

Present Status and Research Needs
In Energy Recovery from Wastes

by

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Introduction

Major metropolitan areas in the United States, as elsewhere, face increasing problems in disposal of solid wastes paralleled by increases in air pollution potential and demand for electric power. While recent advances have been made, there has been rather limited use of available technology for solid waste disposal and certainly full advantage has not been taken of the proven practices in each of the three areas that could resolve common problems.

Historically, raw municipal refuse has been charged to the furnaces in the form in which it was delivered, with no effort to maintain uniformity. For the most part, recovery of resulting waste heat is the exception rather than the rule and auxiliary fuel used to maintain furnace temperature when refuse composition or load is insufficient.

Corrosion can be a problem in the simplest, as well as in the most sophisticated waste disposal system, but the approach to potential problems in this session will be directed primarily toward those systems that incorporate waste heat recovery.

Refuse incineration equipment incorporating waste heat recovery can be categorized as a) new equipment designed specifically for industrial or municipal waste or b) existing equipment modified for refuse or for mixed refuse firing.

On the basis of the somewhat inconsistent operating data available from both the United States and elsewhere, refuse incinerators with waste heat boilers are troubled with corrosion accompanied by slagging and tube deposits in varying degrees in the same general areas in which these problems occur during normal operation of some utility boilers. Wastage has occurred primarily a) in the high temperature superheater and reheater sections and b) on waterwalls near the firing zone and c) in the low temperature gas passes and air heaters (Figure 1). Specific wastage problems are also associated with flue gas treatment equipment.

The similarity between corrosion patterns observed in waste fired systems and those in conventional steam generators led investigators to conclude that the causes might be similar. "Liquid phase" corrosion in

superheaters and "reducing zone" corrosion in waterwall areas and "dew point" or "acid attack" are generally accepted as explanations for the causes of wastage in those principal areas.

Fireside Wastage

The liquid-phase coal-ash corrosion associated with high-temperature superheater and reheater surfaces is an industry-wide problem and has been under intensive study by Combustion Engineering and other major steam generator manufacturers since 1955, when widespread observation of this type of wastage was reported (1-8).

Continuing research programs were undertaken to determine causes and suggest remedies for this type of wastage. Both austenitic (stainless) and ferritic steel were shown to be subject to this wastage, which was taking place under tightly bonded deposits. It was further shown that excessive deposit type wastage of austenitic alloys was related to temperature. The "bell-shaped" curve shows that corrosion is limited to a temperature range of about 538 to 705° C (1,000 to 1,300° F) (Figure 2). Visual observation revealed a thin white or yellow layer next to the tube surface which contained a high concentration of alkali and sulfur.

Simultaneous field and laboratory studies were designed to determine the corrosion mechanism. Careful analysis, including X-ray diffraction analysis, showed that complex alkali iron trisulfates were major constituents of the white inner layers associated with wastage on both superheater and reheater tubes, and on corrosion probes. This same complex sulfate was formed as a by-product of waterwall wastage described later (9, 10).

With the principle corrodent defined, efforts have been turned toward establishing the mechanism of complex sulfate formation to assist in recommendation of adequate protective measures. It is significant that the content of compounds thought to be responsible for corrosion is considerably greater in probe and tube deposits than in the coal ash or fly ash from which they originate.

An important explanation advanced by early investigators is that the initial deposits may be a powder-like material containing alkalis and iron oxide that react with sulfur trioxide to form alkali iron trisulfates.⁽¹⁾ Concentration of alkalis on the tube surface may also occur by thermal migration of molten material through the deposits to the tube surface.⁽⁷⁾

On the basis of the selective deposition observed, it is felt that individual particles of fly ash vary in composition and, therefore, have different fusion temperatures. Some of the particles that are molten or semi-molten at relatively low temperatures continue to stick to the tubes. Sodium and potassium compounds released during the combustion process in

the form capable of reaction with SO_3 in the flue gas may condense or deposit on the tubes as the initial layer. This explains the formation of bonded deposits in regions where the gas temperature is significantly lower than the fusion temperature of the total coal ash.

Research performed by C-E in establishing the mechanism of the liquid phase deposit-type high temperature corrosion has not shown any significant chloride effect at the chloride levels (0.1 to 0.2%) (11) normally encountered in coal firing. However, several recent developments in the American utility fuels market have resulted in a need for renewed investigative efforts to better understand the role that chlorides play in tube metal corrosion and fouling.

Accelerated environmental cleanup, use of fuels with higher chloride content and the firing of refuse containing increasing amounts of polyvinyl chloride (PVC) separately, or mixed with fossil fuels, have resulted in an increasing concern about the effect of chloride on corrosion potential.

Also, steam generation experience to date has been based on the tube metal temperatures below 593°C ($1,100^\circ\text{F}$). If higher steam pressures are to be considered for increased efficiencies, the necessity for evaluation of corrosion performance at higher temperatures becomes more imperative.

High-temperature deposit-type corrosion of superheater and reheater tubes occurring in pulverized coal-fired boilers can be avoided by:

- a. operating with critical surfaces below 593°C ($1,100^\circ\text{F}$)
- b. use of properly installed shields on surfaces falling within 538 to 705°C ($1,000$ to $1,300^\circ\text{F}$) critical temperature range.
- c. suitable corrosion resistant alloys or coatings on superheater and reheater surfaces.

Development of new materials is continuing. In addition, work is continuing on firing modifications, fuel preparation and use of additives as methods of preventing formation of corrosive deposits.

Waterwall Wastage

In the 1940's, waterwall tube thinning was found to be the result of chemical reaction between the normal oxide on the tubes, alkali-metal sulfates comprising the enamel deposits on the tube, and SO_3 in the furnace atmosphere in contact with the deposits. (9, 10)

A second type is observed when the tube deposit contains a sufficiently high ratio of potassium-to-sodium sulfate so as to produce a molten phase. In this case, SO_3 reacts directly with the sulfate mixture to form pyrosulfate, which attacks the oxide at a higher rate than the dry reaction previously described.

The melting point of a mixed alkali pyrosulfate ($K_{1.5}Na_{0.5}S_2O_7$) is 280 C (535 F) when SO_3 is above 7 ppm. The low melting pyrosulfates, as well as the complex sulfates, are considered primary agents in superheater corrosion as previously noted.

In general, waterwall corrosion [tube metal 260 - 427° C (500 - 800° F)] is associated with external deposits and also with flame impingement. Adherence to proper operating techniques has reduced the concentration of pyrites and SO_3 near the walls, and waterwall wastage is infrequent in normal coal firing.

These techniques include a) maintenance of burners to avoid excessive flame impingement b) close attention to coal fineness to prevent coarse coal from reaching the furnace c) maintenance of the distribution of coal feeding systems and d) good air distribution.⁽⁸⁾

Refuse contains considerably less sulfur (0.1-1%) than coal and there is no obvious reason why mixed fuel firing should alter the situation with regard to this type of corrosion.⁽¹¹⁾

The presence of chlorine or chlorides (<0.3%) in the mixed refuse from incineration of vinyl plastics, as well as the presence of some heavy metal oxides which might be present in refuse ash but which would not normally be observed in coal ash could affect both high and low temperature corrosion potential.

Incinerators in both Europe and the U.S. have reported excessive corrosion^(12, 13) rates, and combinations of sulfur, chlorine, lead and zinc have been judged to be the corrosive agents.

In these studies where unprepared refuse is fired, the concentrating of lead, tin and zinc in deposits has been thought to result in a lowering of the deposit melting point with a resulting acceleration of liquid phase corrosion.

Battelle researchers have conducted investigations that show opposing effects of chlorine and sulfur in refuse.⁽¹⁴⁾ An increase in chlorine increases the corrosion rates of low alloy steels, while an increase of sulfur decreased the corrosion rates of all the steels investigated. They reported that the major contribution to the corrosion reaction is in the type of compounds that are deposited on the corrosion probe. Their investigation confirms the importance of the chloride reaction as reported by other investigators.

Experiences to date in mixed refuse firing in the U.S., where refuse is providing 10 percent of the heat input, indicate that the corrosion rates are not excessive. The results with higher chlorine levels introduced with either the coal, refuse or with higher metal temperatures are not known.

C-E investigations reported that the probe corrosion rate for clean coal increased by a factor of 3.3 when firing raw and clean coals from the same mine source. In this case, the coal had been cleaned by a gravity separation in carbon tetrachloride, therefore, the residual chloride in the cleaned coal was 1.3 percent as opposed to a 0.05 percent level in the raw coal. This corrosion rate was confirmed by subsequent testing. (15)

The role of chloride in increased corrosion may take several paths. Chloride occurs naturally in coal as an inorganic material and may be carried over with the fly ash, or released by strong sulfur acid as HCl (Figure 3). It can also be volatilized as NaCl. More importantly, chloride can enter with refuse in either an organic or inorganic form. The resulting chloride compounds usually are concentrated on cooled tube surfaces where additional reactions may occur.

Two major adverse mechanisms are thought to be involved in the potential increase in corrosion rate in incinerators and/or fossil fuel fired boilers in the presence of chloride. One involves formation of eutectics or complexes resulting in a lowering of melting point of deposits. This phenomena is of particular concern in waterwall wastage, where the temperature range of any molten salts would be increased.

The second mechanism---probably of greater concern in superheaters---involves the reaction of gas phase sulfuric acid with deposited chloride to release HCl near the heated tube surface. Subsequent reaction may involve stepwise formation of volatile ferric chloride(16, 17) and/or unstable chloride or oxy-chlorides of other alloy components (Figures 3&4).

In general, boiler surfaces operating in temperature ranges above 316°C (600°F), where refuse is the principal fuel, appear to be subject to wastage although superheater metals appear to be able to operate with tolerable corrosion rates of up to 427°C (800°F). Localized overheating may result in drastic variations in these general statements.

Low Temperature Corrosion

In usual combustion processes, sulfur is released as SO₂, but a similar percentage (~1%) is oxidized to SO₃. In the cooler flue gases in the back passes, this SO₃ reacts with water to form sulfuric acid. If the gas temperature is below the dewpoint, condensation occurs and the resulting acid attacks exposed metal surfaces in airheaters, duct work and pollution control equipment. This type of wastage is controlled or eliminated by maintaining metal and gas temperatures above the dewpoint, elimination of SO₃ from the flue gas or sometimes by use of alloys and coatings resistant to acid attack.

Generally, refuse is a low sulfur fuel, hence dewpoint wastage should be minimized and mixed refuse-fossil fuel firing would be expected to result in a reduction of SO₃ in the flue gas.

However, the presence of HCl in the effluent gas stream during refuse firing might be expected to increase corrosion potential due to general acid attack or stress corrosion fatigue.

Proper operating procedures probably have as much effect as any other in minimizing wastage. Many plants, especially in Europe, have found that less vigorous use of sootblowers will reduce the probability of exposure of cleaned tube surfaces to more rapid attack. The deposits may be considered protective unless the tube surfaces are at such a temperature that the accelerated molten phase or chloride attack can occur.

Erratic combustion and poor distribution of both air and refuse may combine to produce random slag or deposit buildup.

In addition, the firing of prepared refuse has generally considered to result in a reduction in corrosion potential by reducing the concentration of heavy metals and glass, both of which may reduce the melting point of deposits, thus accelerating their fluxing action on protective oxides.

In the formal presentations which follow, we shall hear about specific experience in waste fuel firing---both problems and solutions. It is the purpose of this session to define continuing unknowns and to set a course for future research needs.

The challenge of the conference is to establish priorities in overall progress and continuing needs in the recovery of energy from wastes.

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HIGH
TEMPERATURE
CORROSION

LOW
TEMPERATURE
CORROSION

WATERWALL
CORROSION

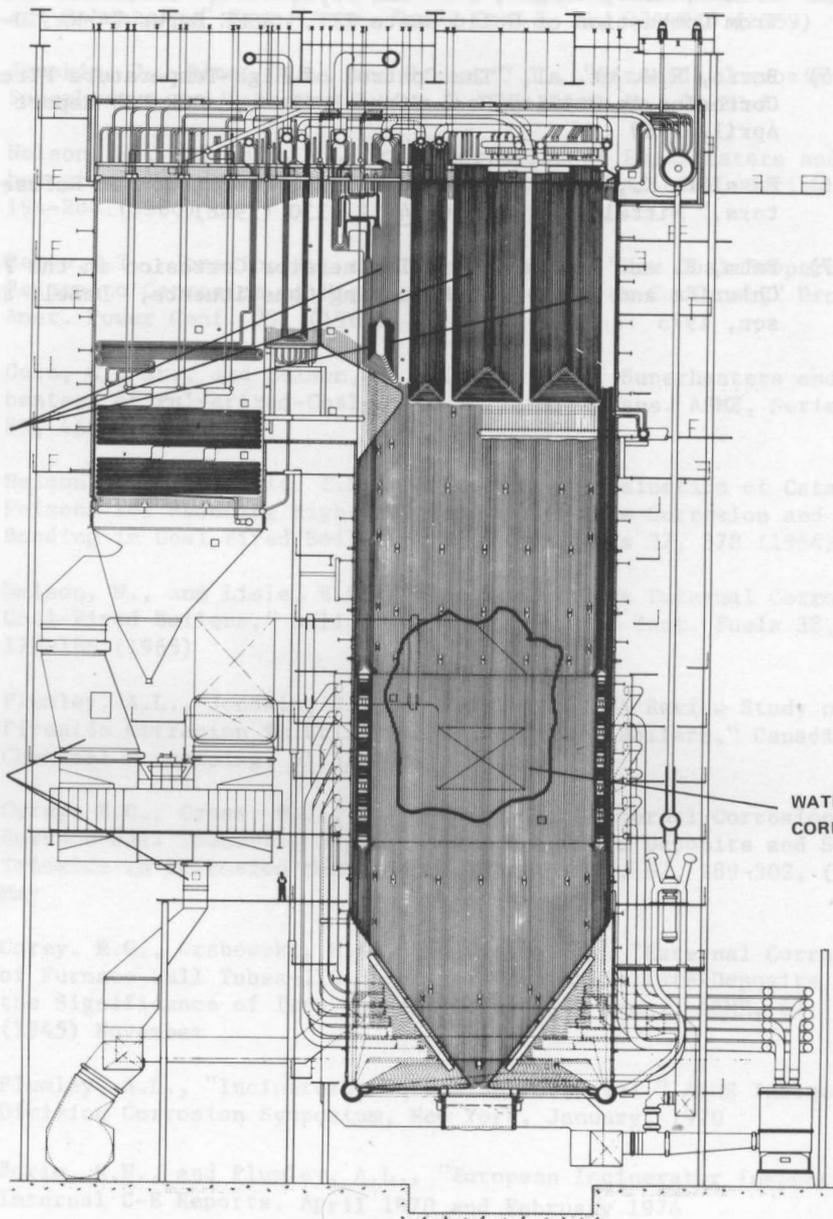
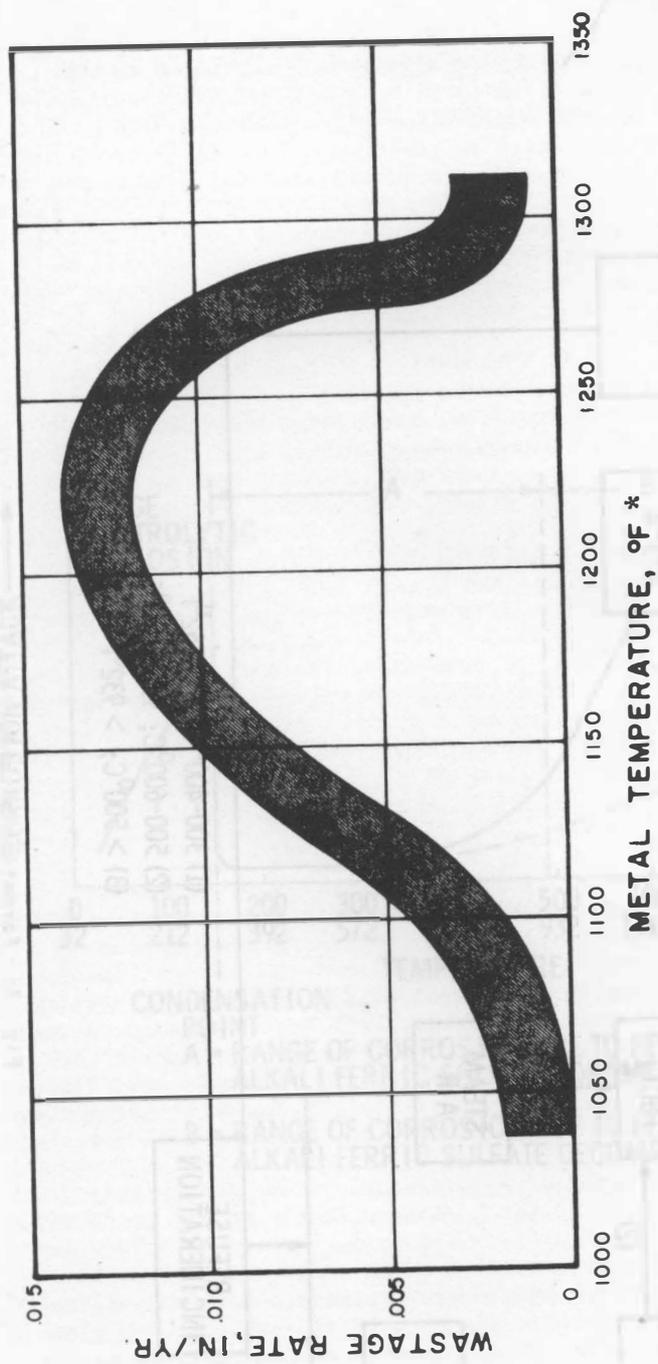


Fig. 1: Areas susceptible to wastage



*Conversion factor: $(^{\circ}\text{C}) = 5/9(^{\circ}\text{F} - 32)$

Fig. 2: Coal-ash corrosion of austenitic alloys as a function of temperature

TUBE SURFACE

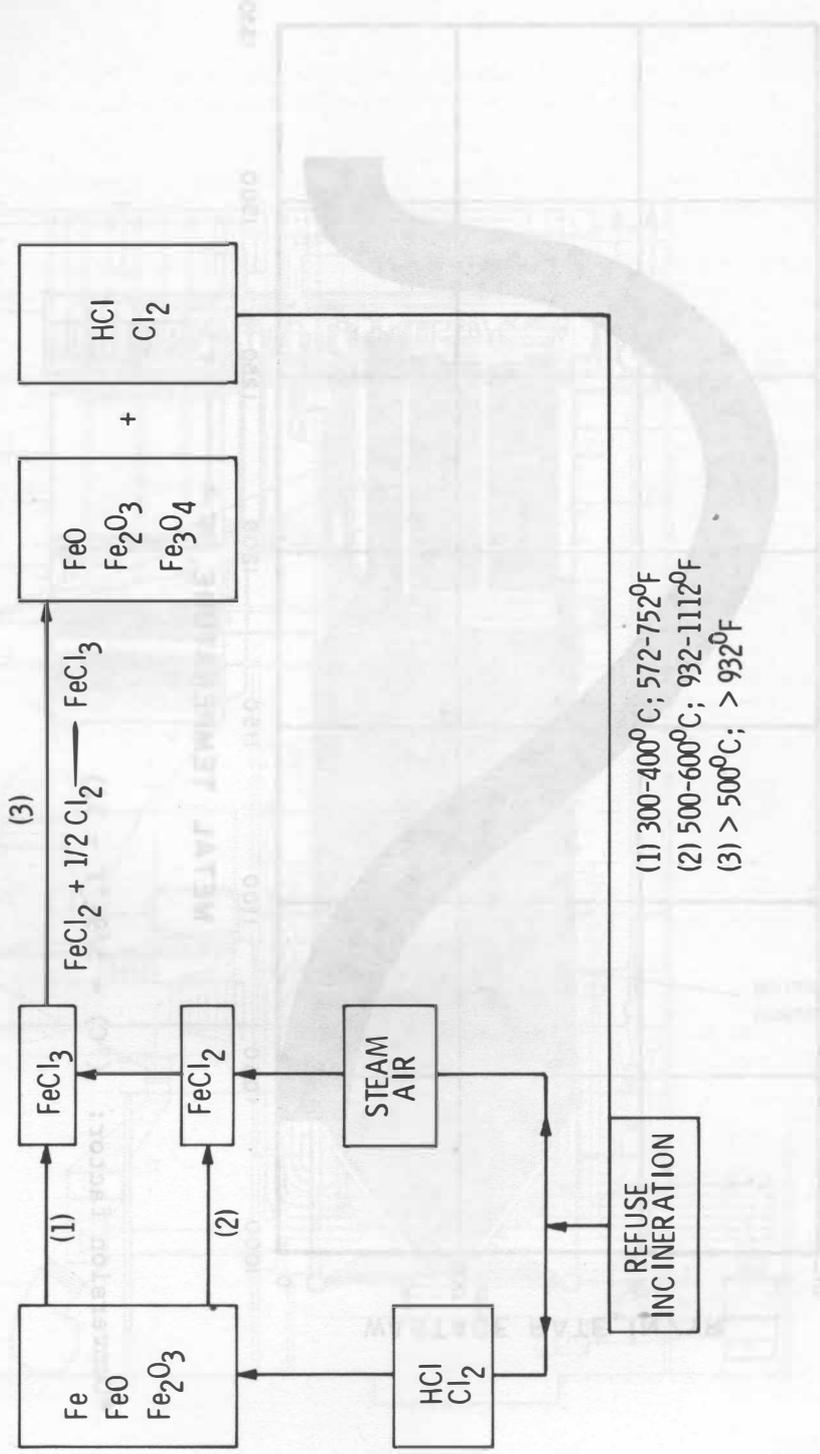
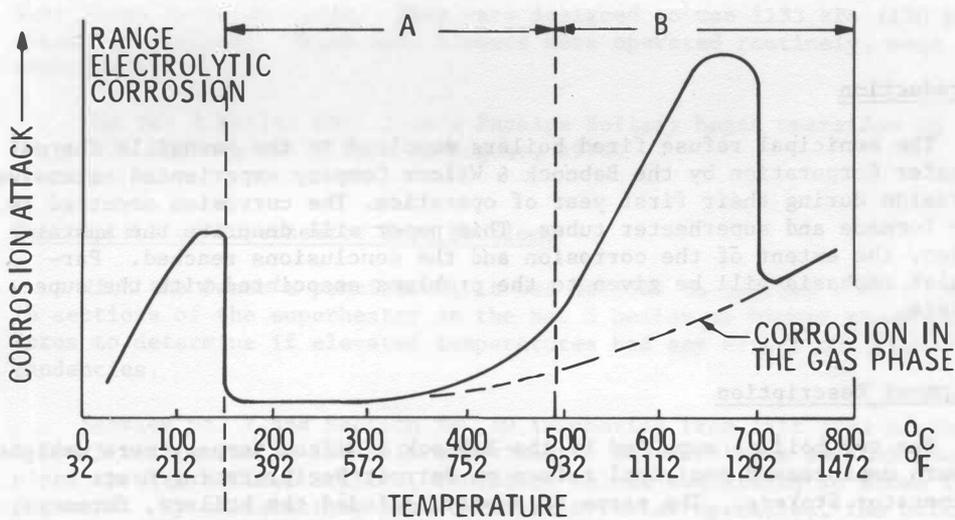


Fig. 3: Formation of chlorides



CONDENSATION POINT

A = RANGE OF CORROSION DUE TO FERRIC CHLORIDE OR ALKALI FERRIC SULFATE FORMATION

B = RANGE OF CORROSION DUE TO FERRIC CHLORIDE OR ALKALI FERRIC SULFATE DECOMPOSITION

Fig. 4: Rate of corrosion as a function of the tube wall temperature