USE OF THE DEW POINT METER AND ASH SAMPLER IN ASSESSING PERFORMANCE OF FUEL OIL ADDITIVES

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INTRODUCTION

Many severe problems are associated with sulfuric acid corrosion caused by conversion of a portion of sulfur in heavy fuel oils to sulfur trioxide by the combustion process in steam boilers. In order to evaluate various practical means of minimizing the problem at the plant level, meaningful but relatively easy tests had to be developed. This paper shows that acid dew point measurements of the flue gases before and after the air preheater are fairly predictive of the acid condensation occurring and its corrosion potential. Use of fuel oil additives can complicate the data collection and interpretation, necessitating supplemental techniques to gauge the neutralization which can take place, both in the gas stream and on the heat exchange surfaces. One such supplemental technique, based on ash collected from the gas stream after the air preheater, is described and a case history presented to show its application in evaluating additives in a modern power station where more sophisticated techniques cannot be readily applied. Results of these techniques quickly show if an additive is effective in controlling sulfuric acid corrosion.

EXPERIMENTAL

The boiler used for the experimental work is a 600-Mw Combustion Engineering utility boiler designed to burn residual fuel oil and equipped with two regenerative type air preheaters. The fuel oil throughout the test period consisted of a typical Venezuelan residual oil containing 0.1 percent ash, an average of 2 percent sulfur and 350 to 500 ppm vanadium.

All measurements and samples included correlation of the boiler operating data which are known to directly affect the amount of sulfur trioxide formed and resulting acid condensation. These data are: rate of firing (load), excess air, and average metal temperature of the heat exchange elements in the air preheaters. Fuel oil flow varies directly with load and is typically half pound per hour per kw of load.

Measurements were taken at various firing rates and with two chemical treatments. One treatment was supplied as fuel oil additive and the other as a "cold end" treatment by injection of chemicals into the hot gases ahead of the air preheaters.

To reduce the total experimental time, two cold end treatments were run simultaneously by treating each air preheater separately. Testing was done with no chemical treatment and also with the following single or combination of treatments:

1. Injection into the fuel oil of a commercial fuel oil additive consisting of a dispersion of an inorganic manganese compound.

2. Injection of a commercial fuel oil additive consisting of a combination magnesium/aluminum in a ratio of 10:1 Mg/Al as magnesium oxide and aluminum hydroxide.

3. Injection of the manganese fuel oil additive with concurrent treatment of the air preheaters. One air preheater with a proprietary aqueous magnesium hydroxide slurry and the other with a proprietary powdered additive.

4. The magnesium/alumina combination fuel oil additive with the cold end treatments.

Dew point measurements were taken both before and after the air preheaters with a Land Instruments Inc., Model 200 Dew Point Meter. This instrument was also used to determine the rate of acid condensation (rate of acid build-up or RBU) at various temperatures by controlled cooling with air of the sensor probe inserted into the gas stream.

The dew point meter has been employed for many years in investigations of the corrosion and fouling of low-temperature heat transfer surfaces on both coal and oil-fired boilers. In a 1963 ASME paper, Clark and Childs described its use in developing a "guide" for air heater temperature control.* They showed the importance of low excess air operation, boiler cleanliness and magnesia additives on flue gas corrosion potential. Operation of the dew point meter has been described in previously published material.

Ash sampling was accomplished by collecting a "grab sample" of particulate from the gas stream by insertion of a proprietary aspirator type sampler (Figure 1) into the gas stream after the air preheater.

The ash sample was ground and a one-gram sample was stirred into sufficient distilled water to make a 1 percent slurry. The pH of this slurry was measured one minute after agitation was stopped using a conventional pH meter.

RESULTS AND DISCUSSION

Operational history of this unit indicated a continuing degradation of "cold end" conditions resulting in increased sulfuric acid condensation. These conditions caused accelerated corrosion and fouling of the air preheater, necessitating washing every six weeks.

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* N. D. Childs, G. D. Clark, "Boiler Flue Gas Measurements Using a Dew Point Meter" -- ASME 63-WA-109, November, 1963.

This fouling of air preheaters is a typical result of condensed sulfuric acid permitting wet air preheater elements to act as a trap for fly ash.

Design factors in the heat exchange surface of the unit encouraged plant operators to select a manganese type fuel oil additive. Dew points with the manganese fuel oil additive averaged 285°F. (141°C.) and the rate of acid condensation (hereafter referred to as rate of acid build-up -- RBU) measured 1,200 to 1,500 microamps per minute. (Figure 2, 12-6-74) Clark and Childs reported that they found very rapid corrosion on boilers showing an RBU in excess of 500 microamps per minute and relatively minimal problems when this reading was below 100.

The significance of these dew point measurements can be seen by analyzing the data in the first entry on Table I. The pH of fly ash samples measured 1.4 and confirms the high acid dew point and RBU values. It is evident that the manganese fuel oil additive was doing very little to ameliorate severe acidic conditions.

This dew point and pH data in conjunction with the fouling frequency of the air preheater and the marked corrosion noted during visual inspections convinced station personnel that additional steps had to be taken to protect the cold end. They chose to evaluate two proprietary cold end treatments -- an aqueous magnesium hydroxide slurry and an alkaline dry powder product. Each of these were introduced upstream of the air preheater into a zone where flue gas temperatures range from 600-700°F. (316-371°C.)

These chemical treatments lowered the acid dew point to 260°F. (127°C.) and 270°F. (132°C.) respectively and the peak acid condensation temperatures to 220°F. (104°C.) and 240°F. (116°C.) respectively. The RBU values also were lowered to 120 and 110 microamps per minute (Figures 2 and 3). Little acid will condense and little corrosion will occur even though the exit gas temperatures are below the acid dew point. Raising the exit gas temperature to about 279°F. (137°C.) would have the same effect on the RBU value as the alkali, but at a considerable cost in fuel dollars. At 279°F. (137°C.), the rate of acid condensation would be the same as it is with alkali at the present exit gas temperature of 245°F. (118°C.), i.e., 68 microamps per minute.

This data indicates the aqueous magnesium hydroxide slurry to be more effective than the dry powdered product when compared on an equivalent weight basis. Both products depressed the dew point and RBU readings but not to the same degree (Figure 4).

Fireside conditions, after prolonged use of the manganese fuel oil additive, convinced the operators to replace it with the magnesium/aluminum front end treatment. Data with this treatment and no cold end additive show that the dew point was unchanged at both high and low load operations, i.e., 285°F. (141°C.). However, the potential for cold end corrosion did improve as indicated by the rate of acid condensation and ash pH data. The RBU values at high and low loads were in the ranges of 500 and 120 microamps per minute and the corresponding ash pH readings were about 3.0 and 2.5 respectively. These compare with much higher peak rates of condensation (approximately 1,500 microamps per minute) and lower pH values (approximately 1.4) when manganese was fed on the front end.

The need to supplement front end additives in this particular case is evidenced by the decreased pH at low load. Addition of both the powder cold end additive to one air preheater and the magnesium hydroxide slurry to the other yielded higher pH ash samples. The slurry was generally more effective at lower magnesium-oxide equivalent feed rates. Emphasis is placed on the ash pH measurements at low load and low RBU values because the dew point meter is less sensitive to chemical changes in this range.

This work and the data collected (Table I) show that the dew point meter can be very useful in selecting boiler operating conditions, evaluating additives, additive feed rates, etc. However, one should be aware of the meter's limitations. For example, measurements should be made before and after the air preheater because acid condensed on air heater exchange surfaces will not be detected if the probe is inserted downstream only.

If the alkali has sufficient time to react with the acid before reaching the dew point probe, the instrument will reflect it. However, in many cases neutralization occurs on the air preheater elements and cannot be detected by the dew point meter.

The relatively short and fixed length of the dew point probe makes it difficult to obtain a profile of the acid distribution in a duct. This is of significance in assessing the performance of cold end chemical additives because gas mixing can be surprisingly poor in those ducts.

Consequently, pH of fly ash samples taken after the air heater will then show if the chemical additive has neutralized sulfuric acid. Long years of experience have shown that when the ash pH is above about 3.5, sufficient acid has been neutralized to minimize corrosion problems and fouling of the air preheaters will not occur.

The results of this work demonstrate that dew point meters and fly ash sampling are viable tools for power plant operation to quickly evaluate both the potential for sulfuric acid corrosion and the effect of chemical treatment. This can be done in a short period of time so money is not needlessly spent for ineffective additives and more importantly, before severe corrosion and acidic stack discharges occur.

FIGURE 1 **Probe For Collecting Oil Ash Samples For pH Determinations**

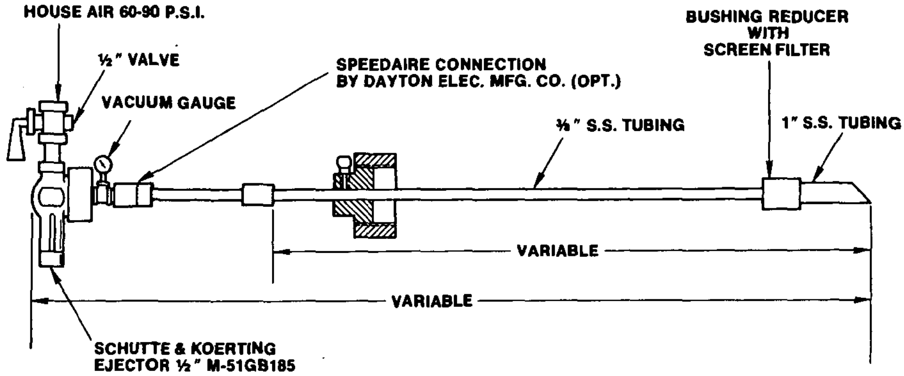

FIGURE 2

Comparison of acid dew point and rate of acid condensation on a 600-MW Oil-Fired boiler with and without Magnesium Hydroxide slurry Cold-End additive on B-Duct

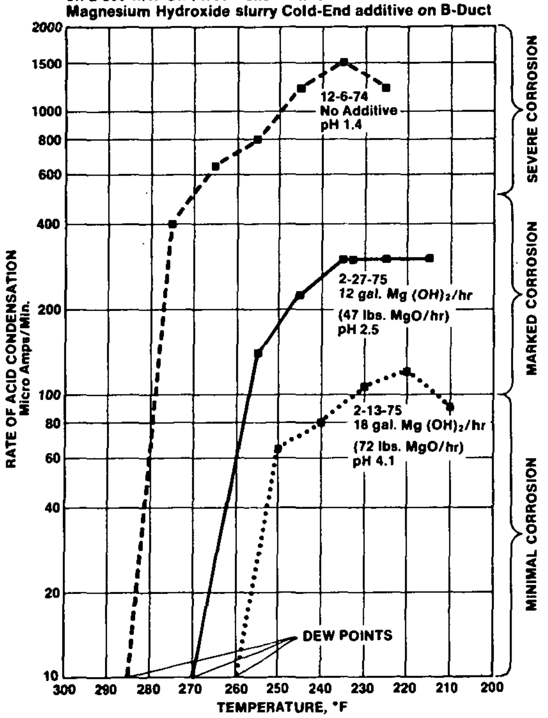

FIGURE 3

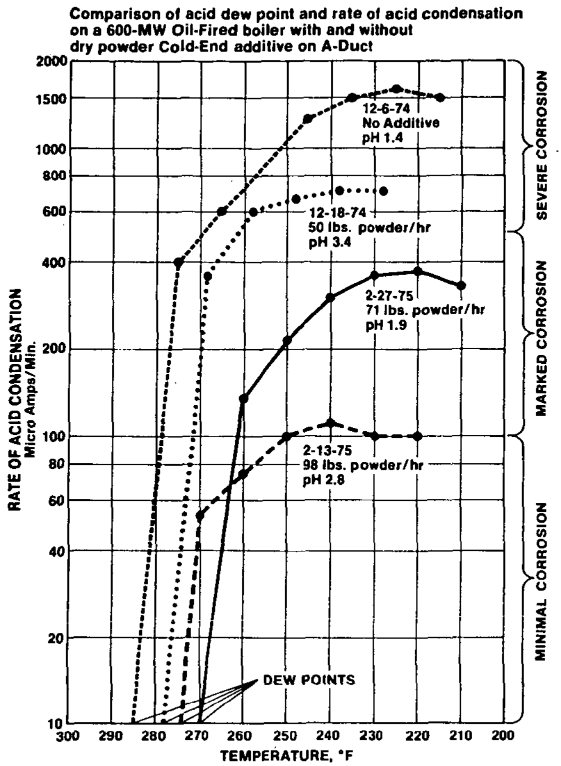

FIGURE 4

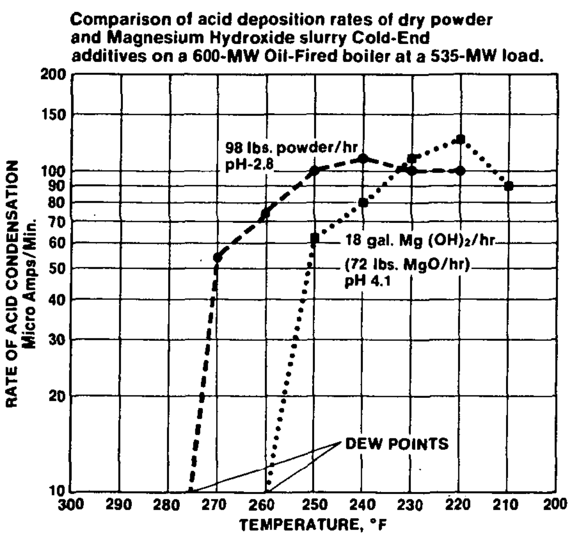

TABLE I

DEW POINT DATA AND ASH pH AS A FUNCTION OF ADDITIVE FEED ON A 600-MW OIL-FIRED BOILER

Date	Fuel Oil Addtv	POWDER ADDITIVE "A" DUCT							MAGNESIUM HYDROXIDE SLURRY "B" DUCT							
		Feed Rate (lb/hr)	Dew Point		RBU (micro amps/min)	Peak Temp		Ash pH	Feed Rate		Dew Point		RBU (micro amps/min)	Peak Temp		Ash pH
			°C	°F		°C	°F		(gph)	MgO Eqv (lb/hr)	°C	°F		°C	°F	
12-6-74	Manganese	0	141	285	1,600	107	225	1.4	0	0	141	285	1,500	116	235	1.4
12-18-74	↓	--	137	278	725	114	238	--	--	--	--	--	--	--	--	--
2-3-75		68.5	--	--	--	--	--	--	0	0	--	--	--	--	--	1.7
2-7-75		41.7	--	--	--	--	--	1.8	24.1	96.3	--	--	--	--	--	4.1*
2-9-75		98	--	--	--	--	--	2.8	16	64	--	--	--	--	--	4.0
2-11-75		98	--	--	--	--	--	--	18.2	72.7	--	--	--	--	--	4.6
2-13-75		98	137	278	118	116	240	2.8	18.2	72.7	127	260	126	104	220	4.1*
2-27-75		71	132	270	390	104	220	1.9*	12	47	132	270	238	116	240	2.5*
3-6-75		50	--	--	--	--	--	3.2	0	0	--	--	--	--	--	2.3
5-15-75	↓	50	--	--	--	--	--	3.2	16	64	--	--	--	--	--	4.2
6-6-75	Magnesium plus Aluminum	0	141	285	590	124	255	3.4	0	0	141	285	420	118	245	2.7
8-5-75		0	141	285	108	106	222	2.4	0	0	141	285	135	106	223	2.4*
8-6-75		60-80	141	285	170	121	249	3.3*	7-8	28-33	141	285	190	113	235	4.5*

*Denotes data collected at low load operation -- 300-320MW. All data on 8-5-75 and 8-6-75 is on low load and compares two cold end treatments with Magnesium Oxide/Aluminum Hydroxide fuel oil additive.