High Temperature Corrosion of Stainless Steel by Fuel Oil Ash*

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Summary: Laboratory corrosion tests on stainless steel were carried out to determine the effects of the oil ash deposits taken from the tube surfaces in four boilers. The chemical constituents and the fusing characteristics were also determined.

Conclusions after testing were as follows:

- (a) The higher the V_2O_5/Na_2O ratio of the deposits the greater the corrosion.
- (b) Many deposits contained a constituent fusing at about 570°C .
- (c) All of the deposits, which were taken from the superheater tube surfaces, were less corrosive at below 570°C .

Introduction

High temperature corrosion in boilers has long been a major problem in firing residual fuels. Since 1955 in Japan, in many oil-fired boilers steam temperatures were limited to 540°C , to prevent serious corrosion by fuel oil ash. However, it is necessary to know the effect of residual oil ash deposits on the corrosion if one desires to raise the efficiency of steam generating plant by increasing the steam temperature.

Many researchers reported the effects of Na_2SO_4 in V_2O_5 - Na_2SO_4 mixtures¹⁾⁻³⁾, the effects of additives^{2), 4), 5), -9)} and the evaluation of corrosion resisting alloys.^{10), 11)}

However, from those reports one could not learn adequate details on the corrosion of superheater tubes in commercial steam power plants.

To obtain this information, laboratory corrosion tests by fuel oil ash deposits were carried out. The present paper describes the examinations of oil ash deposits taken from four boilers and the corrosion tests of SUS 27 stainless steels by the deposits or by the synthetic mixtures simulating such the deposits.

Fuel Oil Ash and V_2O_5 - Na_2SO_4 Mixtures

Oil ash deposits were taken from four oil fired boilers prior to cleaning. The boiler specifications are shown in Table 1.

Impurities in fuel oil consumed in those boilers are shown in the table below:

Sulfur (S)	2.5-2.7%
Vanadium (V_2O_5)	40-100 ppm
Sodium (Na_2O)	20-40 ppm

The deposits consisted mainly of V_2O_5 , Na_2O and SO_3 , and the total was about 70-90%, as shown in Table 2. The ratios V_2O_5/Na_2O and SO_3/Na_2O in the deposits from the three boilers (A, B and C) are distributed around the straight lines represented by $Na_2SO_4 + xV_2O_5 + ySO_3$ (Fig. 1). The V_2O_5/Na_2O ratio of the deposits was decreased with increasing the tube surface temperatures from which the deposits were taken. But the deposits from D boiler were not distributed on those lines.

V_2O_5 - Na_2SO_4 mixtures shown below were prepared and used for corrosion tests, and the effect on corrosion was compared with the oil ash deposits.

Table 1. Specification of Power Plant Boilers

Name of Power Station	A	B	C	D
Capacity (t/h)	435	590	435	260
Pressure (kg/cm^2)	148	186	149	135
Steam Temperature,				
Superheater, $^\circ\text{C}$	541	571	541	541
Reheater, $^\circ\text{C}$	541	544	541	541
$O_2\%$ in Combustion Gas	2.0	2.0	2.5	1~1.2
Date Sample Deposits	'62-6-2	'63-6-3	'63-6-14	'63-7-10
Period of Operation	7 months	5,300hr	21months	6,165hr

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Table 2. Chemical Analysis and Melting Points of Oil Ash Deposits in Oil-Fired Boilers

Sampling Position	Steam Temp. (°C)	Constituents of deposits (wt%)			V ₂ O ₅ /Na ₂ O (mole ratio)	SO ₃ /Na ₂ O (mole ratio)	Melting Point (°C)
		V ₂ O ₅	Na ₂ O	SO ₃			
Power Station A							
Secondary SH, Outlet Tube	541	31.6	18.9	27.5	0.57	1.12	580 735
High temp. RH, Outlet Tube	541	29.5	18.2	24.4	0.55	1.12	570 715
Primary SH	419	49.7	10.5	20.6	1.62	1.53	{550 630 735
Power Station B							
Secondary SH, Outlet Tube	571	36.9	17.3	19.2	0.73	0.86	580 730
Secondary SH, Middle Tube	530	42.3	12.8	16.8	1.13	1.15	575
High temp. RH, Outlet Tube	541	40.8	14.7	18.4	0.95	0.97	565 735
Radiation SH, 4 Floor	480	42.7	6.4	6.8	2.29	0.83	{570 700 730 800
Water Wall Tube, Back Wall, 2 Floor	450	62.1	7.8	8.0	2.79	0.80	—
Water Wall Tube, Front Wall, 2 Floor	350	77.1	7.5	3.4	3.52	0.35	590
Power Station C							
Secondary SH	541	6.8	31.0	41.8	0.07	1.05	550 845
High Temp. RH, Lower Row	541	25.0	17.8	31.5	0.48	1.37	560 735
High Temp. RH, Upper Row	541	16.5	23.2	38.4	0.24	1.28	{560 740 870
Primary SH, Outlet Tube	453	32.4	8.1	28.1	1.36	2.68	{550 610 740
Low Temp. RH, Outlet Tube	421	44.1	11.9	33.4	1.27	2.19	{540 610 720
Low Temp. RH, Inlet Tube	370	32.8	15.5	28.8	0.72	1.44	{530 630 740
Power Station D							
Secondary SH, Outlet Tube	541	39.1	13.1	28.8	1.02	1.71	530 730
RH, Middle Tube	500	43.8	7.9	6.8	1.89	0.67	575
RH, Inlet Tube	341	41.5	11.0	19.6	1.28	1.38	465

Fig. 1 Distribution of Chemical Compositions in Deposits Taken from Four Boilers

Weight Percent of V ₂ O ₅	Weight Percent of Na ₂ SO ₄	Mole Ratio of V ₂ O ₅ /Na ₂ O
30	70	0.34
40	60	0.52
56	44	1.01
70	30	1.82
80	20	3.12
90	10	7.02

Experimental Procedure

Corrosion tests were carried out in an electric furnace, and the temperature was held constant during the test period.

Specimens used in those tests were 12.9×12.9×0.29 mm 18Cr-8Ni stainless steel (SUS 27), polished with sand paper.

Three grams of oil ash deposits or synthetic ash (mixtures of V₂O₅ and Na₂SO₄) were added to 15 ml porcelain crucibles, in which the specimens were immersed. The crucibles containing specimens and ash were put into the electric furnace.

After completion of tests, the corroded specimens were immersed in molten caustic soda bath and cathodically descaled. The descaled specimens were washed, dried and re-weighed.

Results and Discussion

1. Fusion Characteristics of Fuel Oil Ash Deposits

The fusion characteristics of the oil ash deposits were determined by the Leitz high temperature microscope using a similar technique which is used for the determination of the fusibility of coal ash.

The deposits were pressed in 3 mmφ×3 mm, and heated in the electric furnace. When the temperature increased to the fusion points of a constituent in the deposit, the sample bulk was

Fig. 2 Fusion Characteristics of the Deposits on High Temperature Superheater and Reheater in Power Stations A and B

shrunk, and the height was decreased as shown in Fig. 2. Four deposits from A and B Power Station have the two constituents, which fuse at the same temperature, 580°C and 720–730°C. Other deposits also have a constituent fusing at below 600°C. The fusion points of the deposits are shown in Table 2.

Fusion characteristics of V_2O_5 - Na_2SO_4 mixtures were shown in Fig. 3. The fusion points of V_2O_5 - Na_2SO_4 mixtures, which were given between 610–655°C, coincided with those obtained by Cunningham.¹⁾

Low melting constituents in the oil ash deposits are examined in detail¹²⁾, its compositions are assumed to be vanadyl vanadate ($Na_2O \cdot V_2O_4 \cdot 5V_2O_5$, $5Na_2O \cdot V_2O_4 \cdot 11V_2O_5$)^{13),14)}

2. Effect of Oil Ash Composition

Corrosion tests used with the oil ash deposits and V_2O_5 - Na_2SO_4 mixtures were carried out at 600°C or 550°C for 200 hours.

Table 3. Comparison on Air Corrosion of SUS 27 Stainless Steel with Boiler Deposits at 600°C and 550°C in 200 Hours

Sampling position	Weight Loss (mg/cm ²)	
	550°C	600°C
Power Station B		
Secondary SH, Outlet Tube	2.2	3.9
Water Wall Tube, back Wall, 2 Floor	1.0	79.1
Power Station C		
High Temp. RH, Lower Row	8.6	16.8
Primary SH, Outlet Tube	2.6	34.4
Low Temp. RH, Outlet Tube	2.1	20.0
Low Temp. RH, Inlet Tube	1.3	22.9
Power Station D		
Secondary SH, Outlet Tube	0.3	1.0
RH, Middle Tube	0.8	46.2
RH, Inlet Tube	3.6	38.2

Fig. 4 Effect of V_2O_5/Na_2O Ratio on Air Corrosion of SUS 27 Stainless Steel with Boiler Deposits at 600°C in 200 Hours

These results are shown in Table 3, and illustrated in Fig. 4. From the figure, it is found that:

(1) Weight losses of specimens exposed at 600°C

Fig. 3 Fusion Characteristics of V_2O_5 - Na_2SO_4 Mixtures

were increased with increasing V_2O_5/Na_2O ratios of the deposits.

- (2) Specimen weight losses by the deposits taken from the highest tube surface temperature zone were below 20 mg/cm^2 .
- (3) Weight losses by oil ash deposits were smaller than those by the $V_2O_5-Na_2SO_4$ mixtures having the same V_2O_5/Na_2O ratios.

In (2), it is considered that 10–30% of metal oxides in the deposits, consisting of Fe, Ni, Mg, Ca, Si etc., decreased the corrosion rate because they react with vanadium oxides and decrease the amount of fusing constituents.

The most corrosive $V_2O_5-Na_2SO_4$ mixtures were those made up to contain 15–20 percent Na_2SO_4 , or those having a mole ratio of 6 to 1.³⁾ As the V_2O_5/Na_2O ratios of the deposits taken from four boilers decreased below 3.5, corrosion weight losses decreased with the decreasing ratio (Fig. 4).

Fig. 5 Effect of Presumed Steam Temperature in the Tube on Air Corrosion of SUS 27 Stainless Steel with Boiler Deposits at 600°C and 550°C in 200 Hours

3. Effect of Temperature

In most of the oil fired boilers, steam temperatures are designed to be 540°C or 570°C.

If the steam temperature is 570°C, external surface temperature of superheater tube will reach approximately 600°C.

To examine the effect of temperature on corrosion weight losses by oil ash deposits, experiments were carried out at 600°C and 550°C for 200 hours. The temperature of 600°C corresponds to the highest metal temperatures on superheater tubes, and 550°C corresponds to a non-fusing temperature of the deposits.

Effect of the Tube Surface Temperature

The corrosion weight losses of specimens by the deposits taken from the highest tube surface temperature zones were lower than those taken from the lower temperature zones, as shown in Fig. 5.

Effect of Melting Point

Corrosion weight losses by the deposits were all below 5 mg/cm^2 at 550° (Fig. 5). Thus, it is apparent that oil ash corrosion did not occur at 550°C.

Temperatures at which Corrosion Occurred

To determine the temperature at which oil ash corrosion occurs, corrosion tests were carried out at various temperatures between 550–700°C.

As shown in Fig. 6, corrossions occurred at above 570–580°C, and the weight losses increased sharply with increase of the temperatures. In Fig. (c), it is shown that the weight losses at 650°C were

Fig. 6 Effect of Temperature on Air Corrosion of SUS 27 Stainless Steel with Boiler Deposits in 200 Hours

lower than at 600°C. The reasons will be explained below.

4. Corrosion Rate

Corrosion weight losses of specimens increased with the length of the test period. To determine its relationship, corrosion tests were carried out at 600°C and 700°C using both the deposits from the superheater tubes and the V_2O_5 - Na_2SO_4 mixtures. The results are shown in Fig. 7. Weight losses by the deposits from secondary superheater tube increased sharply at 700°C, but at 600°C the weight losses caused by the same deposits were very small. From the log-log plot, it is considered that the weight losses increased proportionally at 700°C, however at 600°C, they increased proportionally with the root test period.

Fig. 7 Corrosion of SUS 27 Stainless Steel with Various Deposits at 600°C and 700°C

Corrosion weight losses of specimens caused by a mixture of 70% V_2O_5 +30% Na_2SO_4 varied with temperature and test period, as shown in Fig. 8. As the mixture did not melt, weight losses were slight at 550°C. Although the corrosion rate in the earlier test period at 575°C was very slow, it was accelerated with progressive corrosion.

The corrosion weight losses at 650°C was larger than those at 600°C in the earlier test period, but after 130 hours, weight losses at 650°C decreased at 600°C (Fig. 8). Corrosion weight losses after 200 hours increased as follows: $550^\circ < 575^\circ < 650^\circ$

Fig. 8 Corrosion of SUS 27 Stainless Steel in 70% V_2O_5 +30% Na_2SO_4 mixture at various Temperatures

$< 600^\circ < 700^\circ$, as shown in Fig. 6(c).

It is considered that the corrosion mechanisms changed at those temperatures.

5. Effect of Oxygen Concentration in Gases

The corrosion tests described above were carried out in air. As of oxygen concentrations in combustion gases are only 1/10–1/20 those in air, corrosion tests were carried out at various oxygen concentrations to determine the effect on corrosion.

As shown in Fig. 9, the corrosion weight losses caused by the V_2O_5 - Na_2SO_4 mixtures at 700°C were constant at oxygen concentration above 2%, but below 2% they decreased. Corrosion weight losses caused by the mixtures at 650°C increased proportionally with the oxygen concentration, and the weight losses by the superheater deposits at 700°C were only slightly affected by the oxygen concentrations.

From these results and the corrosion rate discussed in 4.4, it is believed that corrosion weight loss was similar at above 2% oxygen concentration when the weight loss increased linearly with the test period. However when it increased parabolically, weight loss increased linearly with increase of the concentration.

From the above results, it is conjectured that high temperature corrosion by fuel oil ash in a boiler will decrease with the low excess air firing.

No. 1: $V_2O_5-Na_2SO_4$ (20%), 700°C, 24hr

No. 2: $V_2O_5-Na_2SO_4$ (30%), 700°C, 24hr

No. 3: Power station B
secondary superheater deposit, 700°C, 24hr

No. 4: $V_2O_5-Na_2SO_4$ (30%), 650°C, 100hr

Fig. 9 Effect of Oxygen Concentrations on Air Corrosion of SUS-27 Stainless Steel by Fuel Oil Ash and Synthetic Ash

Conclusion

From the analysis and fusing characteristics of the oil ash deposits taken from four boilers, the following results were obtained.

- (1) The sum of V_2O_5 , Na_2O and SO_3 in the oil ash deposits were 70–90%.
- (2) Ratios of V_2O_5/Na_2O and SO_3/Na_2O in the deposits were distributed around the straight lines represented as $Na_2SO_4 + xV_2O_5 + ySO_3$.
- (3) All of the deposits contained the same constituents, fusing at about 570°C.

Corrosion tests with those deposits were carried out to find the relation between the corrosion weight losses and the deposit characteristics. The conclusions are as follows:

- 1) Corrosion weight losses by oil ash deposits increased with the increase of the molar ratio of V_2O_5/Na_2O in the deposits.
- 2) Corrosion weight losses by the oil ash deposits taken from the higher temperature zones,

secondary superheater and high temperature reheater, were less than those taken from lower temperature zones.

- 3) Corrosion weight losses by the deposits and $V_2O_5-Na_2SO_4$ mixtures occurred at above 570–580°C.
- 4) Corrosion weight losses at oxygen concentration above 2% were similar if the corrosion weight losses would increase linearly with the time. However, if the weight losses would increase parabolically with the time, they increased proportionally with the oxygen concentration.

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