R. (Jr), Baxter, L.L., Bryers, R.W., Jenkins, B.M. and Oden, L.L., "Alkali Deposits Found in Biomass Power Plants: A Preliminary Investigation of their Extent and Nature", National Renewable Energy Laboratory Report, April 15, 1995.
11. Anthony, E.J., Jia, L., Preto, F., Woods, J. and Rocque, W., "Pacification of High Calcic Residues Using Carbon Dioxide", CETC Division Report, ERL 96-20(CF), 1996.

Table 1: Sample Descriptions

Sample	Location and Description	Date Collected
AD - "B" COMPT	Access Door (Large pieces, light brown, and white. Shortly after being in contact with air and humidity, the pieces began to disintegrate into smaller pieces).	4/26/95
TT	Unground Piece of TVA-SH2, Top Tubes (Pieces of hard deposits with colored layers, dark brown, beige, reddish, which kept their form and shape).	
TTB	SH1, Near Tube Bends, Top Tubes (A dark brown powder).	4/24/95
NW	Convective Pass, SH-NW Door (A pinkish powder with some solid pieces).	4/26/95
NNW	Convective Pass, SH, Near NW Door (A pinkish powder).	4/26/95

Table 2: Fuel Analysis

Fuels	Warrior coal	Freeman coal	Pine Bend coke
Proximate analysis, wt %			
Moisture	6.56	10.03	0.63
Ash	11.00	10.17	0.48
Volatiles	31.65	33.93	10.17
Fixed carbon	50.79	45.87	88.72
Ultimate analysis, wt %			
Carbon	65.28	63.09	86.84
Hydrogen	4.57	4.36	3.42
Nitrogen	1.44	1.19	1.48
Sulphur	2.88	3.95	5.57
Oxygen (by difference)	8.27	7.21	1.58
Heating value (MJ/kg)	26.71	26.22	-

Table 3: Major Components (wt %)

Components	BA	FA	AD	TT	TTB	NW	NNW
SiO <sub>2</sub>	3.27	4.44	3.20	8.39	4.99	7.74	8.74
Al <sub>2</sub> O <sub>3</sub>	0.61	1.13	0.75	4.29	2.58	2.47	2.37
Fe <sub>2</sub> O <sub>3</sub>	0.82	1.85	0.91	2.98	1.86	4.01	4.35
CaO	60.3	63.5	59.5	34.6	34.1	32.3	31.8
MgO	3.5	1.92	3.48	1.67	1.20	2.03	2.02
Na <sub>2</sub> O	0.02	0.08	0.41	1.54	1.98	0.18	0.15
K <sub>2</sub> O	<0.01	0.1	<0.01	1.02	1.04	0.34	0.33
TiO <sub>2</sub>	0.042	0.048	0.05	0.37	0.28	0.13	0.12
MnO	0.01	0.02	0.01	0.03	0.02	0.02	0.02
Cr <sub>2</sub> O <sub>3</sub>	<0.01	<0.01	<0.01	0.02	0.03	<0.01	<0.01
P <sub>2</sub> O <sub>5</sub>	0.05	0.04	0.03	0.15	0.07	0.04	0.03
SO <sub>3</sub>	30.70	23.5	28.3	46.5	49.3	46.3	46.5
LOI	1.05	4.62	4.6	-0.30	1.05	3.3	3.1
SUM	100.37	101.25	101.2	101.3	98.5	98.9	99.6
Ni (ppm)	69	30	-	-	831	155	119
V (ppm)	329	127	447	3034	3008	533	367

Table 4: Phase Composition of Deposits (wt %)

Component	AD	TT	TTB	NW	NNW
CaSO <sub>4</sub>	48.0	79.0	80.3	75.6	75.2
CaO	28.5	0.8	0.2	0.1	0.0
CaCO <sub>3</sub>	5.9	0.3	0.5	5.8	5.3
SUM	82.4	80.1	81.0	81.5	80.5
R <sup>1</sup>	33	94	97	96	97

1. R is the degree of conversion of Ca compounds to CaSO<sub>4</sub> on a % molar basis

Table 5: Phase Composition of Lower-temperature Deposits (wt%)

Sample/Component	CaSO <sub>4</sub>	CaO <sup>1</sup>	CaCO <sub>3</sub>	Δ <sup>2</sup>
White coating on sloped walls	49.9	4.7	12.0	23.7
Light coat on waterwall tubes	40.9	9.9	19.0	22.7
Near Manway G on compt. waterwalls, 8 ft. from feed	51.4	9.7	25.7	9.4

1. Includes both CaO and OCC

2. Δ represents non-Ca-based components

Table 6: Phase Composition of Very-low-temperature Deposits (wt%)

Sample/Component	CaSO <sub>4</sub>	OCC <sup>1</sup>	Ca(OH) <sub>2</sub>	CaO	CaCO <sub>3</sub>	Δ <sup>2</sup>
Tenacious coat starting in compartment 8 ft. above feed	23.6	10.6	6.2	4.9	45.3	11.7
Multiclone deposits	14.5	16.3	16.3	0	32.9	18.5

1. OCC are expressed as CaO

2. Δ represents non-Ca-based components