

FIRESIDE TUBE CORROSION IN AN INDUSTRIAL RDF-FIRED BOILER — KODAK'S EXPERIENCE

ROBERT D. BLAKLEY

Eastman Kodak Company
Rochester, New York

ABSTRACT

Kodak's industrial refuse and wastewater treatment sludge are prepared, then burned in a "first generation" modern waterwall boiler located at the Kodak Park site. The tangential injection, full suspension-fired design, and composition of the wastes are unique when compared to recent refuse-derived-fuel, spreader-stoker type boilers burning municipal solid wastes.

Potential fireside tube corrosion and fouling problems were recognized during design stages in 1969. These were not expected to be serious for the predicted operating conditions of Kodak's boiler.

Actual experience has demonstrated where original predictions were optimistic. Tube wastage has become increasingly severe in localized areas of lower furnace waterwalls near the bottom ash grate and lower superheater platen bends in the upper furnace.

Kodak's attempts to address tube corrosion have focused mainly on keeping track of tube wall thicknesses, using pad welding and removal/replacement to maintain reliability. Coatings, shields, alloy weld overlays, and refractory coverings to protect the underlying carbon steel have been tried in wastage prone areas. Combustion air and waste injection nozzles' modifications have attempted to reduce flame and particle impingement on the furnace walls. Corrosion probe and fireside deposit analyses have identified major constituents associated with corrosion due to various waste firing conditions. This paper summarizes

the major efforts undertaken over the nearly 20 years of Kodak's boiler service.

Recent experiences in municipal RDF-fired boilers indicate alloy superheaters and clad waterwalls may be effective solutions to Kodak's tube wastage problems.

INTRODUCTION

Historically, Kodak has preferred to manage wastes from manufacturing photographic film, paper, chemicals, and imaging products by reuse, recycling, and incineration with recovery. In the late 1960s, Kodak wanted to expand the capacity to burn its nonhazardous solid wastes and industrial wastewater treatment plant sludge coming from its various Rochester, New York facilities. Demand for steam production at Kodak's largest Rochester facility (Kodak Park) was growing. More stringent air pollution regulations were being proposed. This meant highly effective combustion and air pollution control equipment would be required.

These combined needs led Kodak to select a waterwall boiler capable of burning shredded refuse and/or #6 fuel oil, while cofiring flash-dried wastewater sludge. In 1968, these were new concepts which Kodak believed would best match its unique situation.

It is important to note that typical refuse disposal practices in the United States at this time were land-

filling or by mass burning in refractory-lined incinerators without emission controls or heat recovery.

Boiler Design Problems

A 1970 technical paper described the introduction of such boilers designed to burn shredded refuse and generate steam [1]. Two basic boiler design problems were discussed—fouling of heating surfaces and potential corrosion. These problems had to be carefully considered to insure high boiler availability without extremely high maintenance costs. They are briefly discussed below.

The first problem would be addressed through designs with proper furnace sizing and arrangement of heating surfaces for adequate combustion completion and flue gas temperature reduction. Wide spacing of inline convection tubes and correct use of retractable sootblowers would further reduce fouling to acceptable levels [1].

Four types of corrosion from refuse incineration were recognized by designers of Kodak's boiler. These were:

- (a) High temperature, liquid phase corrosion.
- (b) Corrosion due to a non-uniform furnace atmosphere.
- (c) Corrosion by HCl.
- (d) Low temperature or dew-point corrosion.

High temperature corrosion was believed caused by molten alkali-metal sulfates an occurred at metal temperatures above 900°F (480°C). This could be avoided by selecting modest steam pressures without superheat [1].

The second type of corrosion results from incomplete refuse combustion products such as carbon monoxide and hydrogen sulfide, in a locally reducing atmosphere. Normally protective iron oxides on the tubes' fireside surfaces can be reduced by CO and H₂S, thus forming nonprotective scale which is then attacked. Proper air distribution and turbulence within the furnace would prevent such combustion deficiencies and resulting corrosion [1].

The third type, corrosion by hydrogen chloride and chlorine gases, was not expected to be severe at operating metal temperatures above dew point and below 550°F (290°C) [1].

Low temperature or dew point corrosion would be minimized by designing the waterwalls as membrane/tube panels (self-cased) and by selection of economizer and air heater clean side inlet temperatures to avoid flue gas acid condensation. Water washing or auxiliary heat would reduce potential standby corrosion from hygroscopic deposits during lengthy boiler outages [1].

Kodak's boiler was designed alone these ideals in 1969. This unit is believed to be the first application of tangential-injection, suspension-burning design for 100% boiler firing from prepared refuse and sludge.

Kodak's boiler was originally furnished as a saturated steam generator without superheat. Refuse throughput at 180 TPD (164 t/d) with sludge flash-dried and fired at a rate of 114 wet TPD (104 tpd) was expected to produce 77,000 lb/hr (35,000 kg/h) of steam at 400 psig (2760 kPa) [1]. No. 6 fuel oil alone would produce 150,000 lb/hr (68,000 kg/h) at full load [2].

Waterwalls of 2.5 in. O.D. × 0.188 in. (63.5 mm × 4.8 mm) wall thickness SA178 grade A tubing on 3 in. (76 mm) centers form a furnace 9 ft 11 in. wide by 11 ft 2 in. deep (3.0 m × 3.4 m). Furnace height from the bottom ash grate to the upper drum centerline is roughly 63 ft (19.2 m).

The boiler convection bank is a single pass design, with 2 in. (51 mm) O.D. tubes on 4 in. (102 mm) centers. Two retractable sootblowers in front and two between the upper and lower drums each operate once every four hours.

A slipstream of hot flue gas is taken from between the convection bank outlet and economizer inlet at 950–1000°F (510–540°C) and routed to the flash drier where it reduces the moisture content of the sludge from 80% to 15% [1]. The warm sludge and 300°F (150°C) gas are separated in a cyclone, with a portion of the dried product returned to be blended with the incoming wet material. The remainder is pneumatically injected through two individual feed nozzles for suspension burning, while the vapor is ducted to the upper furnace through screen tube openings in the rear wall. Dried sludge can be cofired with RDF and/or #6 fuel oil. The latter are fed through separate burner nozzles in each of the four corner wind boxes located at approximately 20 ft (6 m) elevation of the furnace.

A radiant platen superheater, consisting of 2.125 in. × 0.203 in. M.W.T. (54 mm × 5.2 mm) SA213 T22 (2.25% Cr, 0.5% Mo) low alloy carbon steel tubes, was retrofitted to the boiler in 1973, after 3 years of saturated steam service. This raised the design outlet steam temperature by approximately 100°F (38°C) to 550°F (290°C). Figure 1 shows a sectional side elevation view of the boiler's original configuration with the added superheater.

UNIQUE CONDITIONS

Conditions unique to Kodak's boiler application which relate to fireside tube wastage are:

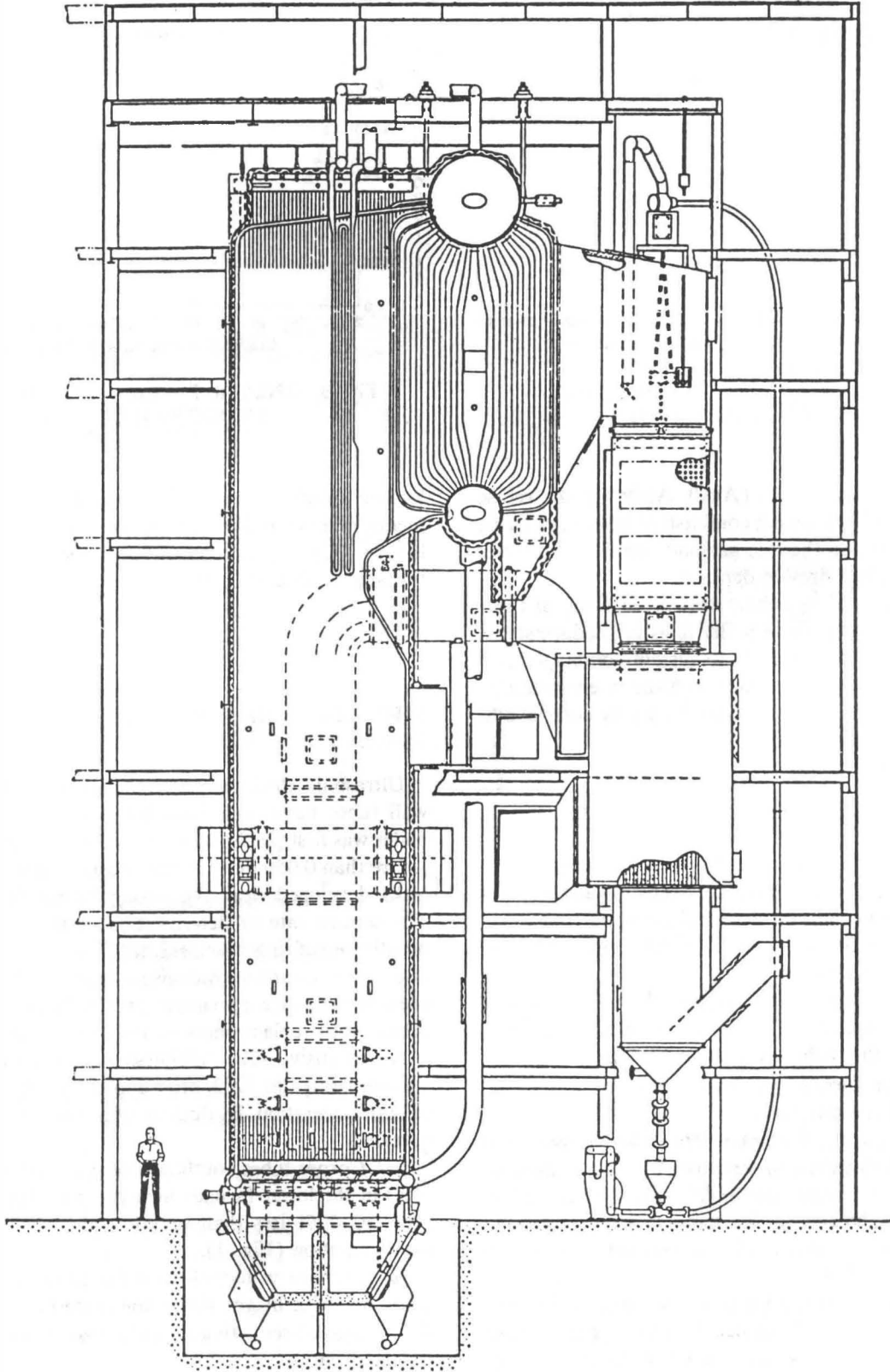


FIG. 1 ORIGINAL BOILER CONFIGURATION W/ SUPERHEATER

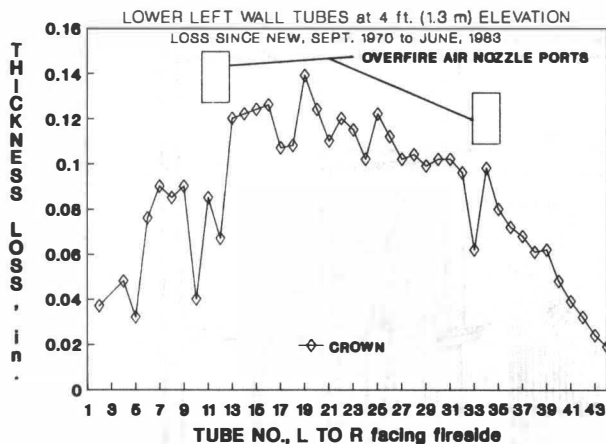


FIG. 2 ORIGINAL FURNACE WALL TUBES—WASTAGE VS TUBE NUMBER

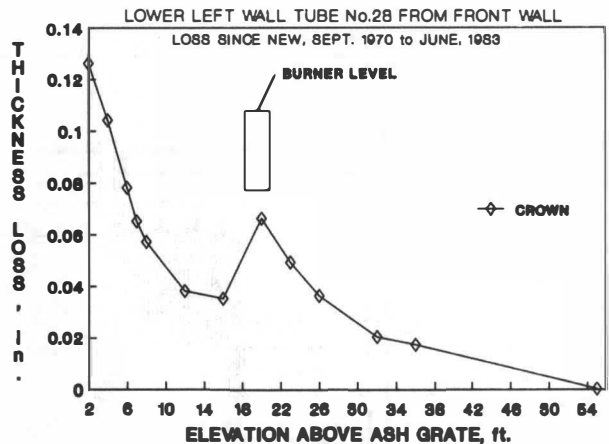


FIG. 3 ORIGINAL FURNACE WALL TUBES—WASTAGE VS ELEVATION

(a) Silver halide salts (AgCl , AgBr) in the refuse and sludge, which during combustion liberate chlorine and bromine into the flue gas and leave behind silver in the ashes and fireside deposits.

(b) Tangential injection, suspension firing of these prepared wastes as main boiler fuels to produce steam without cofiring fossil fuels to sustain combustion.

These conditions produce a furnace environment and fireside deposits which can be highly corrosive to carbon steel boiler tubes.

CHRONOLOGY

Three major areas of Kodak's boiler have experienced significant tube wastage, repairs, and various corrosion protection methods. These are:

(a) Middle furnace waterwalls adjacent to the corner burner/windboxes.

(b) Lower superheater platen tubes near the rear wall furnace arch ("U" bends), and sootblower lanes (in front of the boiler convection bank).

(c) Lower furnace waterwalls within several feet (1–2 m) of the ash grate.

Chronologically, the first efforts involved assessment of tube wall thicknesses, weld overlay tube protection, and corrosion probes after leaks developed in the furnace walls adjacent to the burner/windboxes. This coincided with cofiring a chloride-containing waste solvent in 1975–1976.

Then leaks in lower superheater tubes began in 1978, after 5 years of reliable service. Frequent platen repairs and piecemeal replacements continue to require constant attention.

In 1983, the lower waterwall tubes showed severe thinning just above the ash grate. Weld overlays, re-

located overfire air injection nozzles, panel replacements, and protective coatings have all been tried over the past 10 years to maintain tube integrity in the lower furnace. Such efforts will be described later.

FIRESIDE TUBE WASTAGE

Furnace Waterwalls

Ultrasonic thickness measurements of the furnace wall tubes have been recorded since 1970 when the boiler was first placed into service. Significant thinning [more than 0.050 in. (1.3 mm)] was noticed after tube leaks developed near the corner burner/windboxes. The serious rate of deterioration occurred after 3–9 months of cofiring waste solvent. This wastage slowed after solvent burning was discontinued in 1976. However, the damage remained (in the form of thinned tubes) until replacements in 1987 and 1988.

An extensive tube thickness measurement survey was performed in 1983, after approximately 80,000 hr of boiler operation. Evaluation of nearly 1000 readings revealed:

(a) Corner tubes (outboard of the overfire air nozzles) in the lower furnace near the grate had wastage rates 30–70% less than middle wall locations at the same elevation (Fig. 2).

(b) Furnace waterwall tube deterioration typically decreases with height above the grate (Fig. 3). Note the significant reduction in metal loss above the 12 ft (4 m) elevation.

The increased wastage at 19 and 23 ft (5.8 and 7.0 m) elevations includes some thinning from the brief period of solvent firing in 1975–1976.

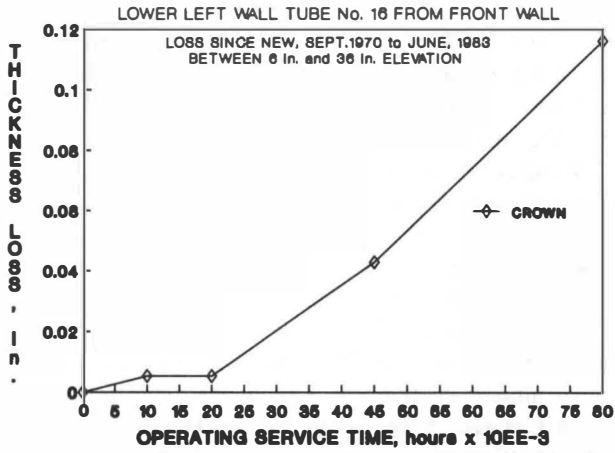


FIG. 4 ORIGINAL FURNACE WALL TUBES—WASTAGE VS TIME

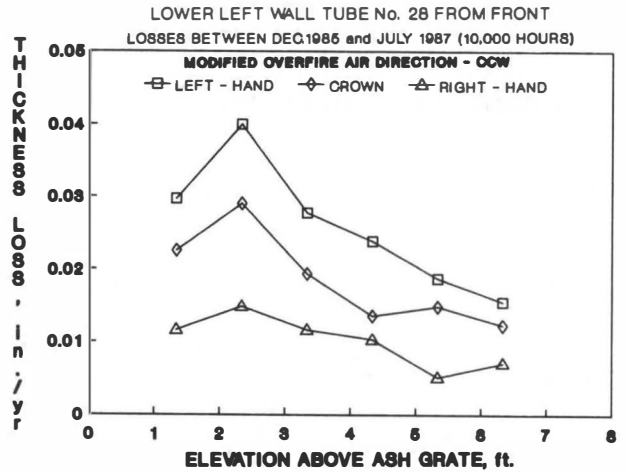


FIG. 6 STUDY TUBE, ANNUALIZED WASTAGE VS ELEVATION

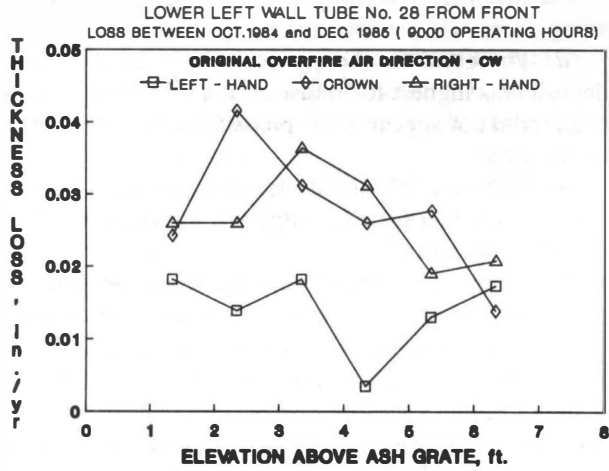


FIG. 5 STUDY TUBE, ANNUALIZED WASTAGE VS ELEVATION

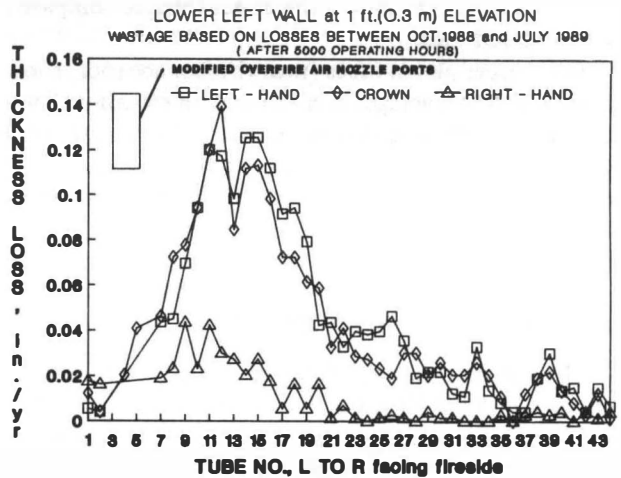


FIG. 7 HEAVYWALL/OVERSIZE TUBES WASTAGE VS ELEVATION

(c) Left and right furnace sidewalls near the grate show larger wastage rates at higher elevations than the front and rear walls.

(d) Metal loss rates are increasing with time (Fig. 4).

Note the dramatic rise coincides with increased refuse quantities burned for longer periods of time between boiler outages, starting in 1975.

Between 1984 and 1987, two individual lower furnace tubes in the left waterwall were periodically measured for thickness. The most significant finding was the pronounced wastage which occurred on the portion of the tubes' firesides facing away from the direction of overfire (OFA) air injection (Fig. 5). This continued

even after overfire air nozzles were relocated and changed the direction of swirl from clockwise to counter clockwise (Fig. 6).

Oversize, heavy wall carbon steel tubes [2.625 in. O.D. x 0.270 in. nominal thickness (66.7 x 6.9 mm)] replaced deteriorated left and right sidewalls in October, 1988. More restrictive overfire air nozzles were also retrofitted at that time. Readings after several months of service indicate severe localized thinning on the left and crown surfaces of these tubes near the grate (Fig. 7). Standard [0.210 in. (5.3 mm) nominal] thickness tubes in the lower front and rear waterwalls

have also shown similar patterns of wastage, albeit at smaller rates [up to 0.120 in. (3.0 mm) loss in 2 years] since replacement in August, 1987.

SUPERHEATER TUBE WASTAGE

Tube thickness readings have also been periodically taken for the lower 10 ft (3 m) of the superheater platens since 1978. Superheater tube wastage patterns are not entirely consistent from platen to platen or year to year. However, the findings have shown:

(a) Bottom and sides of the lower outer loops experience wall loss rates up to 0.050 in. (1.3 mm) per year.

(b) Rear surfaces of unprotected platen tubes in the vicinity of traversing sootblowers can have loss rates up to 5 times greater than the sides of tubes at the same elevation.

(c) Wastage rates are typically 2–3 times larger for platens in the right half of the upper furnace compared with the left half.

(d) Upper platen tubes (near the furnace roof) show more uniform wastage, decreasing with elevation. Typical total thickness losses between 1973 and 1989 (100,000 estimated hours of superheater operation) are only 0.005–0.040 in. (0.1–1.0 mm) except in sootblower lanes.

CORROSION PROBE STUDY

The serious thinning of the waterwall tubes near the burners in 1975 raised concerns over the viability of waste solvent firing. Corrosion probes were used to measure the relative corrosivity of the upper furnace environment during #6 fuel oil firing alone, cofiring with sludge with and without solvent waste, and with refuse in four different tests. Furnace gases and particulate, probe deposits, and specimen weight losses were evaluated in this study, conducted with Battelle Columbus Laboratories [3].

The corrosion probes' weight losses of carbon steel specimens showed relative corrosivity ranges increased in order: (a) #6 oil only; (b) #6 oil with sludge; (c) #6 oil with sludge and solvent waste; and (d) #6 oil with refuse. Refuse and #6 oil produced corrosion seven to ten times greater than #6 oil with and without sludge and twice as much as when solvent was cofired with #6 oil and sludge [3].

Corrosion rates of stainless steel alloys were 10 times lower than carbon steel for all combustion conditions tested. Resistance to corrosion at metal temperatures up to 800°F (430°C) increased in order: AISI 446, 347,

310, and RA333. The possibility of stress corrosion cracking during downtime with chloride-containing deposits made the use of stainless steels for boiler tube fireside surfaces questionable [3].

Analyses of corrosion probe deposits, scale layers, particulate and flue gas samples confirmed that chlorine and bromine were primarily responsible for the corrosion beyond that caused by sulfur in the #6 fuel oil. Zinc, sodium and lead were also noted, with the following results [3]:

(a) Cl in the scale increased with fuel combustion environment corrosivity. The probe deposits did not show this due to the conversion of chlorides to sulfates at a location where HCl could vaporize away.

(b) Na and Zn contents increased in deposits, scale layers, and particulate samples as furnace environment corrosivity increased.

(c) Cl content of the particulate was highest during refuse burning, followed by oil, sludge and solvent firing.

(d) Pb found in the particulate, scale, and bulk deposit was highest for refuse and #6 oil firing. However, it did not appear in the phase (compound) studies of the scale.

(e) HCl and SO₂ in the furnace gas were two to four times higher for oil, sludge and solvent firing than for oil with refuse.

One factor mentioned as a possible explanation for the corrosion probe findings and actual furnace tube deterioration was the tendency of the wastes to be in close proximity and in contact with the waterwalls while burning. This would expose the boiler tubes to higher concentrations of corrosive gases and particulate than if combustion was centered in the middle of the furnace [3].

TUBE FIRESIDE DEPOSIT ANALYSES

In 1979, samples of tube deposits and scale layers taken from the lower superheater, convection bank tubes, and upper waterwalls were analyzed by Kodak. Very high concentrations of lead (some greater than 25%) were found in both bulk deposits and scale layers. Sodium contents were comparable to those levels found in the corrosion probe oil plus refuse deposits. Chlorine was not measured, but a sample of superheater tube scale was highly acidic (pH = 3). Sulfides and chlorides appeared to be present in the solution.

In September 1984, two 8 ft (2.4 m) long waterwall tube sections were removed from the lower left waterwall. Two adjacent tubes from a rear wall test panel (just above burner level) and one lower superheater

bend were also removed with deposits intact. Furnace deposits were removed from a waterwall tube at various elevations between the grate and burner level. These tubes and deposits were analyzed by the boiler manufacturer to try to determine what was causing the general tube wastage.

Evaluation of these tubes and deposits in 1984–1985 found [4]:

(a) Very high (10–30%) concentrations of lead in waterwall deposits and outer superheater deposits (15%), with highest levels on lower furnace left wall tubes near the grate midway between OFA nozzles (high wastage area).

(b) Low levels of lead in the superheater tube scale (0.3%) and inner deposits (1.2%).

(c) High levels of chloride (Cl^-) in the waterwall deposits below the burners (18–21%), moderate at burner level (2–4%), and virtually nil in the superheater scale and deposits (0–1%).

(d) Sodium, zinc, and potassium contents were highest in waterwall deposits in the lower furnace away from high wastage areas near the grate [i.e., above 7–9 ft (2–3 m) elevation] and lowest in the inner layer of superheater deposits.

(e) Silica, aluminum, and calcium were abundant in the superheater surface layer (16–33%) but virtually absent in the lower waterwall deposits (<3%).

(f) Iron (Fe_2O_3) was highest in deposits near the grate and superheater surface (15–22%).

(g) Sulfur (SO_3) levels were low near the grate and superheater surfaces (<3%) but high in burner level (8–17%) and outer superheater deposits (29%).

(h) Melting points were in the range of 710–750°F (375–400°C) near the grate but above 1600°F (870°C) in burner level and superheater surface deposits.

(i) Chlorine was compounded mostly with lead and bromine ($\text{PbBr}_x \text{Cl}_{2-x}$ [$x < 1$]), lead and potassium (KPb_2Cl_5 , K-basis), and sodium (NaCl , Na-basis), with a minor amount of zinc (ZnCl_2 , Zn-basis) and silver (AgCl , Ag-basis). These ranged from 19–30%, 16–18%, 15–26%, 4–6%, and 3–4% respectively, totalling more than 70% of the deposits on each of the two lower furnace tubes removed from the left waterwall within 8 ft (2.4 m) of the grate. Iron oxide (Fe_3O_4 , Fe-basis, 13%) and char (C, H, N, 8–14%) were the next most common analytes.

Deposit scrapings were removed from the two lower furnace study tubes in June 1985. Melting point temperatures were 1080–1150°F (580–620°C) [5]. Elimination of a minor waste stream containing lead and polyvinyl chloride in early 1985 may have caused the rise of 400°F (200°C) in the deposits' melting points.

The hygroscopic nature of the boiler's fireside de-

posits cause strong acids to form at the tubes' surfaces during cold shutdowns. This is particularly prevalent during warm, humid ambient conditions. A check of lower superheater tubes during the 1984 shutdown showed visible liquid seeping through cracks in the deposits. Litmus paper confirmed a pH of 2–3 had developed 36 hr after the boiler was shut down to remove the tubes and deposits.

COMPARISON TO MUNICIPAL RDF-FIRED BOILERS

After Kodak's boiler was designed and built, other RDF-fired designs followed. Those involving suspension burning were usually existing coal-fired utility boilers adapted to cofire 10–20% municipal refuse, or dedicated RDF spreader-stoker type with a travelling grate. Recent RDF-fired designs favor the latter approach. Several boilers of such designs included carbon steel furnace walls and low alloy superheater tubes which have reported high tube wastage rates [6, 7, 8].

A comparison with one municipal solid waste RDF-fired boiler shows Kodak's lower waterwall fireside tube deposits have similar concentrations of most minerals and metals, such as Si, Al, Mg, Zn, Ti, plus Cl, C, and SO_3 , with three to four times less Na, K, and Ca but twenty times more Pb [4, 6,]. Also, silver is present in significant amounts in Kodak's boiler deposits and absent elsewhere.

Furnace waterwall tube wastage rates for Kodak's boiler are of the same order of magnitude as those for the MSW RDF-fired case [0.080 in./year (2.0 mm/year)] [6]. Corrosion of carbon steel waterwalls of these two RDF boilers is comparable, even with obvious differences in waste compositions, steam conditions, firing practices, tube locations, and major deposit metal concentrations.

FIRESIDE TUBE PROTECTION EVALUATION

Various means of protecting fireside tube surfaces from deterioration have been attempted since 1975. These are:

(a) Carbon steel and alloy weld overlay of waterwall tubes.

(b) Carbon and alloy shields on superheater platens and boiler convection and waterwall (burner area) tubes.

(c) Shop-applied and field-applied plasma-sprayed coatings.

(d) Cast refractory tiles and pin studs with castable refractory.

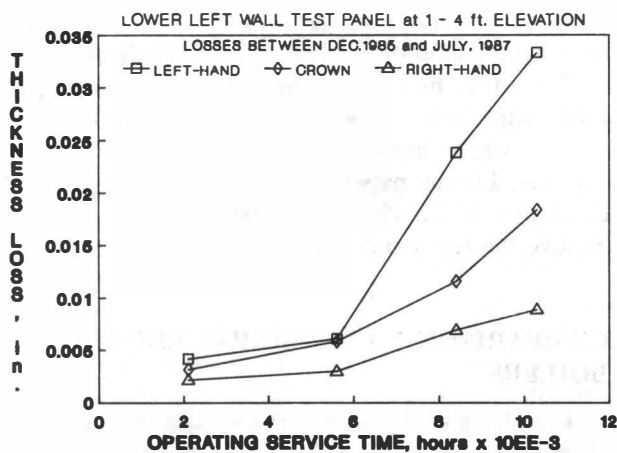


FIG. 8 CHROMIZED FURNACE WALL TUBES—WASTAGE vs TIME

Table 1 summarizes Kodak's evaluations of these methods. Figure 8 shows how the chromized tubes' wastage rates increased with service time and preferential thinning of the left-hand and crown portions of the tubes, similar to the carbon steel waterwalls.

The latest approach to reduce waterwall fireside tube wastage in the lower furnace has been to return to weld overlays in areas with locally severe losses. This was done in July 1989, by using ultrasonic thickness measurement surveys to pinpoint these areas, primarily on the left and right waterwalls within 3 ft (0.9 m) of the grate.

Stainless steel metal wire containing 21% Cr and 10% Ni (ER308LSi) was applied using a submerged metal arc (MIG) welding process after preparing the surface by sandblasting to "white" metal. By adding 0.040–0.100 in. (1.0–2.5 mm) thickness to tubes still approximately 0.180 in.+ (4.6 mm) wall, less heat input and subsequent cross section distortion would be realized. This could avoid weld burn-through and cracking experienced during previous carbon steel pad weld repairs to tubes typically less than 0.100 in. (2.5 mm) wall thickness.

The objective is to monitor such weld overlay areas for wastage over the next 1–2 years to assess the corrosion resistance of this alloy. There is concern that stress corrosion cracking may occur in the stainless steel material due to out-of-service corrosion in the chloride-containing environment near the grates. This will be addressed by periodic inspection, possibly including removal of short tube sections for microscopic analysis.

WASTAGE THEORIES

The previous sections presented findings from measurements, analyses, and evaluations which generally reflect "how much of what and when it occurred" regarding tube wastage in Kodak's boiler. A look at two major concepts may explain "why" such conditions, both unique and in common with municipal RDF-fired boilers, cause the metal loss.

The first relates to actual furnace conditions being different than original design concepts and performance predictions. This is summarized by noting the following:

- A single "fireball" of fuels/wastes and air does not occur, with or without #6 oil cofiring.
- Excess air levels are 75–100+ % (vs 30% originally expected).
- Highly reactive combustion process, with wide swings of furnace exit oxygen concentration and rapid draft fluctuations.
- Pneumatic injection of wastes at 50–100 ft/sec (15–30 m/s).

With the above conditions, it is impossible to prevent particle and flame impingement on the furnace walls. Furnace gas temperatures and heat liberation rates are highest within several feet (1–2 m) of the ash grate where heavy particles burn during refuse firing, or at burner level when firing #6 fuel oil. Attempts to lower excess air volumes trade off reducing fly ash carryover from the furnace against ash slagging and static piles of burning refuse on the grate.

The second part of the tube wastage theory involves the unique constituents in the various wastes plus known corrosion mechanisms. Several possible explanations are:

- Kodak's refuse and flash-dried sludge contain silver halides (Ag Cl, Ag Br). The halides become molten when the wastes burn, becoming part of the flyash, bottom ash, and fireside deposits. Lead, potassium, sodium, and zinc are present in the wastes as well. The halides can combine with these non-precious metals, creating low melting point mixtures. Chlorine (and bromine) may then be volatilized as acid (HCl, HBr) or elemental gases (Cl₂, Br₂). If oxygen is temporarily lacking at the tube surface, these gases will react with the iron in the carbon steel to form FeCl₂ or FeBr₂. When oxygen is available, iron chlorides are oxidized, creating iron oxides and possibly iron oxychloride releasing Cl₂, Br₂. FeOCl is stable between 400 and 750°F (200–400°C), bracketing the expected tube metal temperature range [450 to 600°F (230–315°C)]. Corrosion by HCl gas alone is not expected to be severe below 600°F so it is likely that molten salts and elemental chlorine gas are the primary reasons for wastage

TABLE 1 SUMMARY OF KODAK'S FIRESIDE TUBE PROTECTION METHODS' EVALUATIONS

Description	Location	Time Frame	Results
1. Alloy Weld Overlay	Burner Area	1975-1976	Inconel 182 (60% Ni, 15% Cr) best, 310 stainless next, 312/347 least durable. Coincided with waste solvent firing and corrosion studies.
2. Pin Studs w/Cast. Refractory	Burner Area	1976-1979	Frequent loss of refractory. Discontinued after 1979.
3. Plasma-Sprayed Coating			
a. Cr and WgC "Test" Panel	Burner Area	1976-1987	Middle pair of tubes removed 9/84. Partial failure to remain intact. Tungsten carbide better than chromium.
b. Stainless Steel "444"	Lower Superheater & Burner Area	1980-1981	Significant lack of bonding after 3500 hours of boiler operation.
c. "Chromized" Test Panel, 9 Tubes Wide ⁽¹⁾	Lower Furnace (Left Waterwall)	1985-1988	Brazed sst fiber-rein. refractory failed to remain bonded after 2100 hours. Fused WgC coating suffered minor lack of bonding. Chromized layer reduced wastage rates initially but effectiveness lasted only 10,000 boiler operating hours (18 months) (Figure 8).
d. "Test" Coatings	Lower Furnace	1987	8 different metallic and ceramic coatings. WgC had best bonding. Others failed in 1900 hours.
e. Tungsten Carbide (45% Ni, 11% Cr, 35% WgC)	Lower & Mid Furnace (Front & Rear Walls)	1987 - Present	WgC (field-applied) failed to remain bonded, 5-15% of area attacked after 2400 hours. Up to 90% of area unprotected after 15,000 hours. Caused by corrosion of Ni-Cr-Bo matrix.
4. SiC Cast Refr. Tube Blocks	Lower Furnace (Left Wall @ Grate)	1988 - Present	6-10 Tiles missing after 3200 hours, 18 (50% of total) gone within 5350 hours. Failed by cracking and threaded stud overheating.
5. Sheet Metal Half-Shields	Lower Superheater Bends	1979 - Present	Carbon steel weld-on type last 1-2 years in sootblower areas. 309 SST shields on lower bends 50% missing or burnt within 2700 hours.

(1) "Chromizing" alters the carbon steel surface to approach AISI 442 stainless steel (35-45% Cr), 0.010-0.020 in. (0.25 - 0.5 mm) thick. Three tubes were fused WgC coated, 3 tubes were stainless fiber-reinforced refractory covered, and three were "bare" chromized tubes.

of the lower furnace walls. The mixed iron oxides in the molten salt layers limit the availability of oxygen and retain the chlorine within the adherent scale [9].

(b) Sulfur from #6 oil firing is likely involved only around the burners and lower superheater tubes (not significant in the lower furnace). SO₂ in the gas phase can convert alkali chlorides/bromides to alkali sulfates and HCl/HBr [9]. This may explain the lack of chlorides in the superheater tube scale layers while outer deposits contained large amounts of sulfur and lead.

(c) Preferential wastage on the sides of the lower waterwall tubes and lower superheater bends result from high gas velocities and entrained refuse particles sweeping across the tubes' surfaces. This is inherent in the tangential injection design for fuels/wastes and combustion air.

(d) Frequent boiler outages allow strong acids to form within the moisture-absorbing fireside deposits.

The key to the accelerating tube wastage rates are operating trends throughout the history of Kodak's boiler. Increases in annual amounts and durations of refuse burning occurred as preparation and feed equipment improvements took place in the mid 1970s and early 1980s. This was followed by segregated burns of special photographic materials during low refuse receipt time frames (weekends). Both of these and other changes decreased #6 oil cofiring and sludge burning by the mid 1980s. Combustion hardware modifications in 1986 increased furnace turbulence, initially creating substantial lower furnace wall slagging and particulate carryover into the superheater platens and convection bank tubes.

CONCLUSIONS

Kodak's boiler has experienced severe wastage of carbon steel tubes within 6 ft (1.8 m) of the ash grate, in the vicinity of fuel/waste injection nozzles, and the lower superheater tube 'U' bends. Rates as high as 0.140 in. per year (3.6 mm/year) have been measured in localized areas of the lower furnace walls. Low alloy steel superheater tubes have also required frequent piecemeal replacements and repairs due to thinning in sootblown areas and bends exposed to radiant heating and heavy fireside deposit accumulations.

Corrosion probe and tube specimen analyses have identified chlorine and lead as major constituents associated with the severe wastage. Potassium, sodium, zinc, and silver are other metals which are present in waterwall deposits, mostly as chloride/bromide salt mixtures. Superheater deposits contain sulfur and typ-

ical "fly ash" compounds such as silica, aluminum, and calcium.

Kodak's nonhazardous industrial refuse (RDF) and flash-dried wastewater treatment sludge is tangentially injected for suspension burning. The boiler's combustion hardware designs and the nature of Kodak's wastes promote a highly reactive furnace environment. This results in flame and burning particle impingement, bringing the corrosive compounds in contact with the furnace walls and superheater pendants. Reduction of annual amounts of sludge and #6 fuel oil firing, with increased photographic scrap materials and refuse quantities coincide with accelerated tube wastage rates.

RECOMMENDATIONS

Due to the factors mentioned above, corrosion of carbon steel waterwalls and low alloy superheater tubes requires:

(a) Frequent periodic tube fireside thickness measurements to:

(1) identify tube wastage patterns; and

(2) forecast remaining tube life throughout the entire boiler, especially for

(3) furnace walls near the ash grate and burner; and

(4) superheater tubes where sootblowers operate and pendants are exposed to high gas temperatures/radiant heating.

(b) Corrosion-resistant materials to protect the wastage-prone areas of the boiler which will:

(1) remain tightly attached to the tubes' fireside surfaces;

(2) not adversely limit heat transfer or promote ash slagging;

(3) allow ease of tube thickness measurement during inspections; and

(4) permit ready repair/replacement of the protection and/or boiler tubes by available, qualified personnel.

As for the corrosion protection methods, alloy weld overlays of Inconel 625 have been very successful in several municipal RDF-fired boilers [6, 7, 8]. Lower furnace waterwalls with this installed had virtually no metal loss after 6 months of service. Clad or composite (coextruded) tubes with carbon steel inside (retains pressure), and corrosion resistant alloy such as AISI 304L or 310 outside (acts as a shield) minimized waterwall corrosion in mass-fired municipal refuse boilers, black liquor recovery units, and bark-fired boilers [10]. Such tubes are also available with Incoloy 825 cladding. They should not be highly susceptible to possible

out-of-service corrosion from chlorides in the fireside deposits.

Superheater tubes can be constructed of composite or solid high-strength alloys such as Incoloy 825, appearing to offer corrosion resistance to chlorine and sulfur attack at metal temperatures above the 625°F (340°C) in Kodak's case.

Kodak's experience with metallic and tungsten carbide coatings and refractory coverings have been troubled by failure to remain bonded to the tubes. They cannot be recommended as long term solutions to tube wastage in RDF-fired units. Sheet metal shields can be a cost effective form of sacrificial tube protection in sootblower lanes as long as periodic inspection and replacement is practiced.

These conclusions and recommendations result from Kodak's own investigations and studies by others since the early 1970s. The likelihood that multiple corrosion mechanisms are responsible for such severe tube wastage problems at Kodak and other refuse-fired boilers shows how difficult it can be to predict such problems during design stages. Sharing of such problems as well as successful solutions will continue to be beneficial to Kodak and other resource recovery facility operators.

REFERENCES

[1] Regan, J. W. "Generating Steam from Prepared Refuse." In *Proceedings of 1970 National Incinerator Conference*. New York: The American Society of Mechanical Engineers, 1970, 216-223.

[2] Original Boiler Predicted Performance (from Instruction Manual) for Eastman Kodak Company, Contract 23568, by Combustion Engineering, Inc.

[3] Krause, H. H., Cover, P. W., and Vaughan, D. A. "Evaluation of the Corrosivity of Furnace Environments Resulting from the Combustion of Kodak Waste Materials." Battelle Columbus Laboratories Research Report (for Kodak), March 31, 1976.

[4] Plumley, A. L., and Crisp, D. D. "Eastman Kodak—Assessment of Waterwall Corrosion Unit 25" (for Kodak), dated December 20, 1984 with Supplement dated May 6, 1985, Combustion Engineering, Inc.

[5] Plumley, A. L. (Letter to Kodak), November 20, 1985, Combustion Engineering, Inc.

[6] Daniel, P. L., Barna, J. L., and Blue, J. D. "Furnace-Wall Corrosion in Refuse Fired Boilers." In *Proceedings of the 12th National Waste Processing Conference*. New York: The American Society of Mechanical Engineers, 1986, 221-228.

[7] Morello, T. J. "Fireside Corrosion at Occidental's Energy from Waste Plant." Presented at the Engineering Foundation Conference on Fireside Problems While Incinerating Municipal and Industrial Waste, Sheraton Palm Coast, Florida, October 8-12, 1989.

[8] Boley, G. L., and Smith, M. L. "Start-up and Operations of the Mid-Connecticut Resource Recovery Project." Presented to the International Conference on Municipal Waste Combustion, Hollywood, Florida, April 11-14, 1989.

[9] Krause, H. H. "Corrosion by Chlorine in Waste-Fueled Boilers" Presented at the Engineering Foundation Conference on Fireside Problems While Incinerating Municipal and Industrial Waste, Sheraton Palm Coast, Florida, October 8-12, 1989.

[10] Odelstam, T., Berglund, G., and Nylof, L. "Experience with Composite Tubes in Waste Incinerators." Presented at the Engineering Foundation Conference on Fireside Problems While Incinerating Municipal and Industrial Waste, Sheraton Palm Coast, Florida, October 8-12, 1989.

Key Words: Boiler; Corrosion; Refuse-Derived Fuels; Sludge; Suspension; Testing