W

MASTER

Conf-820418--7

GAT-S-24

GAT-S--24

DE82 011811

CORROSION IN COAL-FIRED BOILERS

By

A. L. Vausher
Environmental Control Department

Distribution

<u>Internal</u>		<u>DOE</u>	<u>ORNL</u>
R. E. Anderson	MS 1215	ORO-Patent Group	T. W. Oakes (2)
V. S. Emler	MS 1218	TIC (2)	
R. R. Miller	MS 2215		
E. R. Newman	MS 2225		
A. L. Vausher (2)	MS 1215		
B. E. Wilkinson	MS 1108		
Central Files (2)	MS 1101		
X-710 Library	MS 2206		

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.

*To be presented at the 1982 UCCND-GAT Environmental Protection Seminar to be held in Gatlinburg, Tennessee, April 5-7, 1982.

GOODYEAR ATOMIC CORPORATION

P. O. BOX 628

PIKETON, OHIO 45661

ACTING UNDER CONTRACT DE-AC05-76OR00001 WITH THE
U. S. DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

See

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.

CORROSION IN COAL-FIRED BOILERS

A. L. Vausher
Goodyear Atomic Corporation
Piketon, Ohio 45661

KEY WORDS: Coal, Boilers, Corrosion, Dew Point, Fuel Additives

ABSTRACT

The corrosive effect of the flue gas and the fly ash from burning coal on combustion and pollution control equipment has led to extensive research efforts aimed at solving this problem. A wide variety of chemical additives are offered by suppliers to perform corrosion reduction functions when added to the solid or liquid fuel. Protection of equipment by the use of corrosion resistant coatings and improved designs to prevent or reduce slag formation are also well known corrosion reduction techniques. However, the problem facing management is to evaluate the many different alternatives and to define the most effective one for their particular facility. Information gained from previous corrosion reduction attempts, and knowledge of factors which increase the SO_3/SO_2 ratio in the flue gas have resulted in the investigation of methods of controlling the dew point and therefore, reducing the condensation of sulfuric acid. Various methods of avoiding the formation of acid are being evaluated.

INTRODUCTION

The steam plant provides heat for the process gas vaporization, heat to maintain the process temperature, and heat for the buildings and other miscellaneous processes. Each of the three independent systems of the Goodyear Atomic Corporation X-600 Steam Plant consists of a coal-fired boiler followed by an economizer, an electrostatic precipitator and finally an induced draft fan. The electrostatic

precipitators were added to the system to control particulate emissions in April, 1979.

In 1977, experimental work to study corrosion problems in the economizers was conducted using fuel additives. Firemate-8 is a chemical mixture which was used in these experiments. It appeared that the chemical reduced the corrosion rate in the economizers. The experiment was therefore expanded to see if the chemical would remove corrosive sulfur trioxide from the exhaust.

Addition of Firemate-8 has been experimented with for more than a year on a continual basis. The chemical was fed into the steam generating system through ports at different locations to neutralize the corrosive acid deposits. Apparently, the addition of Firemate-8 engendered a thick mud-like material which was collected from stack number two at the steam plant. It was reported that this white sludge was found to be 75% MgO , 20% Al_2O_3 as well as some iron, nickel, and sulfur.² The report stated that the chemical additive did not solve the corrosion problem in the area after the ESP. A couple of months later, this prediction was confirmed when boiler number two was shutdown.³ Holes were found in the expansion joint on the outlet of ESP number two. The new induced draft number two fan which has been in service for a short time, showed that several blades were corroded as well and a hole was found in the fan housing. Repair was initiated and the system was put on line. The same system was shutdown again after three months, because of corrosion problems.

Test corrosion coupons were placed in the fan housing to measure the corrosion rate. Coupons removed from the number two fan housing were completely disintegrated; where as, those removed from the number one fan housing showed small metal loss. Other test strips were placed in the housing of fan number three and showed a high corrosion rate as well.⁴

Along with the long history of experimentation with Firemate-3 there was an attempt made to find some suitable type of stack coating. A vinyl ester called Plasite 4030 was applied. The polymer was degraded in approximately two months after the stack was put in service.⁵ The texture and appearance of the failed coating indicated that Plasite 4030 was exposed to the destructive effect of elevated temperature and/or to heavy concentration of condensed sulfuric acid vapors.

DISCUSSION

Magnesium oxide, aluminum oxide, and dolomite are components of mixtures which could be added to the fuel. The potential benefits of these chemicals include the reduction of SO_3 emissions, and consequently, control of corrosion resulting from condensation of acidic vapors. It is claimed that such additives increase the boiler efficiency by maintaining cleaner convection surfaces. A study conducted by ASME Research Committee on Corrosion and Deposits indicated that corrosion of the fireside is caused by molten alkali iron sulfates and that magnesium oxide powder prevents the corrosive attack by the acid-laden gases.⁶

Magnesium oxide is sold in a wide variety of mixtures under different commercial names. Vendors make extensive claims about their product performance when added to the fuel during combustion.⁷ Consequently, the selection of a suitable chemical additive became a difficult task. Management has to make a decision based on the chemical and physical characteristics of the fuel, the usually encountered fireside problems, the operation and maintenance of the system, and cost effectiveness. Evaluation of performance of the chemical additives requires data such as SO_3 concentration, acid dew

point and operation data. Conclusions should not be drawn from short test periods of one or two weeks because reaching equilibrium will be constrained by the ash inventory of the boiler and the boiler surface area.

Sulfur dioxide is an unavoidable product when any fuel containing sulfur is burned. The concentration of the sulfur dioxide is a function of the sulfur content in the fuel. Further oxidation of sulfur dioxide to sulfur trioxide proceeds under certain conditions. The following equations describe the two step oxidation of sulfur to the trioxide form.

Figure 1 shows that the SO_3/SO_2 ratio increases as the temperature of the flue gas decreases. However, the reaction rate falls rapidly below 700°F. This explains why the major portion of the fuel's sulfur is discharged from the combustion equipment in the dioxide form.⁸ Evidently, the rate of formation of SO_3 in combustion equipment varies widely and is affected by several factors. Such factors include, but are not limited to, the size of the equipment, temperature of the firebox, catalytic agents, level of excess oxygen, and sulfur content on the fuel.

Table 1 presents published range of SO_3 as a function of sulfur content and excess oxygen in the flue gas of coal-fired boilers.⁹ These ranges were estimated from research presented to ASME and to the National Research Council.^{18, 19} Table 2 lists the concentration of SO_3 in the exhaust from the steam plant and %S in the burned coal as determined by GAT laboratory.^{10, 11}

Since data in Table 2 do not represent a valid statistical sample size, GAT laboratories are in the process of compiling more results. However, their results have been stated for the purpose of

Figure 1 Equilibrium Concentrations of SO_3 – SO_2 at Various Oxygen Concentrations as per the Reaction $\text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) = \text{SO}_3(\text{g})$ (Adapted from Haugen and Watson, 1945)

Table 1 Published Data of SO_3 Estimated Concentrations from Coal-Fired Units

% Sulfur in fuel		0.5	1.0	2.0	3.0	4.0	5.0
<u>% Excess</u> <u>Air</u>	<u>%O₂</u> <u>in Gas</u>	<u>Sulfur trioxide expected in gas (ppm)</u>					
25	4.0	3-7	7-14	14-28	20-40	27-54	33-66

Table 2 Concentration of SO_3 in the Flue Gas from Coal-Fired Boiler as Determined by GAT Laboratory

DATE	%SULFUR	SULFUR TRIOXIDE
10-13-81	4.5	14
10-20-81	3.57	25
10-21-81	3.58	20
10-29-81	3.32	20
10-30-81	3.63	23
11-03-81	4.05	19
11-04-81	4.12	17
11-12-81	3.28	28
11-17-81	3.87	20
12-03-81	3.35	25
12-09-81	3.01	26

comparison with the concentration range of SO_3 recorded in Table 1. Comparing SO_3 concentrations in both tables it appears that the measured levels of SO_3 are within the lower limit of published concentrations. Such consideration along with the small number of corrosion incidents in the economizers since using Firemate-8 may support the claim of reducing SO_3 emissions by the Firemate-8.

Sulfur trioxide reacts with moisture to form the corrosive sulfuric acid. The dew point of these acidic vapors can be calculated from equations published in several articles.^{9, 12, 13} Figure 2 illustrates elevation of the dew point as a function of SO_3 concentration where as Figure 3 depicts the dew point in degrees centigrade versus the logarithm of SO_3 concentration. It is believed that any significant disagreement of actual dew point with numbers from Figure 3 will be due to errors in the determination of the SO_3 concentration. The results calculated from the cited equations and data obtained by scientists showed good agreement that the dew points in Figure 3 are in the range of $\pm 3^\circ\text{C}$. Below 10 ppm SO_3 there could be significant disagreements. Also, some results showed dew points between $130\text{--}150^\circ\text{C}$ ($226\text{--}302^\circ\text{F}$) which are predicted by the curves for 5-50 ppm SO_3 . Measurements of these high temperatures are in question because the thermocouple may record an integrated temperature composed of the gas temperature and the adjacent stack wall temperature. Such integrated temperatures are due to inadequate shielding of the thermocouple from the stack wall or inadequate exposure to the gas stream. Because of this problem, precise temperature readings are difficult to obtain and it is always recommended to calculate an arithmetic mean of a statistical valid sample size. Figure 4 is a sketch of the induced draft fan with its double inlet. Temperature was recorded for the inlet/outlet of ESP #2 and the inlet/outlet of induced draft fan number two.¹⁴ Table 3 displays the arithmetic mean of these temperatures which were measured over ten consecutive days by taking three readings per day (one reading per shift).

Figure 2 Dew Point Elevation as a Function of Sulfur Trioxide Concentration
(Adapted from Rendle and Wilsdon, 1956)

Figure 3 Calculated Dew Point versus Sulfur Trioxide Concentration

Figure 4 Average Temperature at the Inlet and Outlet of Induction Draft Fan Number Two

Table 3 Average Inlet/Outlet Temperature of Electrostatic
Precipitator Number Two and Induced Draft Fan Number 2

Electrostatic Precipitator Number Two	ID Fan #2	
	Inlet/Outlet Temperature	
	North Side	South Side
Inlet/Outlet Temperature		
298 $\pm$ 4°F/272 $\pm$ 10°F	278 $\pm$ 8°F/286 $\pm$ 4°F	278 $\pm$ 10°F/268 $\pm$ 15°F

A small temperature difference between the inlet and outlet of the ESP should be expected since the unit has been insulated and potential leakage of a cooling draft at the outlet of the electrostatic precipitator is not a valid assumption. However, the calculated average of 272 $\pm$ 10°F at the outlet of electrostatic precipitator number two in Table 2 is due to some erroneous readings which affected the calculated mean. The list of data in Table 3 shows also that the gases are cooled inside the induced draft fan. Similar results could be deduced from the temperature profile at the inlet of electrostatic precipitator number one, the outlet of electrostatic precipitator number one, and the outlet of induced draft fan number one. Scrutinizing the design of the induced draft fan shows that the cooling sleeves around the shaft (Figure 5) allow for a gap through which air impinges on the rotating blades. Heat transfer analysis at this region should support the cooling effect of the draft from the sleeves on the flue gas. Such an analysis will also explain the condensation of acidic vapors inside the induced draft fan and in the stack thereafter. The unavoidable cooling draft from the sleeves leads to focus on heating the flue gas in this area to or above the acid dew point.

Figure 5 The Gap Between the Cooling Sleeve and the Rotating Bearing Inside the Induction Draft Fan Housing and Corroded Blades by the Sulfuric Acid Vapors

Possible Solutions

The introduction and discussion stated in this article show that corrosion problems in the steam plant may be divided into two sections. The first section is corrosion in the economizers and the second section is corrosion in the induced draft fan and the stack. Corrosion of the economizer tubes is either inside tube surface corrosion or outside tube surface corrosion.¹⁷ The inside surface problems are related to the feed water characteristics. Such corrosive attacks are prohibited by the feed water treatment system in the steam plant. The outside surface corrosion of the tube is caused by condensed acidic vapors. Apparently, the outside surface corrosion has been reduced by the chemical additive.

Efforts are concerned with prohibiting corrosion imparted by condensed sulfuric acid vapors in the induced draft fan and the stack. Heating the flue gas after the electrostatic precipitator should be performed in such a way to compensate for the heat lost by the cooling draft in the induced draft fan. Calculations usually include a safety factor which considers fluctuations in the gas flow rate, changes in sulfur trioxide concentration, and variations in the dew point. One potential method, which is not actively being investigated at the present time, but nevertheless may have potential benefits, is to install infra-red heaters in the duct connecting the electrostatic precipitator and the induced draft fan. With this system, a thermostat would regulate the operation of the heater and minimize energy utilization. Currently efforts at the Portsmouth site are directed at raising the temperature of the flue gas by either blocking some tubes in the present economizers or designing a

bypass. Figure 6 is a sketch of the proposed bypass. These modifications will reduce the efficiency of the economizers, however, and hence a larger amount of coal will be burned. Consideration will therefore need to be given to the impact of the resulting increase in SO_x emissions.

Parallel to the proposed solution of heating the gases above the acid dew point, other studies are being conducted. The objective of these studies is to protect the fan and stack from the condensed acidic vapors. Metallurgical studies are being conducted to characterize the type, the extent, and the probable causes of corrosion.¹⁶ New types of materials to replace some of the components exhibiting the worst corrosion are being investigated. Initial tests included placing samples of corrosion resistant metals such as Hastelloy C-276 and Hastelloy G-3, and others into the induction fan housing.

Application of corrosion resistant liners is one method used in industry as a corrosion control measure. Different types of liners are being evaluated for application to protect the inner surface of the stack and the fan housing.

ACKNOWLEDGMENT

The author is greatly indebted to many groups and individuals who supplied the data upon which this paper is based and who could be considered as co-authors in a general sense. Special acknowledgment should go to: Ms. S. L. Fout for metallurgical analyses; D. L. Chaney and members of his Process Services Section for sampling and SO_3 analyses; O. A. Vita and members of his Environmental and Industrial Hygiene Section for stack gas, coal and sulfur analyses; R. J. Riddle for temperature monitoring; and R. A. Childers and B. E. Wilkinson for overall assistance and cooperation on this problem.

Figure 6 Schematic Showing Proposed Bypass

REFERENCES

1. "Boiler Flue Corrosion Monitoring and Protection" Dearborn Chemical (January 8, 1981).
2. Identification of White Sludge from No. 2 Stack of the X-600 Steam Plant, GAT-521-80-159 (August 19, 1980).
3. Testing of Flue Gas from X-600 Boilers, GAT-852-81-70 (March 23, 1981).
4. Estimation of Steel Test Strips, GAT-523-81-51 (March 31, 1981).
5. Evaluation of Degraded Steam Plant Boiler Stack Coating Report, GAT-521-81-54 (March 25, 1981).
6. J. E. Radway, "Effectiveness of Fireside Additives in Coal-fired Boilers," Power Eng. (April, 1978), pp. 72-75.
7. J. E. Radway, "Selecting and Using Fuel Additives," Chem. Eng. (July 14, 1980), pp. 155-160.
8. J. A. Danielson, Air Pollution Engineering Manual, EPA Publication, No. AP-40, 2nd Ed. (May, 1973), pp. 562-564.
9. R. R. Pierce, "Estimating Acid Dew Points in Stack Gases," Chem. Eng. (April 11, 1977), pp. 125-128.
10. Recorded Strip Chart to Measure SO₃ Concentration, GAT Materials Sampling and Testing Laboratory.
11. Analytical Data of Coal Samples, GAT Chemical Analysis Laboratory.
12. F. H. Verhoff and J. T. Banchero, "Predicting Dew Points of Flue Gases," Chem. Eng. Prog. Vol. 70, No. 8 (August, 1974), pp. 71-72.
13. Yen-Hsiung Kiang, "Predicting Dew Points of Acid Gases," Chem. Eng. (February 9, 1981), pp. 127.
14. Inlet/Outlet Temperature of ESP #1 and ID Fan #1, Data recorded by GAT Utilities Operations (August 12-22, 1981).
15. Temperature Measurements at X-600 Steam Plant Boiler System #1 Report, GAT-T-3129, (December 11, 1981).

16. Materials Technology Involvement in Steam Plant Corrosion Problems Report, GAT-523-81-163 (December 11, 1981).
17. J. S. Smith, Economizers Corrosion and Other Problems. Modern Industrial Energy (October, 1980).
18. J. D. Piper and Van Vliet, Hazen. Trans. ASME (August 1958), p. 1251.
19. Ad Hoc Panel on Control of Sulfur Dioxide from Stationary Combustion Sources Committee on Air Quality Management. National Research Council, "Abatement of Sulfur Oxide Emissions from Stationary Combustion Sources," (1970).

TR-022582-WTB