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OIL ASH DEPOSITS AND LOW TEMPERATURE

CORROSION IN A CLEAVER BROOKS BOILER

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CANADIAN COMBUSTION RESEARCH LABORATORY

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by

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ABSTRACT

As part of the continuing energy conservation research program the Canadian Combustion Research Laboratory has undertaken a short analytical investigation of the effects produced by the use of fuel-oil additives. The problem was raised as a consequence of discussions with B.P. Canada who reported excessive quantities of deposits in Cleaver Brooks four pass boilers burning an additive treated residual fuel oil.

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## INTRODUCTION

As part of the continuing energy conservation research program the Canadian Combustion Research Laboratory (CCRL) has undertaken a short analytical investigation of the effects produced by the use of fuel-oil additives. The problem was raised as a consequence of discussions with BP Canada who reported excessive quantities of deposits in Cleaver Brooks four pass boilers burning an additive treated residual fuel oil.

The additives used, Dursol 31 (anticorrosion) and Dearborn 26 (sludge dispersant) were both added at the rate of 2 gallons to 6000 gallons of fuel. The boiler operators reported a marked increase in the cleaning frequency of the units during additive use. Boiler outages for cleaning were now required every 3500 hrs instead of the previous 5000 hrs interval.

## DESCRIPTION OF THE SAMPLES AS RECEIVED

One pound samples of the fuel additives and of the deposits were examined at CCRL. In addition, independent analyses of the fuel oil used and typical analyses of the fuel oil were supplied. These analyses are shown in Table 1.

TABLE 1

### Analyses of Bunker "C" Heavy Fuel Oil

	Tank	Trailer	Typical BP
API Gravity @60°F	12.58	11.42	17.1
Specific Gravity	0.9821	0.990	0.9718
Flash, °F	180	190	230+
Total Sulphur, % wt	3.87	3.48	2.6
Viscosity @ 122°F, SSF	210	197.3	196
Vanadium, ppm	170	110	80
Water by Distillation, % vol	0.05	0.05	<0.1
Ash, % wt	0.065	0.05	0.06
Heat of Combustion, BTU/IG	181953	182744	178425
Pour Point, °F	40	40	+30

The samples were recovered from 1st/2nd pass and 3rd/4th pass tubes. The deposits from the 1st/2nd pass tubes were 100% - 1/8 in. mesh dry particles that were easily friable to form 100% -200 mesh powder and had the appearance of off-white coloured powder-cake covered lightly with soot. The deposits from the 3rd/4th pass tubes were 100% -30 mesh powder-cake that was dry and coloured off-white. The deposits from both sources contained some particles that had the appearance of hematite, and if this were so, then they must have been removed mechanically from the tube walls. The Cleaver Brooks boiler has four passes and access for cleaning with a wire brush is obtained through doors which cover the tube sheets.

The fuel additives were green coloured liquids of low viscosity and odour similar to those of light petroleum distillates. In particular, the odour was not very different from that of ethylacetoacetate, which is a common inexpensive solvent.

## RESULTS AND DISCUSSION

### The Deposits and the Additives

The deposits were mostly soluble in water and a 1% by weight solution of the 1st/2nd pass deposit had a pH of approximately 2.7 and of the 3rd/4th pass deposit had a pH of approximately 2.2. Since the sulphur content of the fuel was high, 3.48% to 3.87%, sulphur trioxide must have formed in the flame and condensed as sulphuric acid in the tubes. It would appear that the anti-corrosion additive had not completely neutralized this sulphuric acid.

Analyses of the deposits, Table 2 showed the presence of quantities of water soluble iron and sulphate. The iron sulphate hydrates,  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ , are off-white powders that are often found in boiler tubes. The deposits were concluded to be principally iron sulphate hydrates containing excess sulphuric acid formed by the reaction of the iron in the generator tubes with sulphuric acid condensed from the flue gases. The presence of excess sulphuric acid within the deposits confirms that condensation of acid was occurring on tube surfaces that were below the acid dewpoint. This condition would be aggravated as the sulphur content of fuel increased above 2.5%. The deposit from the 1st/2nd pass tubes also contained small quantities of vanadium originating from the fuel ash.

Iron wastage by sulphuric acid is catalyzed by vanadyl, ferrous and ferric ions. Additives that react with the sulphur trioxide and also the

TABLE 2

Analytical Data

Description		Dearborn 26	Dursol 31	Deposit From 1st/2nd pass	Deposit From 3rd/4th pass
		green liquid odour of pet dist	green liquid odour of pet dist	grey/black powder	grey powder
Ash*, %		1.0	3.8		
Ash Analysis,					
Water-Soluble Components	%	11.6	5.9	72.6	98.3
SO <sub>4</sub>	%	6.2	2.6	34.2	49.5
Cl	%	0	t	0	t
Ca	%	0.1	0.1	t	t
Cu	%	1.3	t	t	0.0
Fe	%	0.5	0.3	6.2	20.4
Mg	%	t	0.5	t	t
Mn	%	t	t	t	0.1
K	%	0.2	0.3	t	t
Na	%	0.5	0.1	0.4	t
Acid-Soluble Components	%	87.8	93.7	15.7	0.9
Ca	%	0.0	0.0	0.0	0.0
Cu	%	49.3	8.6	t	0.0
Fe	%	0.3	0.2	7.3	0.2
Mg	%	t	38.7	t	t
Mn	%	t	t	0.0	0.0
K	%	0.0	0.0	t	0.0
Na	%	0.0	t	t	t
V	%	0.0	0.0	0.9	0.0
Acid-Soluble Components					
5SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub>	%				

\* Samples were evaporated to dryness and residue was ignited according to ASTM D482-73

t trace amounts

vanadyl oxides that are formed in the flame are commercially available; most of these contain a magnesium salt. Salts of calcium and other cations can serve to neutralize the sulphuric acid but only magnesia-based additives produce a light friable deposit. Since only trace amounts of sodium, potassium, calcium or magnesium were found in the deposits, it is unlikely that there occurred any neutralization of the sulphuric acid by fuel or fuel additive components.

Dursol 31 is described by its manufacturer as an anticorrosion compound. The analysis of Dursol 31, shown in Table 2, shows that it contained 1.4% by weight magnesium (atomic wt 24.3). This magnesium can neutralize the corrosive action of vanadium and sulphur. The sulphur (atomic wt 32.0) forms 3.48% to 3.87% of the fuel. Most of the sulphur in the flue gas is found as sulphur dioxide,  $\text{SO}_2$ . It is unusual to find more than 5% of the sulphur as  $\text{SO}_3$ . Sulphur dioxide does not contribute directly to metal wastage except below the water dewpoint. Unless this occurs, sulphur dioxide does not contribute to corrosion.

A stoichiometric gas-phase neutralization of the  $\text{SO}_3$  formed in the flame (assumed to be 5% of the total sulphur) would require 0.15 lb Mg per 100 lb of 4% sulphur fuel oil. This requirement is not met by the dosage rate of 2 gal Dursol 31 per 6000 gal fuel which corresponds to approximately 0.28 lb Mg per 60,000 lb or 0.14 lb Mg per 30,000 lb. Thus to achieve stoichiometric neutralization, the dosage rate would have to be increased by a factor of 30.

Several magnesia based additives can provide a measure of protection against low temperature (sulphuric acid) corrosion by accumulation of a protective layer of  $\text{MgO}$  on heat transfer surfaces. Neutralization of the total gas-phase  $\text{SO}_3$  is clearly not necessary if surface protection can be arranged so that any condensed sulphuric acid is immediately neutralized to produce  $\text{MgSO}_4$ . If the additive works in this manner, significantly lower dosage rates than those required for stoichiometric gas-phase neutralization can be used.

There is no evidence from the analysis of the deposits that Dursol 31 acts in this manner. Virtually no magnesium was detected in any of the deposit samples analyzed and it must be concluded therefore that this mechanism of surface protection did not occur. A possible explanation is that the magnesium component of the anti-corrosion additive was present in such a form that it generated angstrom size magnesia particles in the flame which, despite their high surface area, did not significantly reduce the gas-phase  $\text{SO}_3$  concentration.

Particles of this size would follow gas streamlines with minimal deposition and could not provide a neutralizing deposit layer on heat transfer surfaces. The total absence of Mg in the deposits indicates that this could have occurred.

The analysis of Dearborn 26, shown in Table 2, shows that it contained 5.1% by weight copper. The solvent was a light petroleum distillate and had a faint odour resembling ethylacetoacetate. Therefore, the green colour of Dearborn 26 was probably due to copper ethylacetoacetate, which is very soluble in light oils. Copper has been employed as an "aid to combustion". The quantity of copper in the additives was small, consequently, the probable purpose of the copper salt is to colour the additives. Numerous inexpensive lipophilic surfactants (anti-sludging compounds) are available to the food and petroleum industry. Only rarely has their performance been improved by dyestuffs.

#### The Fuel

The analyses of the fuel oils used in the Cleaver Brooks boiler shows a significant difference in both the sulphur and the vanadium between the "typical BP" fuel oil and the "tank" and "trailer" fuel oils. The higher sulphur and vanadium levels of the "tank" and "trailer" fuel oils will lead, firstly, to increased  $\text{SO}_3$  production in the flame (from the increased sulphur content) and secondly to an increased catalytic activity on the tube surfaces.

One consequence of the increased  $\text{SO}_3$  production will be an increase in the acid dewpoint thus allowing sulphuric acid to condense on (and corrode) surfaces which were previously protected by virtue of being above the acid dewpoint. The increase in vanadium content can support this by accelerating the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  within any deposited material. The anticipated consequence of using a fuel with the "trailer" or "tank" specification as opposed to the "typical BP" specification would be an increase in the areas of the heat exchanger exposed to low temperature corrosion and an increase in the low temperature corrosion rates.

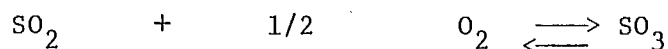
#### The Effect of Excess Air and Tube Temperature on Metal Wastage

High temperature corrosion normally only occurs at temperatures above  $520^\circ\text{C}$  and is not considered likely in this system.



Numerous studies of the causes and cures of low-temperature metal wastage due to oils containing much sulphur have been reported. It is evident that cold end problems are mainly due to the formation of sulphuric acid on the cool metal surfaces.

The most significant oxides of sulphur that are formed in the furnace are  $\text{SO}_2$  and  $\text{SO}_3$ . The equilibrium between these,



favours  $\text{SO}_2$  at high temperatures and  $\text{SO}_3$  at low temperatures provided that the oxygen concentration is that of typical fuel-lean combustion products. The  $\text{SO}_3$  concentration in the immediate post flame gases exceeds the equilibrium level and the  $\text{SO}_3$  concentration in the cool flue gases is far below the level given by the equilibrium expression. This behaviour shows that equilibrium is not achieved and that kinetics are important. Consequently, only a few per cent of the sulphur in the fuel forms  $\text{SO}_3$ ; the remainder forms  $\text{SO}_2$ . This is shown in Figure 1. Note in Figures 1 and 2 that the yield of  $\text{SO}_3$  is minimal for low excess air.

Sulphur trioxide combines readily with the water vapours in the flue gases to form sulphuric acid  $\text{H}_2\text{SO}_4$ . The catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  by rusty iron proceeds very rapidly if the iron is wetted by sulphuric acid. Figure 3 shows the relation between the dewpoint and the  $\text{SO}_3$  concentration in the flue gases. When the wall temperature is below the dewpoint, condensation occurs and the walls become wet with sulphuric acid. A galvanic cell is created. Oxygen is transported to the iron and it is oxidized. Iron ions migrate through the liquid to the surface where they catalyze the formation of more  $\text{SO}_3$ . Also they form  $\text{FeSO}_4$ . The  $\text{FeSO}_4$  that is formed is loose and porous and it restricts the heat flux to the walls. In such a case, the wall temperature decreases and the condensation of sulphuric acid is accelerated. The cycle repeats and more  $\text{FeSO}_4$  is formed. The process is catastrophic. Figure 4 shows typical rates of corrosion as a function of the wall temperature. Note the effect of excess air.

It is evident that the rate of corrosion by sulphuric acid of the steel tubing in the furnace can be minimized by reducing the excess air level and by increasing the metal temperatures. However, most burners do not provide

the efficient mixing of the fuel and the combustion air that is necessary to produce a soot-free flame at all values of excess air. Soot and acid smut are emitted when the excess air values are low. The consequence serious deterioration of the environment and concomitantly the fire hazards and loss of furnace performance associated with soot formation oblige the operating engineer to choose combustion conditions that minimize both soot formation and acid corrosion. An example of this is sketched in Figure 5.

The thermal efficiency of a furnace is a function of the excess air and of the flue gas temperature. This is illustrated in Figure 6. Note that the cross-hatched area in the figure represents that forbidden region of operation where soot formation is excessive. Although minimum excess-air is the desired operating parameter and efficient burners do exist, it may not be possible to reduce the excess air level below 5% or 10% in a Cleaver Brooks furnace. Since the furnace wall temperature is determined by the furnace design, a parameter that is not readily altered, the temperature of the flue gas at the base of the stack should be maintained at a level in excess of 150°C. Indeed, even this value may be too low.

Furnaces that are operated at minimum excess air level require continuous attention or a high-degree of automated combustion controls. Variations of wind pressure on the stack and flue gas buoyancy at start-up and shutdown are of sufficient magnitude to produce sooting unless a safe margin of excess air is permitted. The operating condition is therefore determined by the fan capacity, the stack height and the presence or absence of an inducted draft fan. If the furnace is not operating continuously, then the excess air necessary to produce safe soot-free operation can be as high as 25% excess air.

#### CONCLUSIONS

The deposits supplied to CCRL consisted largely of  $\text{FeSO}_4 \cdot n\text{H}_2\text{O}$  and contained free sulphuric acid. These deposits are a corrosion product from the heat transfer surfaces of the boiler.

The absence of magnesium from the deposits indicates that the anticorrosion additive was not providing a protective  $\text{MgO}$  deposit on the tube surfaces. Further, the dosage rate of the anticorrosion additive was

insufficient to offer a satisfactory gas-phase neutralization of  $\text{SO}_3$  formed in the flame.

The increase in sulphur content of the fuels (above the "typical BP" levels) will lead to increased corrosion throughout the system due to the consequent increase in acid dewpoint.

The results indicate that the increased cleaning frequency is a consequence of a significant increase in corrosion of the heat transfer surfaces that has not been ameliorated by the anticorrosion additive.

#### RECOMMENDATIONS

Since no operating data on the boiler were available explanations and corrective measures can only be tentative, the following items merit investigation.

A minimum flue gas exit temperature of  $180^\circ\text{C}$  is desirable with a fuel oil containing more than 2.5% S.

The use of a magnesia slurry coating, applied periodically to the gas side surfaces, can provide an effective surface protective coating.

Make-up and feedwater temperatures must be controlled to avoid localized tube temperatures below the acid dewpoint.

In view of the metal corrosion problem indicated by the deposit analyses, an examination of tube metal wastage is desirable to determine if replacement is necessary.

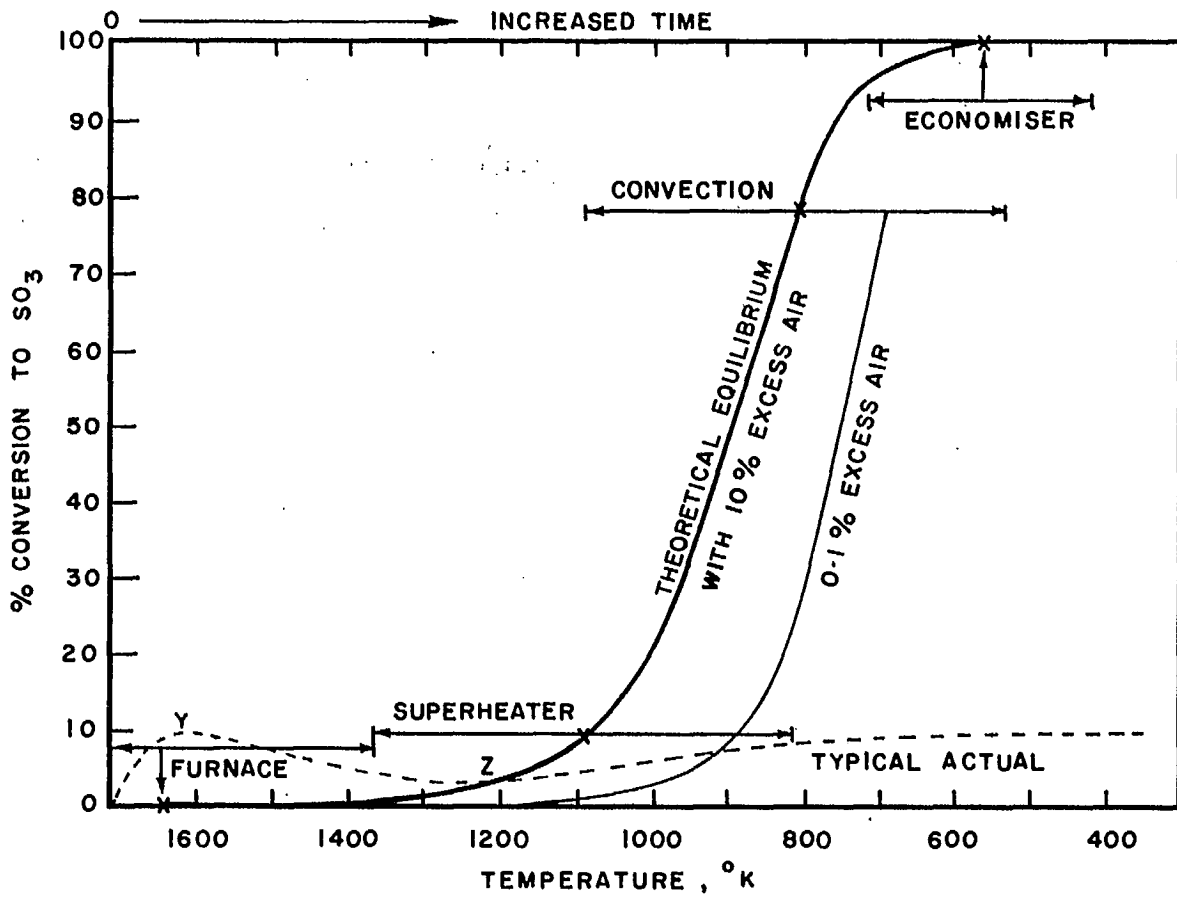


FIGURE 1. Factors Affecting SO<sub>3</sub> in Flames

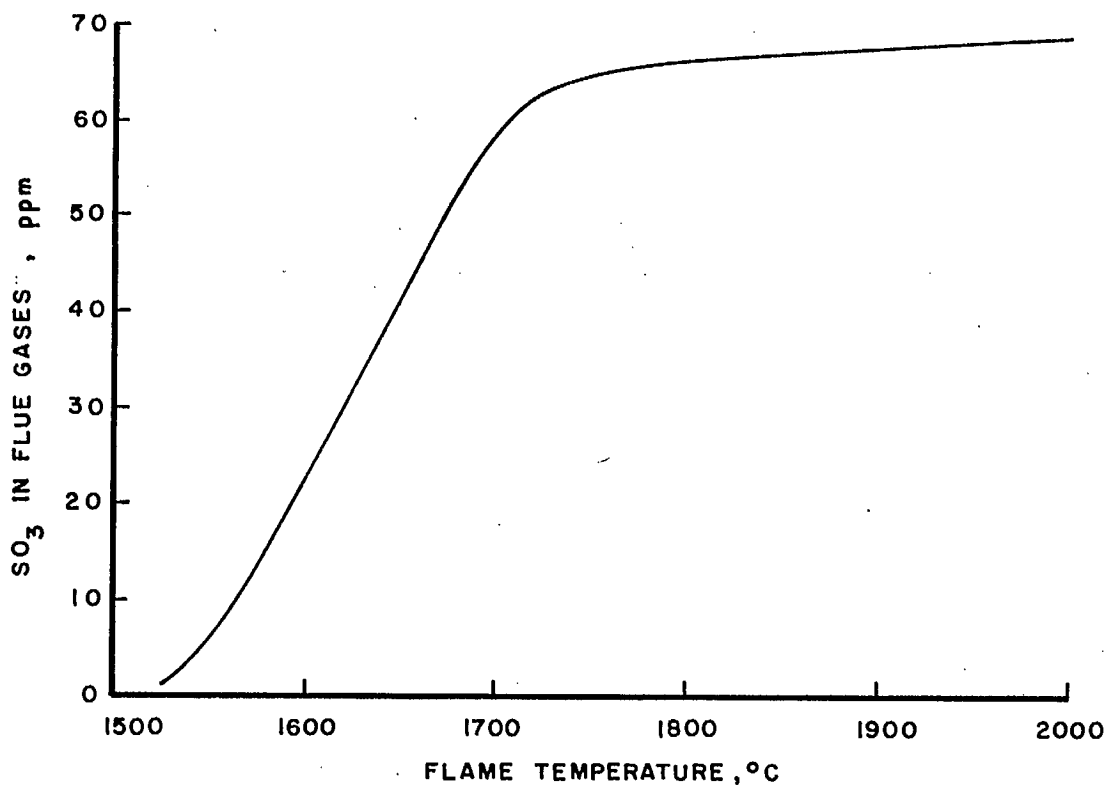


FIGURE 2. Sulphur Trioxide Concentration Evolution as a Function of Flame Temperature. The Fuel is No. 2 Oil Containing 3% Sulphur and the Excess Air is 7%.

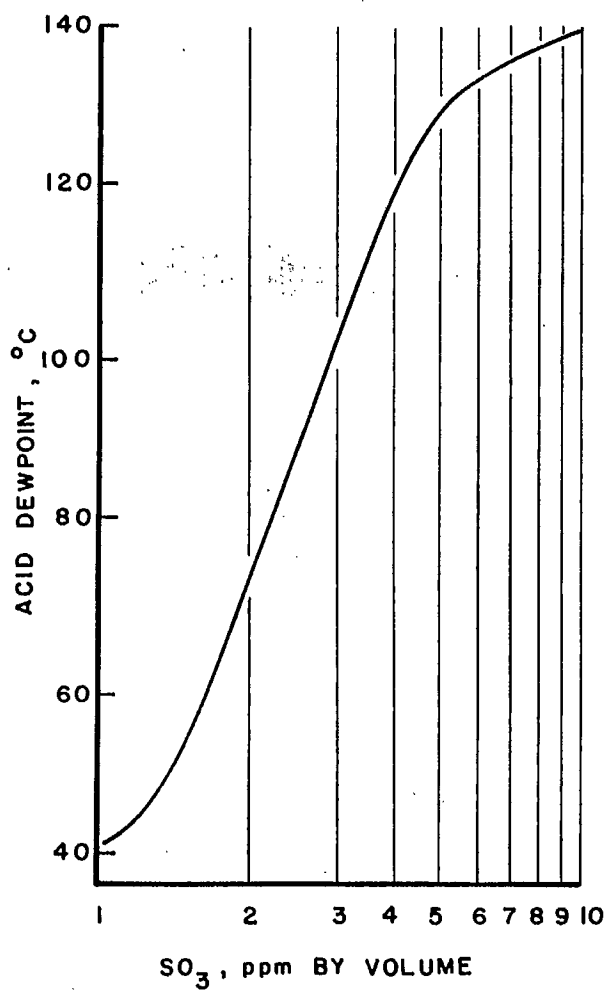


FIGURE 3. A Correlation of Acid Dewpoint With  $\text{SO}_3$  Concentration for Residential Fuel Oil.

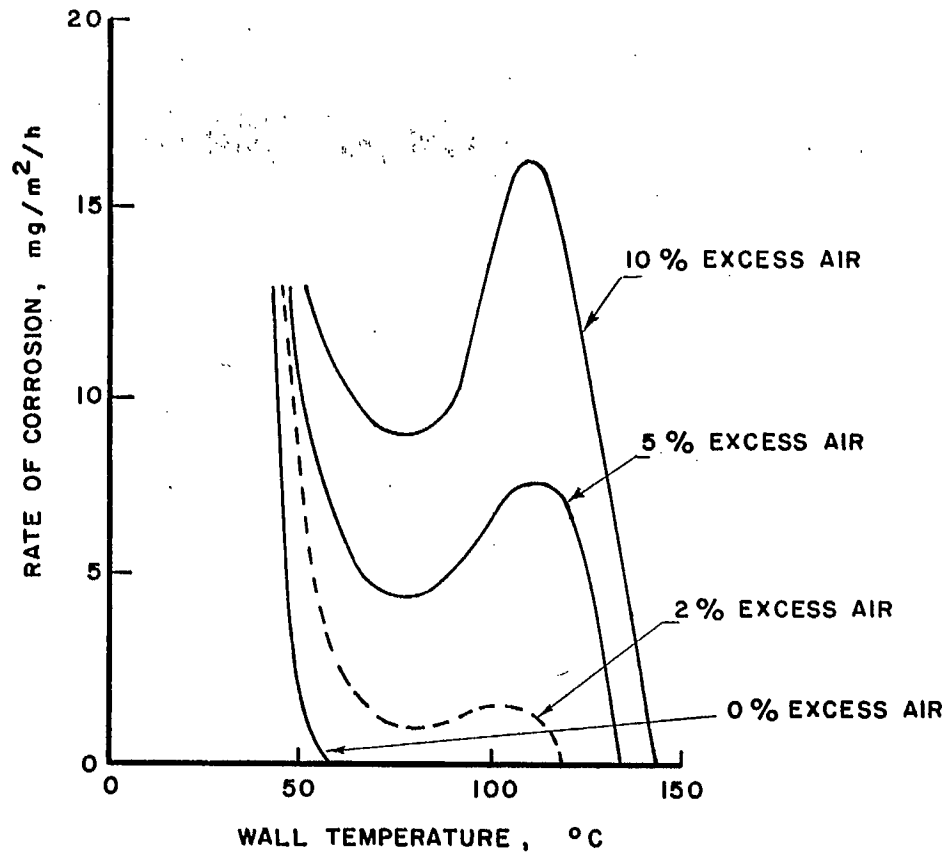


FIGURE 4. Corrosion Rate of Steel Tubing as a Function of Temperature and Excess Air

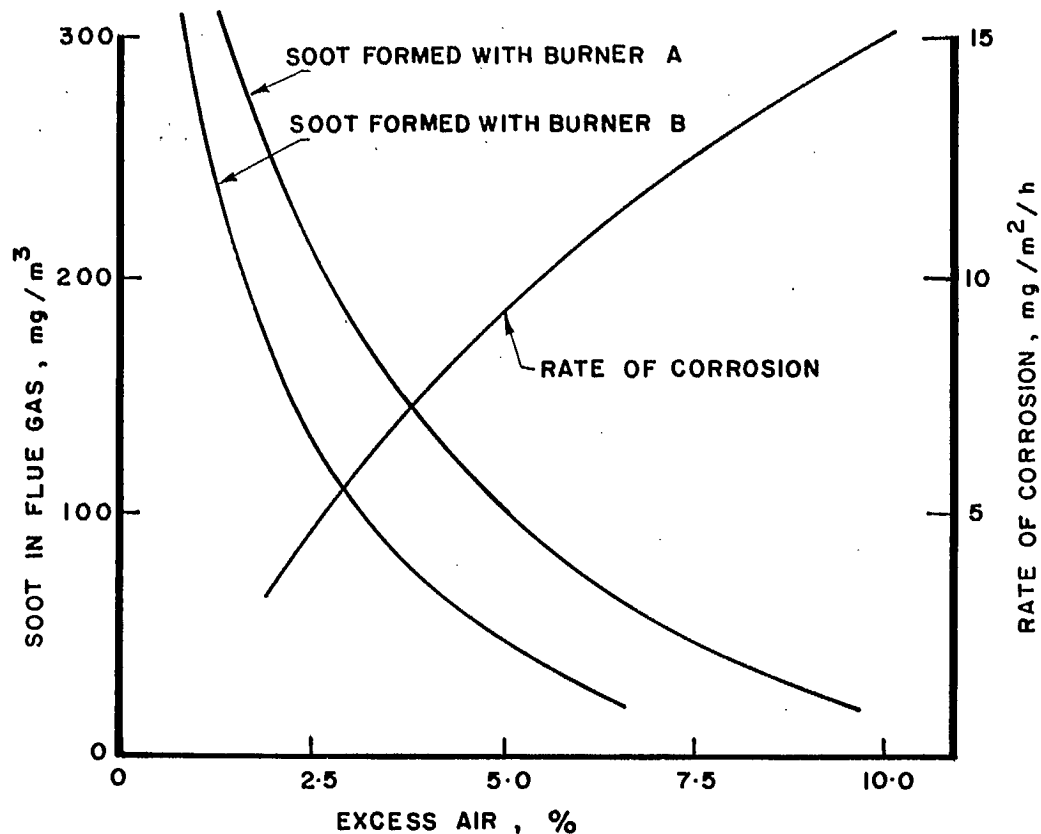


FIGURE 5. Soot Evolution and Rate of Corrosion of Steel as a Function of Excess Air for Typical Burner Configurations



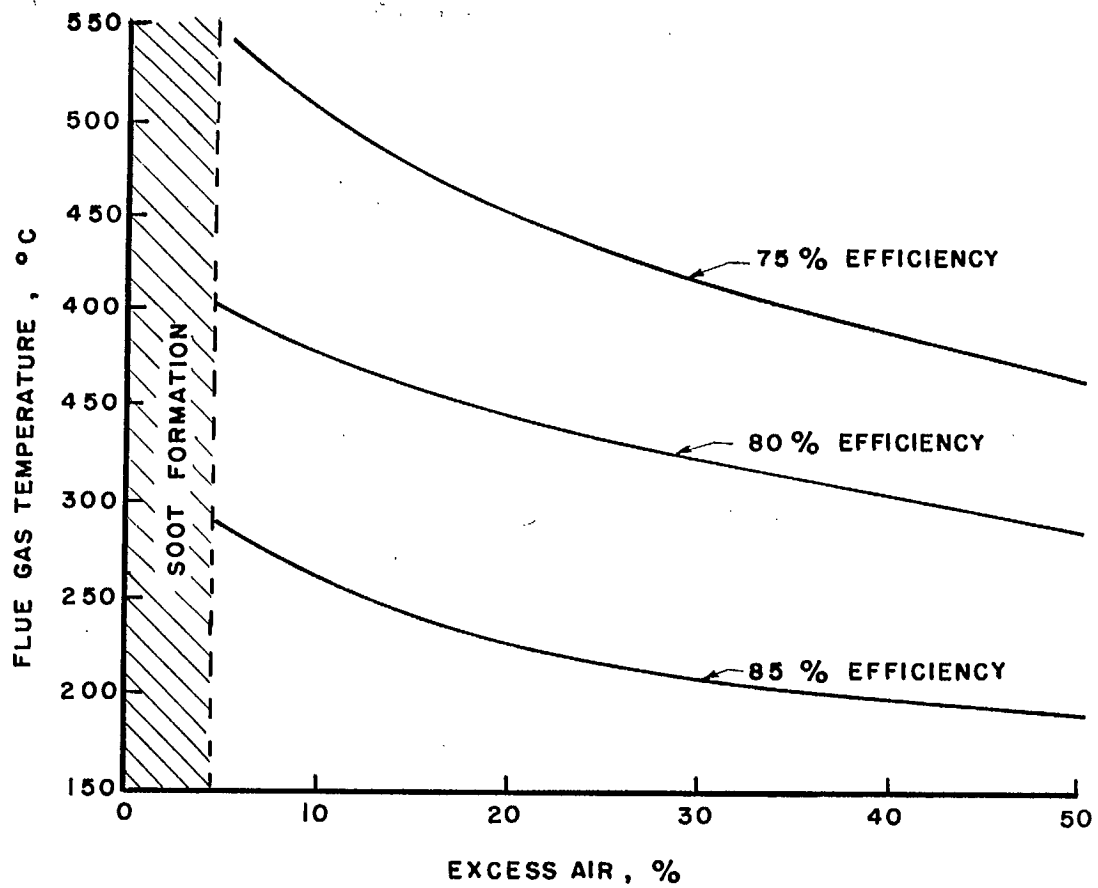


FIGURE 6. The Thermal Efficiency as a Function of Excess Air and Flue Gas Temperature at the Stack Exit