

Recent Experience with Ash Deposits in Refuse-Fired Boilers

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ABSTRACT

The increasing interest in using refuse as a fuel has introduced some new problems to the field of high temperature deposits and corrosion. A literature review indicated that most investigators attribute the fouling and corrosion problems in steam generating incinerators to the presence of alkalis and chlorides despite the presence of some contradictory evidence. Recent field and laboratory experience suggests that minor constituents, such as lead or possibly zinc originating in paint or solder, may be the contributing or even responsible agents.

INTRODUCTION

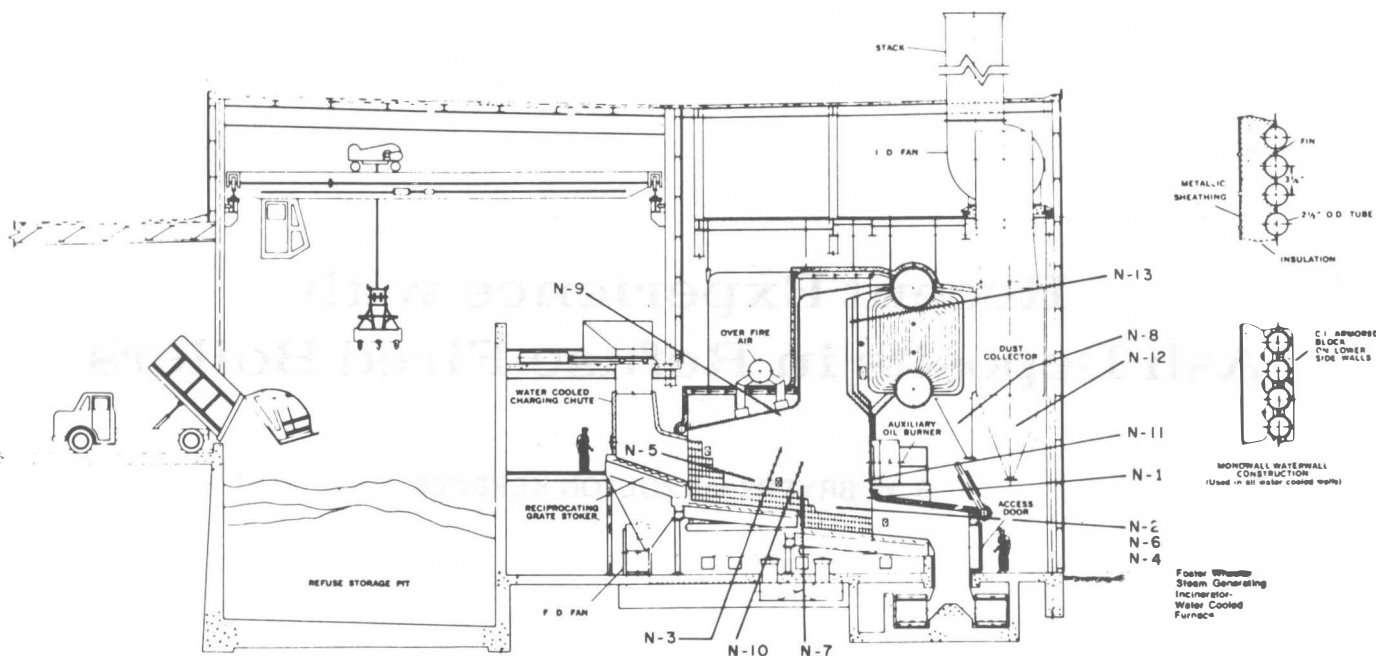
The burning of refuse in water-cooled steam-generating incinerators for the purpose of compacting it and providing an inexpensive source of energy has introduced new problems to the field of ash deposition and corrosion. Recent experience reported in the literature attributes the fouling problems to the alkalis and chlorides. Contradictory evidence suggests minor constituents such as lead or zinc may be responsible agents. In this paper, we briefly review the work that has been done, and introduce a few new ideas based on some laboratory analysis and experimentation that we feel deserves some attention. Admittedly, it is too early to draw any conclusions from these observations. However, in view of the complexity of the ash deposit and corrosion problem

and the heterogeneous nature of refuse as a fuel, we feel it is essential to establish as many of the facts as possible at the very beginning. In this way, all avenues of thought may be explored.

RENEWED INTEREST IN INCINERATION

Refuse burning is not new. Circular, refractory, steel-cased incinerators have been used since the thirties, and other types of devices have been reported in use as early as the 1880's. However, the recent increase in population crowding our communities, the improved standard of living with its attendant increases in waste, and the increased value of land, have stimulated considerable interest in incineration as a means of compacting and disposing of waste materials, rather than the more conventional practice of sanitary land fill. The original incinerators used as much as 400 to 600 percent excess air. No attempts were made to recover the heat. Recent studies showed that absorption of heat through a water-cooled furnace was less expensive than tempering flue gas with large quantities of excess air. This introduced refuse as an attractive fuel to generate inexpensive process steam. Within the last four years, two salvage boilers have been installed in the United States, one in Long Island and the other in Norfolk, Virginia.

In Europe, where the municipality is primarily responsible for providing electricity, steam for heating, and a means of disposing refuse, incineration has



NUMBERS N-1, N-2, ETC., REFER TO ASH SAMPLE LOCATION - SEE ANALYSES TABLE 3

FIG. 1 FOSTER WHEELER STEAM-GENERATING INCINERATOR WATER-COOLED FURNACE, U.S. NAVAL STATION, NORFOLK, VIRGINIA

provided a logical source for cheap energy. That is particularly true where the supply of fossil fuels is short. They have not only used refuse to produce process steam, but they have also used it with coal to produce electricity. It is these applications which require higher steam temperatures that have produced the deposit problems.

FURNACE DESIGN

The modern incinerator differs somewhat from the conventional steam generator. It generally consists of either a refractory-lined furnace and waste-heat boiler in which the furnace flue gas temperatures are maintained at 1400-1700 F by using as much as 500 percent excess air, or a water-cooled furnace in which combustion gas temperatures of 2500 F are experienced with as little as 30 percent excess air. Refuse is laid down on a reciprocating, rotating, or traveling grate adapted from prior coal experience, which provides sufficient refuse turnover to assure proper drying and complete combustion. The moisture is driven off on the first section of the grate, the volatile matter is driven off next, and finally, the full ignition temperature is reached in the combustion

zone. In recent designs overfire air is introduced at the far end of the grate, causing the flame to sweep under an overhanging arch and over the incoming refuse. In this way, it provides heat for drying and preheating. The upsweeping flame rises into the second vertical section of the furnace to a sufficient height to complete combustion. Furnace wall tubes are generally brought down to the grate level to reduce clinkering and costly refractory repair. Furnace wall tube metal temperatures are kept between 300 and 800 F to prevent dewpoint corrosion and high-temperature corrosion, respectively.

The secondary furnace is designed to reduce the gas exit temperatures to the convection passes to between 1400 and 1600 F, and acts as a settling chamber for the larger particles. It also provides sufficient time to ensure complete combustion of gases and solids, particularly pieces of paper and other light particles that may be lifted up off the grate. For these reasons, the primary furnace sections are generally restricted to a volumetric heat release of 13,000 Btu/cu ft-hr. The velocities in the long vertical secondary combustion chamber are usually limited to 30 fps. Fig. 1 illustrates a Foster Wheeler boiler that was built somewhat along the lines just outlined.

ASH-FORMING CHARACTERISTICS OF REFUSE

Prediction of ash deposits and corrosion problems resulting from firing refuse is extremely difficult. Refuse is heterogeneous by nature and undoubtedly varies from time to time, as well as from municipality to municipality. Despite these problems, attempts have been made to provide some guide for predicting problem areas by analyzing individual constituents sorted from the refuse. Although no attempt was made to proportion the results to give a composite analysis, a comparison was made between the individual constituents and the slag and fly ash that resulted. Such a comparison seems particularly appropriate, in view of the problem encountered in predicting the ash contribution of metallic constituents like iron and aluminum. This technique was used by E. R. Kaiser, et al. [1], and the results appear in Table 1.

These results only become useful when they can be interpreted in terms of past experience with other fuels. Elder and Kube [2] have very nicely tabulated the data for other fuels which make such a comparison possible. These results appear in Table 2. Examination of the refuse ash indicates it is high in silica and alumina. We might also expect the iron and calcium content to be high. It is interesting to note the calcium to iron ratio, as indicated by the slag, is greater than one. Previously, this characteristic was peculiar to lignite-type ashes. Duzy and Walker [3] in their work with lignite indicate that fusibility of ash decreases to a minimum when the basic content of the ash, i.e., Fe_2O_3 , MgO , CaO , Na_2O , and K_2O approaches 40 percent. This certainly appears to be the case here. Therefore, care should be taken in burning refuse to avoid high gas temperature in the convection pass or slagging conditions on the furnace walls. Further examination of the ash indicates that the alkali content, i.e., Na_2O and K_2O , are relatively high, about 4 to 10 percent. When the ash content is reported to exceed 5 percent, refuse can be considered in the moderate to severe fouling range. Past experience with Central Illinois coal has indicated that the fuels with Na_2O and K_2O contents in excess of 0.4 percent on a dry coal basis generally cause fouling problems [4]. Chlorine, although it does not appear in the tabulated analysis, may be introduced with the increased consumption of plastic. If the content were to exceed 0.01 percent, we might expect a corrosion and deposit problem associated with this element (b).

The sulfur content of refuse can be expected to run from 0.10 to 0.15 percent. In contrast with

coal and oil, the sulfur content of coal ranges from trace amounts to 10 percent, and the sulfur content of oil ranges from 0.6 to 3 percent. E. R. Kaiser [5] has shown that only 25 percent of the sulfur present in refuse is released as SO_2 in the flue gas. Twenty-five percent is discharged in the fly ash, and 50 percent is discharged with the refuse. In the case of coal and oil, it has been reported that 80 to 100 percent of the sulfur in the fuel is released as oxides in the flue gas. This makes refuse attractive as a low-sulphur fuel for air-pollution control.

LITERATURE REVIEW

As already indicated, the little experience acquired to date has been obtained in Europe. The Germans indicate that they experienced severe corrosion and ash deposition in many but not all of the refuse burning steam generators. The results have been discussed in numerous papers, but unfortunately raw data and operating conditions have been omitted, leaving an unclear picture. For the most part, they have attributed their problems to the deposition of the pyrosulfates, complex alkali metal sulfates, or the chlorides. Certainly some of the circumstantial evidence indicates these prospects to be reasonable choices, as we shall see.

The classical experience of Reid, Corey, Cross, and Grabowski [6,7,8] indicates that the corrosive nature of the alkali compounds depends on the presence of deposits on tube-metal-surfaces in the temperature range of 570 to 1300 F. The temperature and chemical composition must be such that a liquid phase can exist. Furthermore, they indicated that neither iron oxide nor the alkali metal sulfates, alone, will react with the sulfur trioxide at 1000 F. However, mixtures of the three combine to form complex alkali-metal sulfates. The formation of the pyrosulfates also depended upon the presence of at least 0.5 percent sulfur trioxide. The complex alkali sulfates were found at an SO_3 concentration in the gas as low as 0.025 percent. From an operational point of view, it was noted that the pyrosulfates usually formed in areas of flame impingement. To this Nelson and Cain [9, 10] added the definition of temperature ranges in which excessive corrosion was experienced, due to the presence of the pyrosulfates (550-700 F), the complex alkali iron sulfates (950-1300 F), and the alkali sulfates (1600 F).

This information certainly appears applicable to some of the conditions which the Germans encountered. They reported the presence of sodium and potassium in the deposits [11-14]. In some

TABLE 1. ASH ANALYSES AND FUSION TEMPERATURES OF MUNICIPAL REFUSE COMPONENTS AND SLAGS

		Clear Glass	Brown Glass	Green Glass	Garbage, less bones	Card- board, corrug.	Misc. Paper (a)	Grass and dirt	Textiles	Heavy plastics, leather, etc.	Bones & clam shells
ASTM Fusion Temp. °F.											
Initial		1480	1620	1640	2020	2060	2160	2080	2040	2100	2800
Softening		1600	1700	1720	2100	2120	2260	2200	2120	2160	2800
Fluid		1840	2080	2080	2200	2240	2480	2320	2240	2300	2800
Analyses, %											
Silica	SiO ₂	74.11	71.86	75.21	46.35	47.92	48.27	61.50	38.85	34.18	63.40
Alumina	Al ₂ O ₃	4.97	7.21	9.42	4.29	6.97	7.02	6.98	5.71	6.22	0.84
Calcia	CaO	9.36	11.70	8.62	20.70	18.08	11.70	12.87	23.65	31.04	23.90
Ferric oxide	Fe ₂ O ₃	0.09	0.04	0.03	2.86	4.28	3.21	1.69	3.14	2.09	0.98
Titania	TiO ₂	Tr	Tr	Tr	1.04	7.21	8.69	1.83	8.62	9.23	Tr
Magnesia	MgO	8.16	0.43	0.02	11.06	9.62	8.94	7.61	9.34	8.71	4.28
Barium oxide	BaO	0.07	0.08	0.11	0.02	0.41	0.03	0.37	0.07	0.04	0.09
Soda	Na ₂ O	2.09	6.02	4.31	5.01	3.26	5.72	2.09	3.84	4.19	0.70
Potash	K ₂ O	0.05	0.82	0.74	5.16	0.27	4.29	1.14	5.16	1.04	0.04
Zinc oxide	ZnO	0.03	0.02	0.04	0.32	0.39	0.41	0.53	0.01	1.84	0.02
Phos. pentoxide	P ₂ O ₅	0.09	0.08	0.06	2.02	0.14	0.39	2.28	0.06	0.06	3.75
Sulfur trioxide	SO ₃	0.14	0.27	0.18	0.21	0.12	0.14	0.08	0.37	0.16	0.32
Totals		99.16	98.53	98.74	99.04	98.67	98.81	98.97	98.82	98.80	98.32

	Slag C (b) Contin. Feed	Slag F (b) Batch Feed	Avg. 25 Slags (b)	Herbert Slags (c)	Chemical Analysis of Incinerator Fly Ash Taken from Various Locations in the Gas Pass(d)			
					Suspended in Hot Flue Gas	Dust Collector Zone	Stack	
SiO ₂	37.1	20.9	44.73	46.3	47.2	48.7	36.5	SiO ₂
Al ₂ O ₃	7.0	15.2	17.44	18.35	10.2	23.4	25.9	Al ₂ O ₃
CaO	7.7	12.7	10.52	9.94	18.4	9.2	8.9	CaO
Fe ₂ O ₃	40.0	1.8	9.26	8.85	15.6	6.5	7.1	Fe ₂ O ₃
TiO ₂	0.55	2.4	2.92	2.90	—	1.1	0.7	TiO ₂
MgO	1.2	2.4	2.1	2.54	2.9	2.3	2.8	MgO
BaO	Tr	Tr	Tr	0.58	—	—	—	BaO
Na ₂ O	5.36	17.23	8.14	4.61	4.5	5.8	10.5	Na ₂ O
K ₂ O	—	—	—	—	—	—	—	K ₂ O
ZnO	0.20	6.3	*1.54	1.37	—	—	—	ZnO
P ₂ O ₅	0.6	0.7	1.52	2.15	—	—	—	P ₂ O ₅
SO ₃	0.55	20.4	*3.69	**0.96	1.2	3.0	7.6	SO ₃
MnO ₂	0.30	0.44	0.29	—	—	—	—	MnO ₂
CuO	—	0.3	Tr	—	—	—	—	CuO
PbO	—	0.2	Tr	—	—	—	—	PbO
Totals	100.56	100.97	102.15	98.55	100.0	100.0	100.0	

* 6 samples
** 2 samples
Tr Trace

- (a) All paper except newspaper and corrugated carboard, some smeared with garbage
- (b) G. H. Criss and A. R. Olsen, "The Chemistry of Incinerator Slags and Their Compatibility with Fire Clay and Alumina Refractories," Presented at the 1966 National Incinerator Conference ASME, New York
- (c) D. B. Herbert, "The Nature of Incinerator Slags," Proceedings of the 1966 National Incinerator Conference ASME, New York
- (d) Elmer Kaiser, "The Sulfur Balance of Incinerators," Paper 67-160 Air Pollution Control Assoc., Annual Meeting June 11-16, 1967

TABLE 2. APPROXIMATE LIMITS IN ASH COMPOSITION FOR VARIOUS FUELS⁷

	Chemical analysis, weight-percent of ash				
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	P ₂ O ₅
U. S. Coals:					
Anthracite ¹	47.7-67.7	24.7-43.5	2.1-10.2	1.1-1.8	0.08-3.7
Bituminous ¹	7.1-68.5	4.1-38.9	1.8-43.6	0.5-3.7	0.05-3.1
Subbituminous ¹	16.7-58.2	4.1-35.0	2.7-18.9	0.6-2.3	0.02-3.1
Lignite ²	6.8-45.2	6.3-22.5	0.9-17.8	0.1-0.8	0.0-1.3
British coal: Bituminous ³	25-50	20-40	0-30	0-3.0	-
German coals:					
Bituminous	25-45	15-21	20-45	-	-
Brown ⁵	7.0-46.3	6.0-29.4	16.6-26.0	-	-
Victorian coal: Brown ^{5,6}	0.1-41.6	0.4-36.9	2.1-29.8	0.1-0.3	-
Refuse ^{8,9}	20-52	8-25	4.2-19.0	Nil-2.9	1.5-2.2
	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
U. S. Coals:					
Anthracite ¹	0.2-3.7	0.2-1.2	-	-	0.1-1.1
Bituminous ¹	0.7-36.4	0.1-4.2	0.2-2.8	0.2-3.5	0.1-32.3
Subbituminous ¹	2.2-45.1	0.5-8.0	-	-	2.7-16.1
Lignite ²	15.3-44.4	3.0-12.2	0.2-11.3	0.1-1.7	6.2-30.3
British coal: Bituminous ³	1-10	0.5-5.0	⁴ 1-6	-	1-12
German coals:					
Bituminous ³	2-4	0.5-1.0	-	-	4-10
Brown ⁵	4.1-43.0	0.9-4.0	-	-	2.1-22.0
Victorian coal: Brown ^{5,6}	tr.-36.4	0.7-19.5	0.5-6.2	0.1-1.1	8.0-33.1
Refuse ^{8,9}	7.8-22.0	1.8-3.4	2.0-6.1	.27-5.2	.9-9.7

¹ Selvig, W. A., and F. H. Gibson. Analysis of Ash from United States Coals, BuMines Bull. 567, 1956, 33 pp.

² Data from Grand Forks Coal Research Laboratory.

³ Lowry, H. H. Chemistry of Coal Utilization, Supplementary Volume, John Wiley & Sons, 1963, p. 209.

⁴ Includes K₂O.

⁵ Henderson, P. L. Brown Coal: Its Mining and Utilization. Melbourne University Press, Melbourne, Australia, 1953, pp. 53-54.

⁶ Coal from the Australian State of Victoria.

⁷ Elder, James L., and Kube, Wayne R., "Technology and Use of Lignite - Proceedings: Bureau of Mines - University of North Dakota Symposium, Bismarck, N. Dakota, April 29-30, 1965", U.S. Dept. of Interior, Bureau of Mines, 1C-8304, 1966.

⁸ Elmer Kaiser, "The Sulfur Balance of Incinerators", Air Pollution Control Association Annual Meeting, Paper No. 67-160, June 1967.

⁹ E. R. Kaiser, C. D. Zeit, and J. B. Macaffery, "Municipal Incineration, Refuse and Residue", Proceedings of 1968 National Incineration Conference, ASME, May, 1968.

cases, they reported the presence of alkali iron sulfates [11]. Difficulties were encountered in the temperature ranges of 572 and 1112 F [12, 15, 16, 18, 20]. There also appeared to be definite association of corrosion with the presence of ash deposition [12, 13, 15]. The latter often appeared to occur in the area of flame impingement [26].

Part of their problems have been attributed to the firing of large quantities of plastics containing

chlorine. J. Angenend [21] demonstrated in a test facility the increase in corrosive activity of chlorine with temperature. These tests were run in an environment in which chlorine was added by injecting HCl. Chlorine was also added by burning polyvinyl chlorides with refuse. Brown, et al. [22], indicates that the corrosion of iron in a chlorine environment was so severe that iron would ignite at 450-500 F. However, they also indicated that the presence of

alkalis would tend to temper the corrosivity of chlorine. Kohle [13], Huch [12], and Eberheart [27] all have identified the presence of chlorine as ferric chloride $FeCl_3$ in the deposits. It is possible that chlorine could be responsible for corrosion in the temperature range of 680-900 F in which the alkali sulfate compounds may be dry and relatively ineffective.

These original postulations by the various German investigators are not without contradictions or evidence questioning the credibility of this explanation for the deposit problem. The physical characteristics of the deposits such as color, texture, and so forth, were not the same as reported for the alkali sulfates deposits. The level of sulfur in the refuse appears to be well below the level necessary for the formation of complex alkali metal sulfates or pyrosulfates. This, however, is a rather weak point, as recent work by Battelle Memorial Institute [23] has shown that the concentration of SO_3 at the tube

surface may be some 30 times as high as the bulk stream concentration. No liquid phase has been reported in the deposit responsible for this type of corrosion. Recent information in the literature [14] and personal inspection [24] has indicated that:

- 1) The upper safe limit for tube-metal temperature is 850 F, and not 578 deg as reported earlier.
- 2) Corrosion was time dependent. The corrosion was high at first but subsided shortly after start-up and proceeded at a tolerable level.
- 3) Corrosion can take place in the absence of ash deposits.
- 4) As long as the protective covering of corrosion is left intact, the wastage of tube-metal surface is kept under control.
- 5) Corrosion may or may not occur in the presence of chlorine. One plant, which incinerated chemical wastes with a much higher chlorine content than municipal refuse, reported no evidence of corrosion [25].

TABLE 3. ANALYSES OF DEPOSITS FROM REFUSE BOILER NORFOLK, VIRGINIA

Sample No. Analysis	N-1	N-2	N-3	N-4	N-5	N-6	N-7	N-8	N-9	N-10	N-11	N-12	N-13	Sample No. Analysis
SiO_2	1.1	1.2	1.8	1.0	7.00	1.9	8.00	33.3	5.00	29.8	48.3	21.7	36.5	SiO_2
Al_2O_3	0.70	1.2	1.4	1.1	6.50	1.4	4.50	16.4	2.50	12.6	15.9	10.0	17.5	Al_2O_3
Fe_2O_3	78.8	73.5	68.7	64.3	63.0	55.8	30.0	10.2	9.50	9.7	8.5	7.7	12.0	Fe_2O_3
CaO	0.40	0.72	0.70	0.50	0.80	0.98	2.00	9.3	2.60	8.8	7.2	7.0	10.0	CaO
SO_3	6.62	8.40	6.52	8.75	2.13	13.3	18.5	4.12	9.74	15.1	0.34	25.1	8.40	SO_3
K_2O	1.30	1.64	1.55	2.33	2.05	3.89	4.07	1.75	4.22	4.02	2.04	5.60	3.00	K_2O
TiO_2	0.15	0.18	0.32	0.19	0.20	0.28	0.60	3.38	0.50	2.45	2.99	1.87	2.00	TiO_2
Na_2O	1.2	1.9	2.2	3.0	5.39	4.3	6.48	6.35	18.9	4.5	1.5	7.6	3.51	Na_2O
ZnO	1.23	2.20	2.26	4.03	1.62	5.21	7.16	3.74	8.84	5.47	2.43	5.89	7.44	ZnO
P_2O_5	nil	nil	nil	nil	nil	nil	0.14	2.59	0.10	2.75	1.72	1.90	1.71	P_2O_5
MnO_2	0.45	0.45	0.60	0.35	2.35	0.35	0.35	0.65	nil	0.80	0.40	0.50	1.00	MnO_2
CuO	nil	nil	nil	0.19	nil	0.01	0.18	0.12	0.12	0.24	nil	0.19	0.31	CuO
NiO	0.13	0.09	0.10	0.10	0.13	0.10	0.13	0.33	0.13	0.22	0.16	0.32	0.25	NiO
V_2O_5	nil	nil	nil	nil	nil	nil	nil	0.22	nil	0.51	0.03	0.16	0.75	V_2O_5
Cr_2O_3	0.24	0.19	0.41	0.19	nil	0.21	nil	0.40	nil	0.46	0.37	0.31	0.60	Cr_2O_3
MoO_3	0.02	0.03	0.08	0.02	nil	0.03	nil	0.14	nil	0.10	0.14	0.14	0.10	MoO_3
MgO	0.3	0.4	0.4	0.3	0.54	0.4	0.70	2.4	1.67	1.0	1.7	1.5	0.90	MgO
Cl	0.6	1.8	0.8	1.17	5.59	0.6	1.00	0.2	23.4	0.2	1.0	0.2	0.02	Cl
PbO_2	0.68	1.28	2.01	3.98	0.46	5.45	10.1	1.60	9.24	2.35	1.08	3.45	0.75	PbO_2
SnO_2	nil	0.1	nil	nil	nil	nil	0.20	0.3	2.02	0.3	0.3	0.3	0.40	SnO_2
Ag_2O	nil	0.05	0.10	0.03	nil	nil	0.05	0.22	0.12	0.19	0.25	0.15	0.15	Ag_2O
I.D. °F.	2800+	*	*	2800+	2800+	2800+	2800+	2140	2120	2000	2080	2060	2010	I.D. °F.
S.T. °F.	2800+	*	*	2800+	2800+	2800+	2800+	2190	2420	2110	2160	2130	2140	S.T. °F.
F.T. °F.	2800+	*	*	2800+	2800+	2800+	2800+	2440	2540	2160	2460	2380	2300	F.T. °F.
pH	3.7	6.4	6.7	6.9	6.2	5.9	5.5	7.3	5.6	4.8	7.3	6.0	6.1	pH
L.O.I., %	5.92	11.1	16.4	6.57		4.20		16.1		0.19	5.71	0.33	1.38	L.O.I., %
L.C.D., %	0.01	0.06	0.12	0.10		0.01		0.05**		0.01	0.01	0.01	0.56	L.C.D., %
% C		3.41	8.51					12.5					0.05	% C
% H		0.62	1.34					0.73					0.19	% H

* Insufficient sample
 ** Gain

Experience with steam-generating refuse plants in the United States has been limited to just a few units. These include a water-cooled furnace plant installed at Norfolk, Virginia (Fig. 1), and a refractory-lined unit equipped with a waste heat boiler located on Long Island. The latter has experienced some severe tube wastage and ash deposit problem. In view of the complexity of the problem encountered and the uncertainty of the cause, Foster Wheeler began a study of its own.

ASH DEPOSIT SURVEY AND ANALYSIS

The program consisted of examining and analyzing ash samples and running crude sorting type corrosion tests in an attempt to restrict the study to meaningful areas of investigation. The ash deposit phase of the program included a survey of the deposit accumulations in both the Norfolk and Long Island units, followed by a close examination and complete analysis of samples taken from various locations in the boilers. A sample taken from a third boiler located in Germany was also analyzed for comparative purposes. Prior to running detailed chemical analysis, several rather comprehensive surveys were made by qualitative spectrographic emission techniques to identify the major constituents present. These tests were then followed by detail quantitative wet and x-ray fluorescent analysis, the results of which appear in Tables 3, 4, and 5. Where feasible, the samples were also checked for fusion temperature, pH, ignition loss, loss on drying, and percent hydrogen and carbon. Attempts were also made to identify the presence of specific compounds. Fusion tests were run on the samples according to ASTM Standards. To complement the analysis, most of the samples were examined very closely under a microscope at 30-100X for physical characteristics, such as color, structure, homogeneity and so forth.

The ash survey of the Norfolk boiler indicated that accumulations were rather light. Screen tubes with estimated surface temperatures of 600 F and inlet gas temperatures of 1600 F were covered with a thin coating of friable ash. Wedge-shaped deposits, which could easily be removed, collected on the leading edge of the screen tube. The deposit contained what appeared to be a fused outer casing enclosing a cinder-like porous inner structure. The inside layer of the deposit circumscribing the tube consisted of a thin fused layer of material. An extremely thin buffer layer of red-yellow powdery material was left on the tube surface when the deposit was removed. The quantity of material in the layer was too small

TABLE 4. ANALYSES OF ASH DEPOSITS FROM THE LONG ISLAND BOILER

Sample No. Analysis	L-1	L-2	L-3	L-4
SiO ₂	7.50	19.5	6.00	2.00
Al ₂ O ₃	3.50	11.0	4.00	1.00
Fe ₂ O ₃	7.50	4.00	18.0	59.0
CaO	9.00	9.00	1.80	0.60
SO ₃	31.9	20.4	26.1	12.6
K ₂ O	9.64	9.46	13.0	7.03
TiO ₂	0.70	0.50	0.50	0.15
Na ₂ O	7.82	6.21	5.12	4.04
ZnO	7.80	6.72	9.65	4.67
P ₂ O ₅	0.57	2.52	0.68	0.05
MnO ₂	Nil	Nil	Nil	Nil
CuO	Nil	Nil	Nil	Nil
NiO	0.13	0.51	0.13	0.13
V ₂ O ₅	Nil	Nil	Nil	Nil
Cr ₂ O ₃	Nil	Nil	Nil	Nil
NoO ₃	Nil	Nil	Nil	Nil
MgO	2.14	1.48	Nil	Nil
Cl	2.26	5.09	1.58	2.46
PbO ₂	13.1	1.44	5.75	0.92
SnO ₂	1.10	0.84	1.12	0.20
Ag ₂ O	0.05	0.28	0.08	0.08
I.D. °F	1120	2140	850	Insufficient
S.T. °F	1180	2380	1040	Sample
F.T. °F	1500	2540	1490	
pH	5.8	5.9	5.6	5.1
L.O.I. %	5.87	4.20	—	—
L.O.D. %				
% C	Nil	0.40	—	—
% H	.53	0.45	—	—

to remove. Fig. 2 shows a cross-sectional view of the deposit on a macro scale. A photo micrograph of the deposit, shown in Fig. 3, indicates the bulk of the deposit consists of small spherical particles, 10 to 20 microns or less in diameter, bound together at the surface. The photographs clearly illustrated the heterogeneous nature of the ash.

Ash accumulated on furnace walls in areas closest to the flame, essentially outlining its path as it passed on up into the vertical portion of the furnace. The ash was light and friable and crumbled upon touching. The greatest accumulation was between tubes which were part of a monowall construction illustrated in Fig. 1. In those areas re-

TABLE 5. COMPARISON OF ASH DEPOSITS TAKEN FROM THE CONVECTION PASS OF THREE REFUSE BOILERS

	German G-1	Norfolk N-13	Oceanside L-3
SiO ₂	15.0	36.5	6.00
Al ₂ O ₃	7.0	17.5	4.0
Fe ₂ O ₃	7.0	12.0	18.0
CaO	8.0	10.0	1.80
SO ₃	31.7	8.40	26.1
K ₂ O	7.68	3.00	13.0
TiO ₂	0.65	2.00	0.50
Na ₂ O	2.40	3.51	5.12
ZnO	5.61	7.44	9.65
P ₂ O ₅	1.31	1.71	0.60
MnO ₂	0.10	1.00	Nil
CuO	0.12	0.31	Nil
NiO	0.18	0.25	0.13
V ₂ O ₅	Nil	0.75	Nil
Cr ₂ O ₃	0.20	0.60	Nil
MoO ₃	0.15	0.10	Nil
MgO	4.1	0.90	Nil
Cl	0.40	0.02	1.58
PbO ₂	8.98	0.75	5.75
SnO ₂	1.02	0.40	1.12
Ag ₂ O	Nil	0.15	0.08

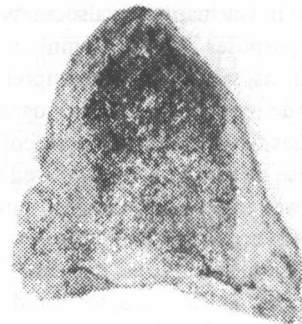
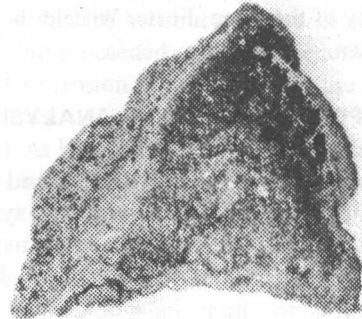
TABLE 6.[29] MELTING AND DECOMPOSITION TEMPERATURES OF SOME LEAD COMPOUNDS

Compound	Melting Temperature, °F.	Decomposition Temperature, °F.
PbO	1610	—
PbO ₂	—	554
Pb ₂ O ₃	—	698
Pb ₃ O ₄	—	932
PbCl ₂ · PbO	975	—
PbCl ₂ · 2 PbO	1270	—

moved from flame impingement or intense radiation, the deposits consisted of a thin fused scale covering the crown of the tube. The remaining portion of the tube and the adjacent fin were covered with a thin brittle scale. A buffer layer of red-yellow powdery material existed between the scale and the tube surface throughout the furnace. In some areas, a white powdery material had accumulated on top of the scale in the areas between the tube. The base

ASH DEPOSITS
SALVAGE FUEL BOILER
NORFOLK, VIRGINIA

CROSS SECTIONAL VIEW



SCREEN SECTION DEPOSIT

FIG. 2 CROSS-SECTIONAL VIEW OF ASH DEPOSIT REMOVED FROM THE LEADING EDGE OF A SCREEN TUBE IN THE NORFOLK BOILER.

metal beneath the ash was smooth and without blemish. The interstices of the beads in the weld joining the fins to the tube and the junction of the weld material and tube surface were visibly sharp, yielding no evidence of corrosion. Tube metal surfaces were estimated at 550 to 600 F.

In contrast to the Norfolk Salvage Boiler, the Long Island unit consists of a horizontal water tube waste heat boiler located in the flue gas pass at the exit of a refractory-lined furnace. The unit is operated with 128 percent excess air which should provide average flue gas temperatures between 1600 and 1800 F at the entrance to the boiler. Tube-metal tem-

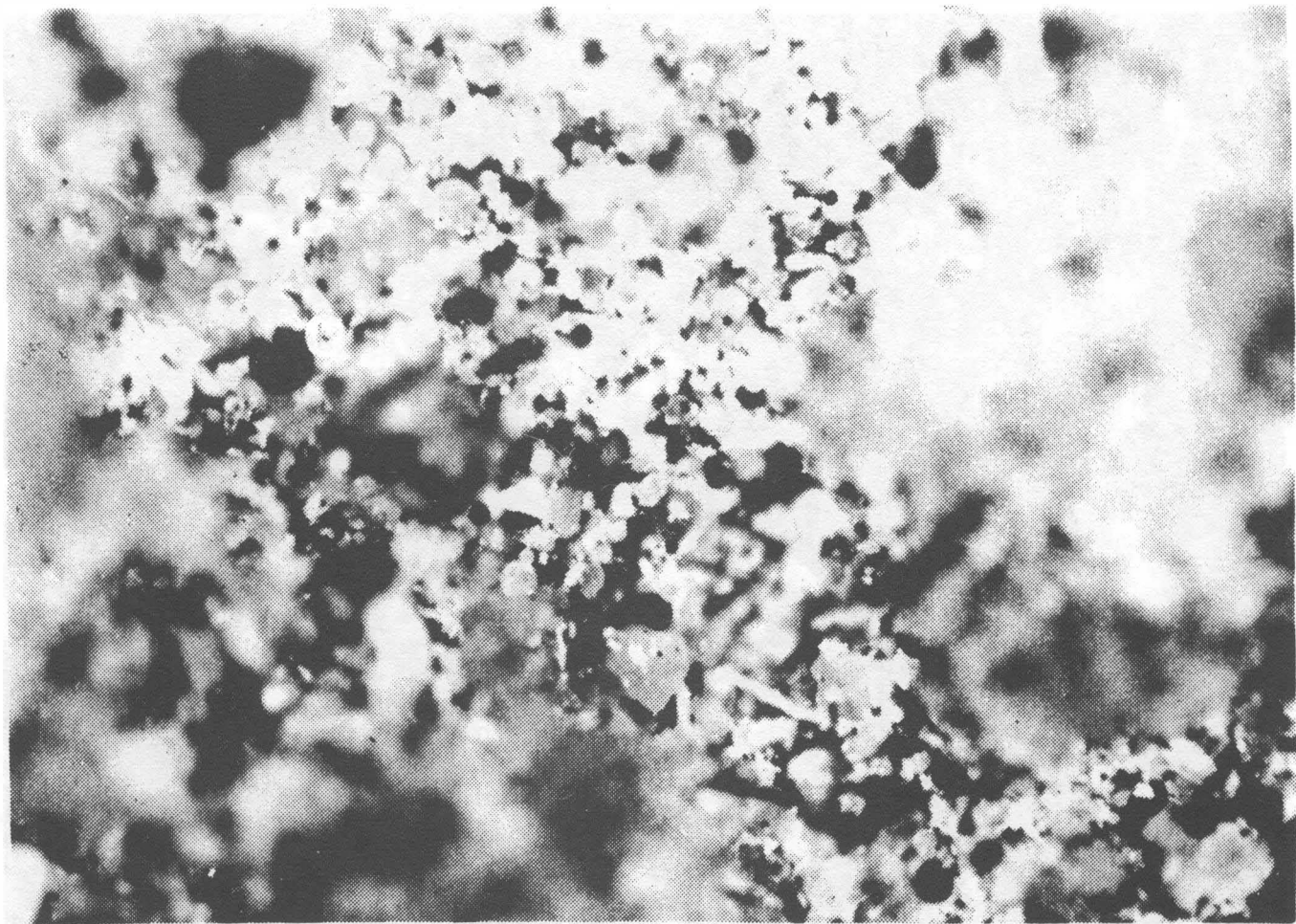


FIG. 3 PHOTOMICROGRAPH OF ASH REMOVED FROM A SCREEN TUBE IN THE NORFOLK BOILER, MAGNIFICATION OF 100.

peratures have been estimated at 512 F on the basis of the drum steam pressure at 460 psig.

Deposit formation appears to coincide with the flow path of the flue gases in the convection pass as well as in the furnace. Accumulations are greatest at the inlet to the convection pass. They decrease as the flue gas temperature decreases. Deposit formation apparently starts on the leading edge of the tube and between adjacent tubes forming the tube platen. With time, this deposit completely fills these spaces and proceeds to grow out into the gas passes. The deposits are hard, dense, white material that appears fused to the naked eye. Under the microscope, at relatively high magnification, the deposit has the appearance of highly compacted spheres or granules. The outside surface of the deposit was black, implying that some reaction may be taking place as the deposit grows and the surface becomes a sub-layer in a stratified accumulation. The inside layer,

binding the deposit to the tube, was a red scale-like material.

Severe tube wastage was reported on the sides, as well as the top and bottom of the tubes, where the gas temperature and mass flow rates were the highest. Some observers reported occasional flame impingement in this area.

Ash samples were taken from various locations in the Norfolk boiler, as indicated by the analysis code numbers material in Fig. 1. Sufficient samples were taken from the Long Island boiler to analyze the inside and outside layers. The results of the chemical analysis are reported in Table 4 as oxides of the constituent present. The tabulation also includes the identification, softening and fusion temperature as determined by ASTM techniques under reducing conditions.

Examination of ash analysis for both boilers reveal the following interesting facts:

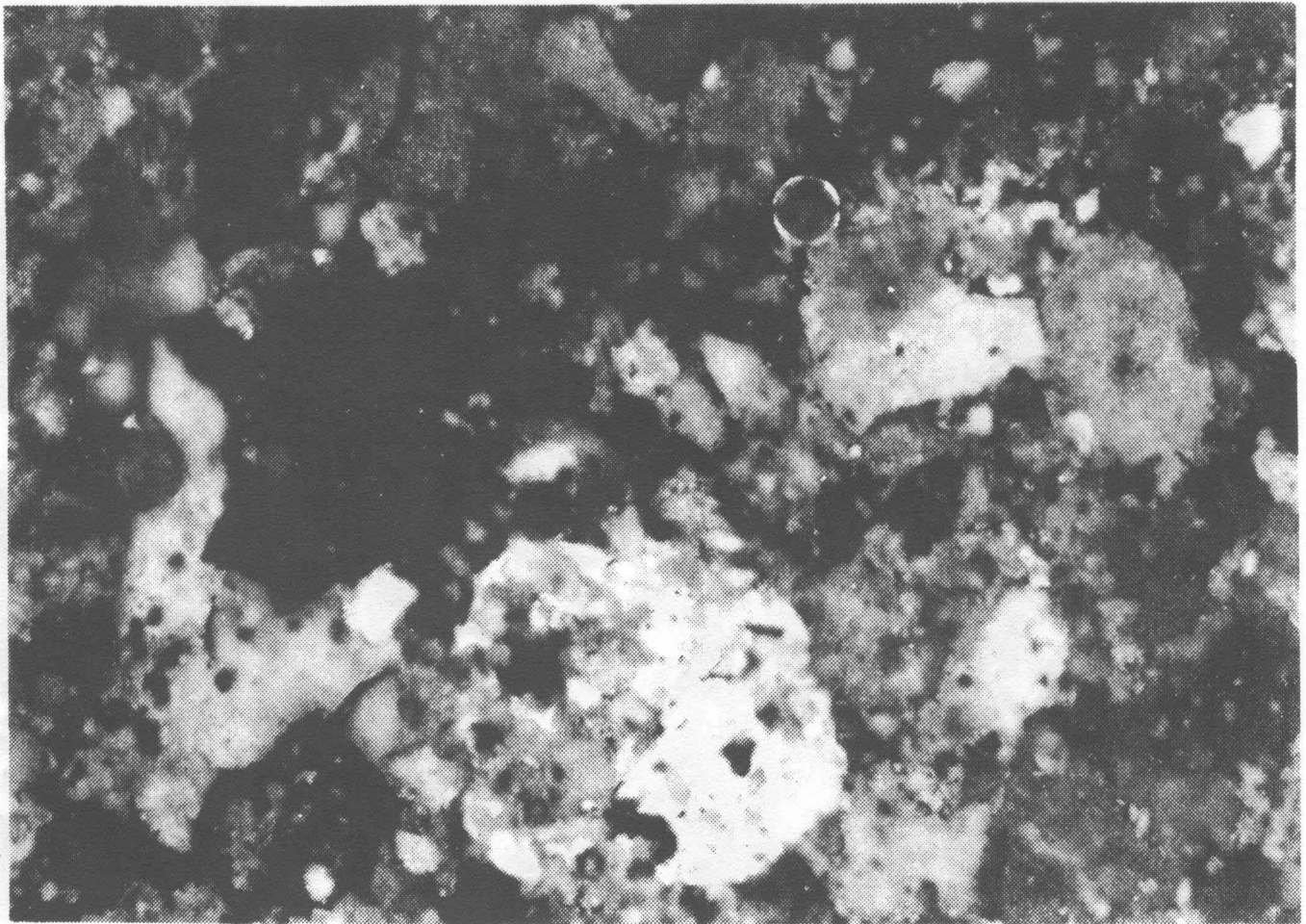


FIG. 4 PHOTOMICROGRAPH OF ASH COLLECTED AT THE ENTRANCE TO THE DUST COLLECTOR OF THE NORFOLK BOILER, MAGNIFICATION OF 100.

1) Chlorine appears to be depositing in both boilers in a rather undefined pattern. The quantity present in most cases is very small.

2) Silica and alumina appear with few exceptions in the same ratio, 2 to 1, respectively. Both appear primarily in composite samples or external layers. This implies that they are probably deposited as entrained particles, once a suitable collecting surface is provided.

3) The sodium and potassium content in the Norfolk deposit varies from about 1 to 5 percent, with a few exceptions. There appears to be a general trend, which indicates that the percentage of alkalis present is inversely proportional to the iron concentration. These specimens have extremely high-fusion temperatures. Similar trends appear in the Long Island deposits with somewhat lower fusion temperatures and slightly higher alkali content.

4) The iron content varied from 12 to approximately 80 percent and, as might be expected, it strongly influenced the increase in fusion temperatures. It should be pointed out that the high iron concentration was not necessarily corrosion product, as the tube surface in the vicinity of the ash sampled was clean and smooth, giving the appearance of unblemished, original tube surface. Furthermore, a very thin buffer layer of powdery material existed between the tube surface and the scale.

5) All the samples contained relatively large quantities of zinc (1.23 to 9.65 percent) expressed as ZnO. Many samples contain lead (1 to 10 percent) expressed as PbO. Lead also appears in relatively large quantities in the German sample. Huch [11] is the only other investigator to report its presence.

6) The calcium reported is unexpectedly low, particularly in the case of the Long Island boiler where

severe fouling was encountered.

7) Phosphorous appears in an irregular pattern and rather low quantities. Therefore, its presence can most likely be considered insignificant.

CORROSION TESTS

Crucible-type corrosion tests were used to supplement the ash analysis data and possibly gain a better understanding of the significance of the presence of some constituents. This sorting type program involved soaking metal specimens in ground ash samples for a period of 135 hr at some given temperature. The errors introduced by using this technique, as well as its inadequacies and shortcomings, were quite apparent from the start. It was selected, despite its faults, as an inexpensive starting point. It was felt this approach was particularly appropriate, in view of the total lack of field data or prior experience.

A total of 25 specimens cut from T-11 stock were used in the test. T-11 was selected, as it was used commercially in the temperature range with which we were concerned. Each specimen weighed approximately 16-20 g, provided about 0.45 sq in. of surface area, and measured 1 by 1/2 by 1/4 in. All specimens, except for the dummy samples, were soaked in about 4 g of ash contained in a number 0 crucible. About 1/4 of the specimens were submerged in the ash, and 3/4 remained exposed to the atmosphere. All the specimens had a ground surface finish. The time of exposure was arbitrarily set at about 135 hr. At the end of the test, each specimen and ash sample was examined, and the test coupons were cleaned first with NaOH and then 8 percent HCl. Dummy specimens were soaked independent of the corrosion test to avoid any possibility of contamination. Heat treated as well as freshly ground specimens were checked under identical conditions to avoid errors, due to a variation in surface condition and to approach actual tube surface conditions.

Tests were run at 500, 600, 750, 850, and 950 F. One sample contained relatively large quantities of zinc, while another contained lead and zinc in somewhat smaller proportions. Samples L-3 and L-4, taken from the inside layer of a deposit removed from the convection gas pass in the Long Island unit, were used in tests run at temperatures of 950 and 750 F. Again, one sample contained relatively large quantities of zinc and lead, while the other contained only relatively large portions of zinc. All samples were high in the alkalis. One series of tests were run using SA-210 coupons soaked in furnace wall samples N-10 and N-13 at 600 F to determine whether the

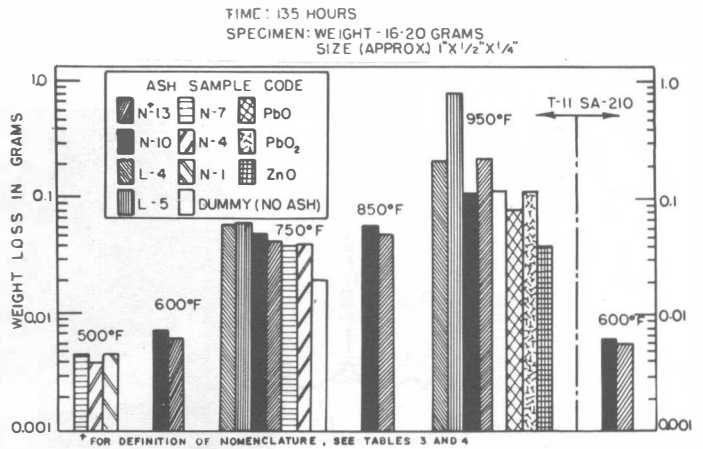


FIG. 5 CORROSION OF T-11 COUPONS SOAKED AT VARIOUS TEMPERATURES FOR 135 HR IN ASH TAKEN FROM REFUSE FIRED BOILERS.

sample was a corrosion product containing portions of the corrosive agent or just ash deposit. The last series of tests were run using PbO, PbO₂, and ZnO at 950 F. The choice of the compounds will become apparent after reviewing the discussion.

The results have been summarized in the form of a bar graph appearing in Fig. 5. Samples N-13, L-3, and L-4, all soaked at 950 F, were the only specimens to experience corrosion. The weight loss of all other descaled coupons did not exceed that which could be attributed to normal oxidation at the corresponding temperatures.

The greatest weight loss was experienced by sample L-3 soaked in ash removed from the Long Island boiler tubes. The ash was noticeably high in lead and zinc. Ash samples N-13 and L-4 produced about the same corrosion effect on T-11 when soaked at 950 F. Both ash samples contain substantial quantities of zinc and alkali. Lead was present, but in minute quantities. In all these cases, the ash showed signs of cohesive bonding, even though the specimen was soaked at temperatures below the initial deformation point. Examination under the microscope confirmed the lack of a liquid phase. Fig. 6 illustrates how the ash could be removed from the crucible as a single unit and yet crumble by the pressure applied by the fingers. The corrosion product consisted of a thin shell of scale that did not adhere to the coupon surface. It also indicates the coupon could be removed gently from the test vehicle leaving the corrosion product and ash intact. The coupon surface showed no visual sign of attack, which suggested that corrosion was possibly caused by a gaseous agent.

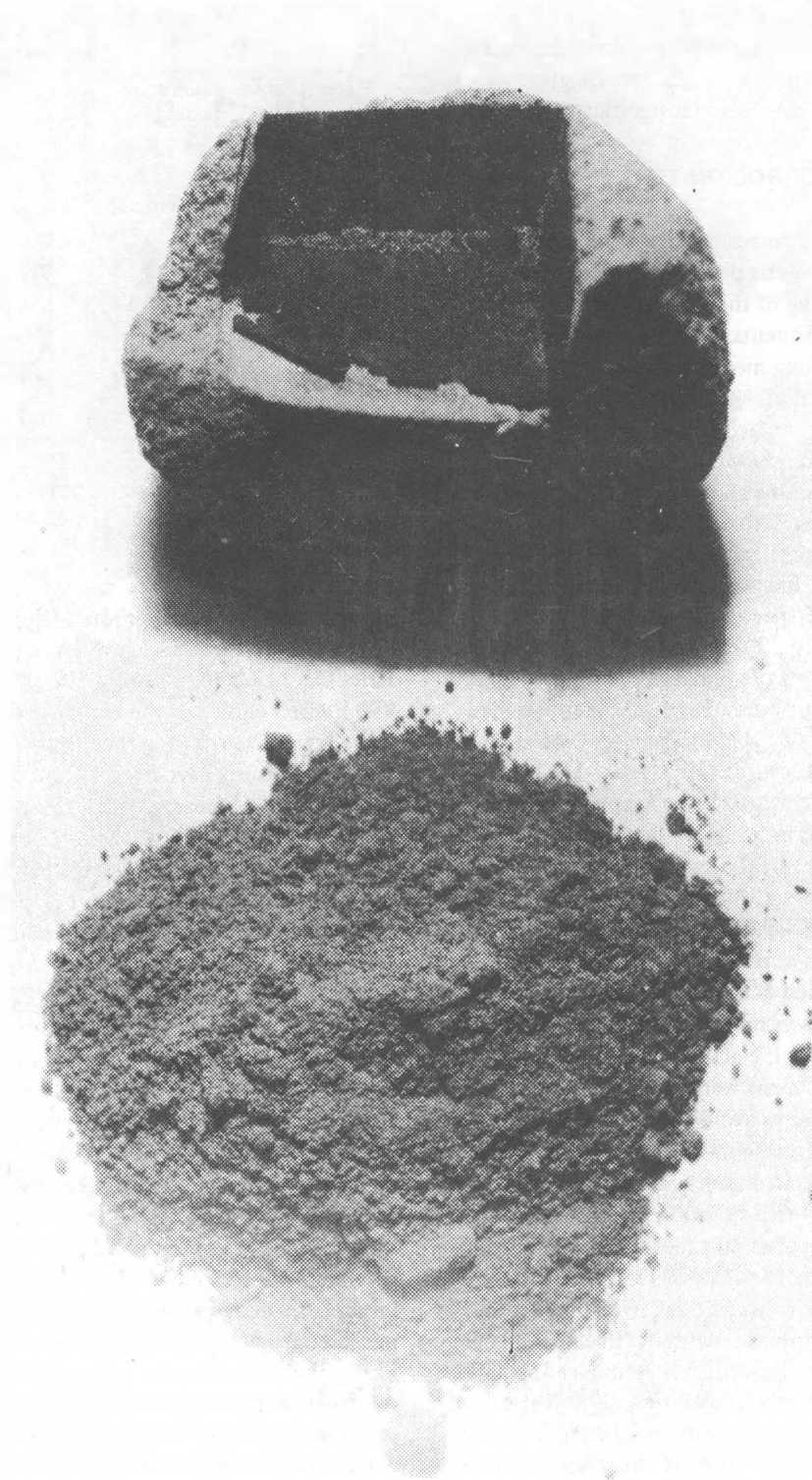


FIG. 6 ASH AND SCALE REMOVED FROM CRUCIBLE
AFTER SOAKING T-11 IN ASH SAMPLE L-3 FOR
135 HR AT 950 F.

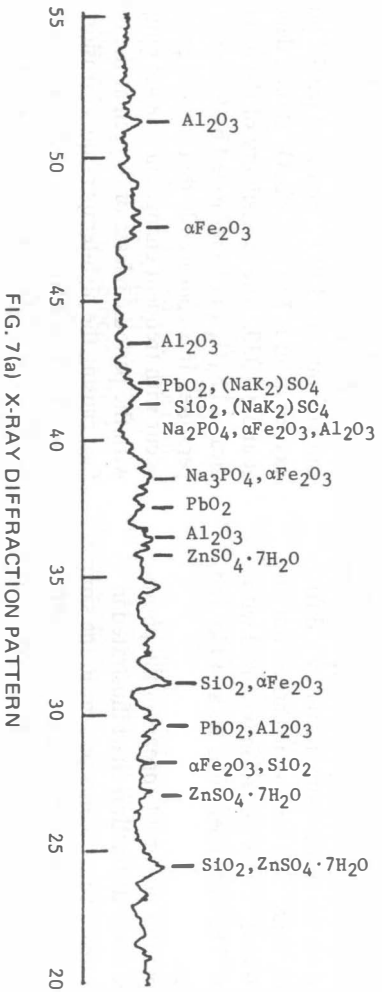


FIG. 7(a) X-RAY DIFFRACTION PATTERN

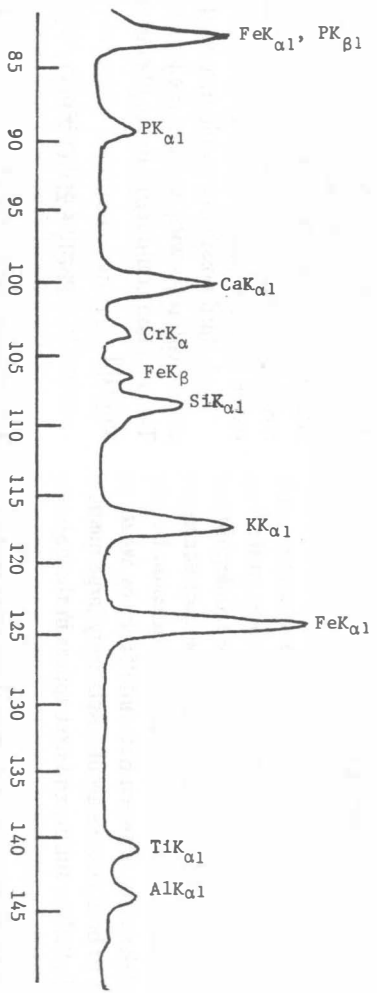


FIG. 7(b) X-RAY FLUORESCENT SCAND 75-145 DEG

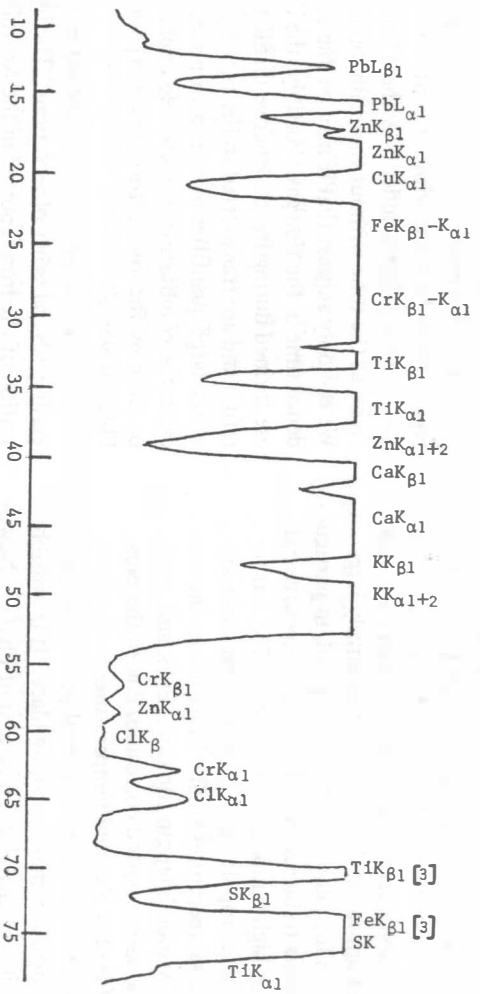


FIG. 7(c) X-RAY FLUORESCENT SCAND 10-75 DEG

FIG. 7 X-RAY DIFFRACTION PATTERN AND X-RAY FLUORESCENT SCAND OF INNER LAYER OF ASH DEPOSIT TAKEN FROM LONG ISLAND BOILER SAMPLE L-3

X-RAY DIFFRACTION ANALYSIS

X-ray diffraction was used in an attempt to determine the phases present in deposit sample L-3. The sample was pulverized and screened through a 325-mesh-size sieve, mounted in the sample holder, and scanned on the spectrogoniometer by a diffractometer technique. The tests were carried out on a G.E. XRD-6 unit. $\text{CuK}\alpha$ radiation was used with a nickel filter. The instrument was set at 40 kv and 20 milliamps.

The pattern produced appears in the photograph of the x-ray diffraction chart illustrated in Fig. 7. The many constituents present in the sample greatly increase the complexity of the x-ray pattern, making it difficult to distinguish which type of lead compounds were present. Unfortunately, the PbO_2 lines were superimposed on the other lines, characteristic of other compounds. It is for this reason that a definite identification could not be made.

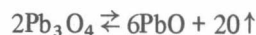
DISCUSSION

Our experimental evidence appears to agree with many of the recent observations made on field trials in Europe. Chlorine occurs in the ash deposits in an irregular pattern. Its presence does not necessarily indicate a corrosible situation. Corrosion begins to take place between 850 and 950 F, by what appears to be a gaseous agent. Relatively large quantities of alkalies, sulfur, and iron appear in the deposits.

In addition to the evidence supporting past experience, we feel we may have contributed a few new factors. Despite the presence of the alkalies, no liquid phase was detected up to 1000 F. There was no obvious relationship between their presence and the corrosion experienced. On the other hand, zinc and lead appear in the deposits in relatively large quantities for minor constituents. Lead, in particular, appears to be associated with the excessive oxidation at high temperatures. Sawyer [28] has reported catastrophic damage of stainless steels at elevated temperatures similar in nature to the corrosion by molybdenum trioxide. Buckland, et al. [31] has also reported corrosion, due to the presence of lead at elevated temperatures.

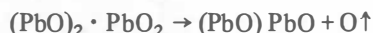
We believe there are several possible ways in which corrosion may be taking place. It is possibly due to the thermal decomposition of Pb_3O_4 . Newby and Dumont [29] have indicated that it decomposes at 932 F, which is certainly in the temperature range of the corrosion problem.

The equilibrium reaction, describing the dissociation of Pb_3O_4 , is as follows:



The dissociation pressure varies with temperature, 5mm at 832 F, 60 mm at 932 F, 183 mm at 1032 F, and 765 mm at 1170 F. Since the partial pressure of oxygen in air is 150 mm, Pb_3O_4 should decompose at about 1030. The reversibility of the reaction indicates Pb_3O_4 can be reformed by lowering the temperature. It is conceivable that a cyclic process may occur with frequent changes in flue gas temperature with the periodic release of oxygen at the tube surface causing the high-temperature corrosion.

Pb_3O_4 is also a common designation for Pb_2PbO_4 or $(\text{PbO})_2 \cdot \text{PbO}_2$. The equilibrium reaction in this case may be described as:



The leading chloride (Matlockite), $\text{PbCl}_2 \cdot \text{PbO}$, is another compound included in Newby and Dumont's test which thermally decomposes in the vicinity of 900 to 1000 F (Table 6). In this case, nascent chlorine, which could be a dangerously corrosive agent, would be released.

A third possibility would involve the reaction of lead chlorides with water at the lower temperature. This reaction could result in the liberation of PbO_2 and HCl.



Either compound would be dangerous, if the temperature were sufficiently high to cause further thermal dissociation.

As in the case of the alkalies, the postulations regarding lead are not without contradictory evidence. One might wonder how these lead compounds arrive at the tube without thermally breaking down. We can only suggest that it may be due to a short residence time in the flue gas. Possibly, the compounds are formed during the destructive distillation of the refuse and are transported to the tube by a portion of the large quantities of excess air present that escapes the combustion process. No explanation can be given by the low-corrosion rate experience with PbO_2 at 950 F.

We feel some comments should be made regarding several other observations. The high concentration of the iron reported in the Norfolk deposit, particularly in the initial layers of the low temperature furnace wall deposits, suggests the presence of corrosion product rather than ash. This possibility

appears to be lessened by the high fusion temperatures of the samples (2800 F), the low temperatures of the collecting surface, and the unblemished conditions of the tube surfaces. It is possible that a portion of the iron oxide contained in this flue gas is reacting with an alkali sulfate, lead or zinc system at the tube surface. It is proposed that, once a buffer layer of some powdery constituent is established at the tube surface, the temperature of the outside surface exposed to flame radiation is raised sufficiently to accommodate a low melting constituent deposited from the flue gas. It is further proposed that the iron, reacting with the low melting constituent and possibly SO_3 at the gas liquid interface, proceeds to diffuse through the liquid film to the cooler surface where it freezes, forming a high melting scale. Such a reaction may proceed, until it is upset by rising temperatures at the liquid vapor interface or deposition of large quantities of silica and alumina. It is possible that the constituents responsible for corrosion and tube fouling selectively react with either iron oxide provided by the flue gas or the tube surface depending upon the tube-metal temperature.

Examination of deposits under the microscope indicate ash collected in high temperature gas zones was comprised of heterogeneous spheres approximately 50 microns in diameter or less. The population density of a given size appeared to vary with diameter. Generally, the particles had a frosted surface, and they frequently consisted of an agglomerate of smaller particles. This implied some sort of surface reaction was taking place on a once-used particle. Ash collected in the cooler gas zones generally consisted of larger size particles which frequently include a large percentage of clear, unattached spheres. The implication here was that the particles have passed through the boiler without reacting with any gaseous phase. The observations made here infer that the high melting constituents, such as CaO , SiO_2 , Al_2O_3 , and so forth, are fused or liquid at one point, but arrive at the tube surface in a dry state by a diffusion mechanism, as opposed to inertial impact. At the surface of the tube or deposit, where the residence time may be extended, they react with the more volatile constituents, forming compounds with somewhat lower melting points. If this were not the case, one could expect a larger concentration of large diameter particles in the hotter zones. It would also seem doubtful that any ash would escape without reacting with the more volatile constituents.

From the observations made of the physical characteristics of the deposit, it might be concluded that:

1) Little can be done in the way of mechanical rearrangement in the convection passes to reduce the deposit problem without a corresponding loss in heat transfer. The same parameters that govern heat transfer govern mass transport.

2) Some benefits may be gained by increasing the portion of the heat transfer by radiation and, at the same time, reducing the mass transport by using adequate ventilation with uncontaminated air. This would require carefully scrutinizing the use of secondary air.

3) Reducing furnace gas velocities may be helpful from an air-pollution point of view by allowing the larger particles to settle out. However, it will do little to alleviate the ash deposit problem.

CONCLUSIONS

It appears that we may be at the beginning of new ash deposit and corrosion problems. Definite analogs exist between firing refuse and fossil fuel. However, there are also many contradictions that cause us to question the credibility of extrapolating this experience directly. Field and laboratory data are lacking, probably due to the infancy of the problem and the unpredictable nature of the fuel. Recent experience indicates that we should be just as suspicious of such minor constituents as zinc and lead as we are of the alkalis and chlorides. To begin to unravel this complex problem, more field data, completely describing the deposit material and corrosion product, are necessary. Once this is done, further laboratory investigations can be made to ascertain the effects of isolated parameters.

ACKNOWLEDGMENTS

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