Investigations into the Air Heater Ash Deposit Formation in Large Scale Pulverised Coal Fired Boiler

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Abstract

A mineralogical study was undertaken of air heater deposits in a 300 MWe pf boiler located in Western Australia to understand the deposit formation in air heater sections of boiler as an aid to implement possible remediation actions. Several air heater deposit samples were collected in the selected regions of the air heater along with samples of the feed coal, bottom ash and fly ash for comparison of ash chemistry and mineralogy. The deposit samples were examined using a combination of ash chemistry and quantitative X-ray diffraction analysis; the ash samples by bulk chemical analysis to determine the major element chemistry and mineralogy by quantitative X-ray diffraction. Samples of the deposits were also analysed using optical microscopy and QEMSCAN, an automated electron beam image analysis system.

Chemical and mineralogical analysis showed that the deposits are unusual in containing high amounts of sulphate, particularly of aluminium and, to a lesser extent, iron. From the analyses it appears that the formation of the deposits is due to the high sulphate content which is acting as a cementing agent. There is an indication that temperature could be another factor in formation of the deposits, with a decrease in temperature leading to the formation of sulphurous acid which then reacts with the reactive glassy amorphous fly ash phase to form the aluminium and iron sulphates. Dew point calculations indicated that this is a possible deposit formation mechanism based upon air heater temperature data obtained from the utility. There was no evidence that unburnt carbon has played a significant role in deposit formation. Large temperature fluctuations resulting from the inherent nature of the operation of the air heater are a significant factor in deposit formation and a practical solution to consider would be the use of an SO_2 absorbent placed prior to the air heater.

Introduction

It has been well established by several researchers over the last few decades that the ash deposition on boiler components and associated equipment within a power utility is a significant problem. The build-up deposit causes several operational problems leading to unnecessary outages requiring periodic maintenance [1-3]. The problems are much more pronounced when ash blockages occur on the heat recovery systems such as the air preheater. The purpose of an air preheater is to recover the heat associated with exit flue gases from the boiler mainly to enhance the thermal efficiency and control the heat likely to be lost in the flue gas. As a consequence of build-up deposits, on these heat recovery systems, the heat transfer rates will be altered significantly, thereby reducing the efficiency of thermal boiler systems.

In this study, an investigation was made of the air preheater of a typical 300 MWe local power utility located in Western Australia. The power utility employs a typical rotary preheater (mainly used for large water tube boilers) wherein hot flue gas flows through one portion of the wheel while cool, clean combustion air passes through the remaining portion. As the wheel revolves, the cold combustion air passes through these hot surfaces and becomes heated which is then sent to the burners to mix with fuel in the firebox [4]. This preheater is often prone to ash build-up within short periods of operation, mainly due to to the wet steam which comes from the soot blower steam supply and the accumulation of hardened ash with flow marks and dribbles. With an effort to upgrade the steam quality supply from the soot blower, the steam temperature is increased via mixing with the main steam to arrive at a mixed steam temperature of 360°C. This enables prolonged operation and the interval between air heater washes increases further. Despite these measures, hardened ash on the bottom cold side of the heat exchange system elements at the cold end basket is reported to occur in this utility. (see Figure 1). The top end of the elements appears to suffer less from ash blockage due to higher flue gas temperatures.

Given these build-up issues in air heater sections, an investigation was carried using detailed mineralogical analysis to understand the interaction between ash particles and the surface of the air heater elements (in terms of how it sticks initially and on the formation of subsequent ash layers) along with the deposit chemistry to establish the factors/mechanisms leading to the formation of hardened consolidated ash eventually causing blockages in the heat exchange elements. The study also examined other contributing factors and precursors for ash build-up as it is a well known fact within the power generation industry that soot from diesel burn, moisture and flue gas temperature below the SO_2 dew point are contributing factors .

Sampling and Analytical Procedures

Five samples of the air heater deposits were provided for analysis. Three subsamples were taken of sample A as an initial visual examination indicated that differences existed between the fragments supplied for analysis (see Table 1 for details). Sub-samples were taken of the coarser fragments for optical and scanning electron microscopy and the reminder was ground and sub-sampled for chemical and X-ray diffraction analysis. The power utility also supplied representative samples of the feed coal, bottom ash and fly ash for chemical and X-ray diffraction analysis..

A mineral matter sample was prepared from the coal sample using low temperature radio-frequency plasma ashing, a technique which minimizes detrimental alteration of the coal mineralogy. Sub-samples of the ashes and deposits selected for X-ray diffraction analysis were ground in an agate mortar and pestle then packed into an aluminium holder. Quantitative X-ray diffraction analysis was performed using SIROQUANT™, a quantitative X-ray diffraction analysis software package that uses Rietveld procedures to generate a synthetic pattern which is then matched to the experimental data using a least squares minimisation fitting procedure. This approach has the advantage that the complete diffraction pattern is used to derive the quantitative results rather than relying upon one or two peaks for the determination. Although application of the Rietveld procedure usually requires that the phases be crystalline in order to calculate the synthetic XRD pattern, SIROQUANT makes use of

experimentally derived structural data (observed hkl files) for amorphous or poorly crystalline phases and thus can be used to determine the amount of amorphous material present in the sample.

Major element analysis of the ash samples was carried out using ICP-AES following fusion of the sample with lithium metaborate/tetraborate and dissolution of the fused sample in acid. The coal sample was ashed at 815°C prior to borate fusion. Loss on fusion was determined at 600°C and 1000°C. Moisture and ash yield were determined using a LECO MAC analyser. Total carbon was determined using a LECO TruSpec CHNS analyser. Following determination of total carbon, carbonate carbon was removed by acid digest and carbon re-determined; the residual carbon assumed to be unburnt carbon and the difference, carbonate carbon. Sulphur was determined using a LECO TruSpec CHNS analyser.
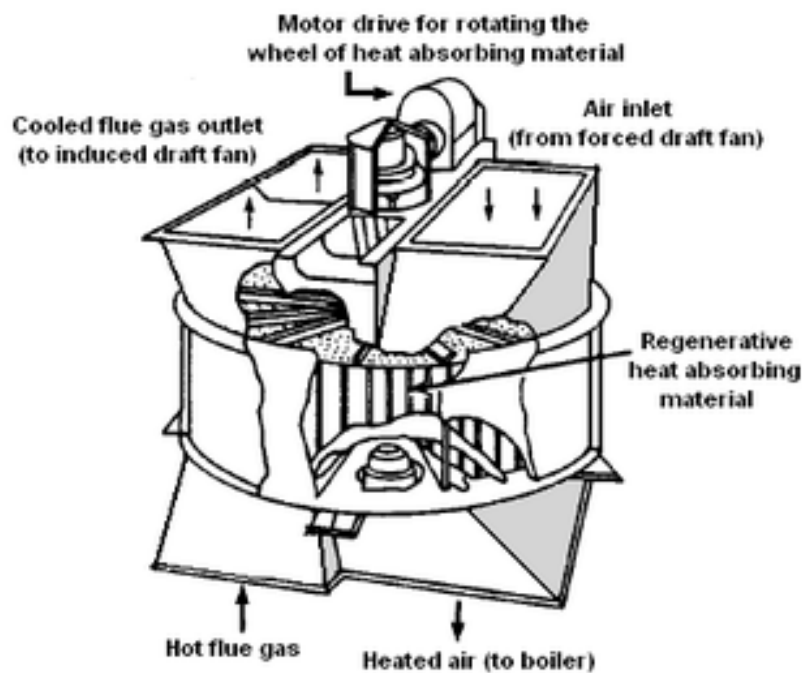
(a)

(b)   (c)

Figure 1. *Figure showing the schematic of an air preheater (a)[adopted from ref 4] and (b) and (c) photographs of hardened ash on the bottom cold side of the heat exchange system*

Table 1. *Details of deposit samples provided for analysis.*

Sample description	Sample Id
Primary cold end hood	A
Primary cold end hood	A
Primary cold end hood	A
Secondary cold end heat exchanger basket elements. Deposit on the leading edges of the elements at the secondary cold air inlet	B
Secondary cold end heat exchanger basket elements. Deposit on the leading edges of the elements at the secondary cold air inlet	C
Secondary cold end heat exchanger basket elements. Deposit located between the elements from a depth of 0mm into the cold end	D
Secondary cold end heat exchanger basket elements. Deposit located between the elements from a depth of 100mm into the cold end	E
Feed Coal	F
Bottom ash	G
Fly ash	H

Results and Discussion

Petrography of deposit samples
As shown in Figures 2 and 3 all samples are grey brown and layering is evident in Sample A, the reddish-brown colour due most likely to hematite. Layering is also evident in samples B and C and less so in sample D. In samples B and C, the layering is defined by alternating reddish-brown and pale-beige layers, whereas in sample D, the layering is defined by alternating pale brown and beige layers. Due to the small quantity of the sample it was not possible to further define the mineralogical nature of the layering and hence possible causes. Layering appears to be absent in sample E, the reasons for which are unknown. Samples A, B, and C are more indurated than the other samples, sample E being very friable and sample D being of intermediate hardness.

Chemistry
The chemistries of the coal ash and fly ash are similar but significantly different from that of the bottom ash which is enriched in silica and depleted in alumina (Table 2). Iron is also enriched in the bottom ash but sodium, potassium, phosphorus and sulphur are depleted.

The ash analyses of the deposit samples used in this study are given in Table 3. Sample A is distinctive in having higher silica and iron contents and significantly lower sulphur contents. Total carbon content is also high, consisting mostly of unburnt carbon. Magnesium, calcium and potassium contents are also slightly higher. In spite of the apparent visual differences, there is no significant difference in the chemistry of the sub-samples. , The chemistry of the other samples is generally similar, apart from sample D which has higher sulphur and lower silica, titanium, aluminium, and phosphorus contents. Sample E has higher iron and silica contents.

The most obvious difference between the chemistry of the ash samples and the deposits is the generally high sulphur contents and LOI values of the latter (Table 3), the exception being sample A, which is closest in composition to the coal and fly ash samples. In comparison to the coal and fly ash,

silica and alumina contents of sample A are slightly lower; iron contents are comparable. Magnesium contents of the deposit A samples are slightly higher. The chemistry of deposit samples B-E are significantly different in that silica and iron contents are significantly lower and alumina contents slightly lower.

Figure 2 Sub samples of sample A(left); top A1, middle A2, bottom A3; from top to bottom (on right), samples B, C, D and E

Mineralogy
The quantitative X-ray diffraction results of coal, fly ash and bottom ash are presented in Table 4a and the corresponding glossary of mineral phases is presented in Table 4 b. The mineralogy of the coal is dominated by quartz and kaolinite (Table 4a). Potash feldspar (microcline) and illite are minor phases, as are anatase and jarosite. The differences in the chemistry of the fly ash and bottom ash are also reflected in the mineralogy, particularly the higher quartz content of the bottom ash. The hematite content of the bottom ash is higher and the amorphous content is much lower. The oxide mineralogy of the fly ash is also more varied, with magnetite, hercynite and spinel being present.

The quantitative X-ray diffraction results for the air heater deposit samples are presented in Table 5. As for the chemistry, sample A also has a distinctive mineralogy, having higher amorphous contents and containing hematite, hercynite, magnesioferrite and spinel. Apart from minor anhydrite, sulphates are absent. Mullite contents are variable. Minor quartz is also present. Mineralogically, sample A is most comparable to the fly ash. In contrast, the other samples are distinguished by their high sulphate content and reduced amorphous abundance. Although variable, quartz and mullite contents are similar to those observed in sample A. Sample E is unusual in containing minor magnesioferrite, thus resembling sample A. Minor voltaite and anhydrite are present in all samples. Significant coquimbite is present in sample D and, to a much lesser extent, in sample E. Anhydrite is ubiquitous and contents

tend to be slightly higher than in the sub-samples of sample A4. Aluminium sulphates are common, sample D having the highest concentration of alunogen.

Table 2. Chemical analyses of the coal, fly ash and bottom ash samples (results expressed in wt%)

CSIRO Sample Number	4274	4276	4278
Description	Coal Ash	Fly Ash	Bottom Ash
Total sulphur	0.25	0.26	0.03
Total sulphur as SO_3	0.62	0.64	0.07
Unburnt Carbon		<0.1	<0.1
Carbonate carbon		0.20	0.10
Total carbon	0.13	0.20	0.10
Moisture		0.20	<0.1
SiO_2	51.49	51.25	65.28
TiO_2	1.58	1.61	0.94
Al_2O_3	26.15	29.78	12.75
Fe_2O_3	14.78	11.19	18.16
MnO	0.03	0.04	0.02
MgO	0.31	0.97	0.39
CaO	0.95	1.66	0.61
Na_2O	<0.01	0.23	0.06
K_2O	0.62	0.42	0.26
P_2O_5	1.46	1.02	0.30
SO_3	0.32	0.46	0.01
ZnO	0.03	0.04	0.01
LOI @600°C	0.20	0.70	0.20
LOI @1000°C	2.15	1.36	1.03
Total LOI 600°C	**97.92**	**99.37**	**98.99**
Total LOI 1000°C	**99.87**	**100.03**	**99.82**

In comparison to the fly ash, the most noticeable feature of the deposit samples is their high sulphate content, in particular aluminium sulphates. There is little evidence of any systematic variation in the deposit samples. Sample A most closely resembles a typical fly ash in chemistry and mineralogy, apart from the presence of anhydrite which is probably acting as a cementing agent, giving the deposit its hardness. The abundant sulphates in the other samples are most likely responsible for the deposit strength, also acting as a cementing agent. The lower amorphous content of samples B-E coupled with the high sulphate content is suggestive of reaction of the reactive glassy amorphous fly ash material with sulphur dioxide in the flue gas to form the aluminium and iron sulphates. As mentioned, although there is little evidence of any systematic trends, the slightly lower sulphate content of sample E and higher amorphous content in comparison to samples B-D suggest that there may be a temperature control on sulphate formation which reaches a maximum at lower temperatures, possibly due to the formation of a sulphurous acid which then reacts with the glassy particles.

Table 3. *Chemical analyses of the air heater deposit samples (results expressed in wt%)*

Description	A1 Boiler deposit	A2 Boiler deposit	A3 Boiler deposit	B Boiler deposit	C Boiler deposit	D Boiler deposit	E Boiler deposit
Total sulphur	0.93	0.68	1.44	10.51	9.41	13.21	8.88
Total sulphur as SO_3	2.32	1.70	3.60	26.24	23.50	32.98	22.17
Unburnt Carbon	3.8	7.3	8.7	0.2	0.2	0.1	0.2
Carbonate carbon	0.1	0.2	0.4	<0.1	<0.1	<0.1	<0.1
Total carbon	3.9	7.5	9.1	0.2	0.2	0.1	0.2
Moisture	2.5	2.2	3.6	11.3	8.3	16.9	7.9
SiO_2	42.2	41.3	33.8	23.1	26.3	14.5	37.1
TiO_2	1.5	1.4	1.3	1.0	1.1	0.6	1.3
Al_2O_3	23.9	23.8	21.9	20.7	22.5	14.6	20.9
Fe_2O_3	15.7	12.6	16.7	6.3	7.0	6.7	13.0
MnO	0.11	0.10	0.12	0.03	0.03	0.03	0.03
MgO	1.40	1.10	1.35	0.62	0.65	0.47	0.73
CaO	1.80	1.40	2.00	0.80	0.86	0.67	0.93
Na_2O	0.24	0.20	0.17	0.14	0.16	0.12	0.25
K_2O	0.67	0.72	0.57	0.37	0.40	0.22	0.39
P_2O_5	0.93	0.79	1.20	1.20	1.20	0.77	1.00
SO_3	0.29	0.26	0.50	8.70	8.10	13.50	7.80
LOI @600°C	11.4	16.2	21.3	24.4	20.2	34.3	19.7
LOI @1000°C	12.2	16.3	22.3	46.3	39.2	61.1	34.5
Total LOI 600°C	**100.1**	**99.9**	**100.9**	**87.4**	**88.5**	**86.5**	**103.1**
Total LOI 1000°C	**100.9**	**100.0**	**101.9**	**109.3**	**107.5**	**113.3**	**117.9**

To test the above hypothesis a series of dew point calculations were performed using information supplied by the utility [7] on sulphur in coal and SO_x in flue gases, the results of which are given in Table 6. All the dew point calculations were performed utilising Okkes method [8] based on the partial pressures of gaseous species. Information provided by the utility in a private communication [7] indicates that temperature in the air heater may vary from ambient to the flue gas temperature of 150°C depending upon movement of the secondary air hood. Therefore, it is possible that condensation may indeed occur as indicated by the dew point calculations which show that condensation is possible over a temperature range of 132 – 152°C depending on gas composition. Another contributing factor may be the possibility that the initial burst of superheated steam used for soot blowing could be wet [7].

There is little evidence that unburnt carbon arising from the initial use of diesel oil firing has any significant influence on deposit formation as total carbon values of the deposit samples are low (0.1-0.2 wt%, ref Table 3.2, being comparable to that found in the fly ash. Although unburnt carbon values are higher in sample A (3.8 -8.7 wt%, ref Table 3.2), it is considered that sulphate is still the primary cementing agent as postulated for the other samples. However, the possibility that unburnt carbon may have played a role in the formation of sample A cannot be entirely discounted but would require a more comprehensive sampling program in order to establish its relative importance. Previous studies [6] have shown that residual carbon has affected deposit formation in the turbine section of a coal-fired turbine.

Table 4a. *Quantitative X-ray diffraction mineralogy of the feed coal, fly ash and bottom ash samples (in wt%).*

Description	Feed coal	Fly Ash	Bottom Ash
Mineral matter wt%	**9.37**		
Quartz	33.8	13.8	43.5
Cristobalite			2.8
Mullite		25.7	21.8
Microcline	2.9	0.5	0.6
Illite	5.9		
Kaolinite	54.7		
Anatase	1.0		
Hematite		2.2	4.4
Magnetite		0.3	
Maghemite		0.7	1.6
Hercynite		0.4	
Spinel		0.6	
$(NH_4)_6P_6O_{18}.(H_2O)$			1.2
Jarosite	1.7		
Amorphous		55.8	24.1
Total	100.0	100.0	100.0

Table 4b *Glossary of mineral names*

Mineral Name	Formula
Quartz	SiO_2
Cristobalite	SiO_2
Mullite	$Al_6Si_2O_{13}$
Microcline	$KAlSi_3O_8$
Illite	$K(AlFe)_2AlSi_3O_{10}(OH)_2 \cdot H_2O$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Anatase	TiO_2
Hematite	Fe_2O_3
Magnetite	Fe_3O_4
Maghemite	Fe_2O_3
Magnesioferrite	$MgFe_2O_4$
Hercynite	$FeAl_2O_4$
Spinel	$MgAl_2O_4$
$(NH_4)_6P_6O_{18}.(H_2O)$	$(NH_4)_6P_6O_{18}.(H_2O)$
Jarosite	$KFe_3(SO_4)_2(OH)_6$
$Al_2(SO_4)3(H_2O)$	$Al_2(SO_4)3(H_2O)$
Alunogen	$Al_2(SO_4)_3 \cdot 12\ H_2O$
Anhydrite	$CaSO_4$
Coquimbite	$Fe_2(SO_4)_3 \cdot 9H_2O$
Voltaite	$K_2Fe_5AlFe_3(SO_4)_{12} \cdot 18H_2O$

Table 5. *Quantitative X-ray diffraction mineralogy of the air heater deposit samples (in wt%)*

Sample Number	AA1	AA2	AA3	B	C	D	E
Description	A1 Boiler deposit	A2 Boiler deposit	A3 Boiler deposit	B Boiler deposit	C Boiler deposit	D Boiler deposit	E Boiler deposit
Quartz	7.4	6.7	4.2	3.4	4.4	2.2	10.1
Cristobalite	0.1						
Mullite	15.8	12.2	9.3	11.4	16.4	5.8	11.7
Hematite	4.9	4.1	4.4				
Magnesioferrite	1.1	0.9	2.9				2.7
Hercynite	2.5	1.2	3.3				
Spinel	1.1	0.3	1.6				
$Al_2(SO_4)3(H_2O)$				17.1	14.8	10.8	15.0
Alunogen $Al_2(SO_4)_3 \cdot 12\,H_2O$				16.1	13.1	32.5	10.7
Anhydrite $CaSO_4$	0.4	0.2	1.0	1.5	0.9	2.1	1.1
Coquimbite $Fe_2^{+3}(SO_4)_3 \cdot 9H_2O$						9.0	0.8
Voltaite $K_2Fe_5AlFe_3(SO_4)_{12} \cdot 18H_2O$				1.2	0.7	1.5	0.9
Amorphous	66.8	74.4	73.4	49.2	49.7	36.0	46.9
Total	100.1	100.0	100.1	99.9	100.0	99.9	99.9

Table 6. *Results of dew point calculations*

Gas	Volume% concentration					
N_2	72	75	75	72	72	72
O_2	3	3	3	3	3	3
CO_2	10	10	13	8	8	8
H_2O	15	12	9	17	17	17
Ar	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001
SO_2	0.001	0.001	0.001	0.001	0.002	0.004
Dew Point (^{o}C)	**138.1**	**135.4**	**132**	**139.6**	**145.6**	**152**

Conclusions

Chemical and mineralogical analysis shows that the deposits are unusual in containing high amounts of sulphate, particularly of aluminium and, to a lesser extent, iron, the chemistry and mineralogy being quite distinct from that of the parent fly ash. It is suggested that the formation of the deposits is due to the high sulphate content which is acting as a cementing agent. There is an indication that temperature may be an important factor in formation of the deposits, decreasing temperature leading to the formation of sulphurous acid which then reacts with the reactive glassy amorphous fly ash phase to form the aluminium and iron sulphates, The dominance of aluminium sulphates over iron sulphates is most likely due to the greater abundance of aluminium in comparison to iron in the reactive glassy phase. Dew point calculations show that this is a possible deposit formation mechanism based upon air heater temperature data supplied by the power utility. There is no evidence that unburnt carbon has played a significant role in deposit formation.

With regard to possible remediation measures, although large temperature fluctuations resulting from the inherent nature of the operation of the air heater are a significant factor in deposit formation, it is considered impractical to address this issue. A more practical solution to consider would be the use of an SO_2 absorbent placed before the air heater.

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