CHLORINE MASS BALANCE IN THE COMBUSTION OF REFUSE-DERIVED FUEL

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ABSTRACT

Chlorine mass balance studies have been carried out in the combustion of refuse-derived fuel (RDF) using the combustor of the NBS multikilogram capacity flow calorimeter. This arrangement allows for a more accurate examination of the combustion chemistry of RDF than is possible in a real-world incinerator. The changes in the distribution of chlorine between the volatile and the nonvolatile combustion products caused by the addition of lime to the RDF are discussed.

INTRODUCTION

The purpose of this study is to determine the distribution of chlorine between the reaction products and to obtain chlorine mass balances for the combustion of refuse-derived fuel (RDF). Three main questions are under consideration:

(a) How is chlorine in a RDF sample distributed during combustion into volatile and ash components?

(b) How does the presence of lime (calcium hydroxide) in the input RDF sample influence the distribution of chlorine in the combustion products?

(c) Is there a difference between the distribution of chlorine in the combustion products when the combustible fraction of RDF contains either an inorganic chlorine or an organic chlorine compound?

The answers to the first and last questions are basic to understanding the transfer of chlorine in the combustion process. The second question is motivated by a study [1] which shows that lime is a suitable binder for RDF to produce densified pellets which are stable and storable.

This chlorine mass balance study is part of a research effort to develop a quantitative understanding of the fundamental processes responsible for the formation and destruction of chlorinated organic compounds found during combustion of municipal solid waste. In a previous study [2], work was initiated on the problem of identifying the optimal operating conditions to control or eliminate the formation of chlorinated organic compounds. The latter study showed that the incomplete combustion characteristics of synthetic RDF doped with polyvinyl chloride (PVC) can be studied in a calorimeter [3] designed to burn 2.5 kg (6 lb) pellets of RDF in 100 mol % oxygen. The synthetic RDF was an 80/20 mass % mixture of cellulose/sand. The doped synthetic RDF contained 1 mass % of PVC. The calorimeter was modified to permit the use of air with varying concentrations[1] of oxygen, rather than 100 mol % oxygen, and to allow sampling of the product gas stream with a Modified Method 5 Sampling Train.

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[1] Gas concentrations are by volume (e.g., here mol % = volume %, ppm by volume) and are on a dry basis.

In the present work, the combustor of the calorimeter is mounted outside the calorimeter proper to simplify assembly. The operation and design were modified in an attempt to have the option of burning a kilogram-size pellet of synthetic or real RDF for one hour in 21 mol % oxygen (air) under complete as well as incomplete combustion conditions. The complete combustion conditions that were sought consisted of a total hydrocarbon concentration (THC) of <10 ppm, a CO concentration of <100 ppm, and a carbon content in the ash of <0.1 mass %. The condition of 1 hr of burning is the approximate time needed to obtain a reasonable detection sensitivity for chlorinated organic compounds with a Modified Method 5 Sampling Train.

We did not achieve the complete combustion condition for CO except for cellulose/sand mixtures, as is discussed later. A single kilogram-size pellet was burned per experiment (e.g., batch mode) in excess air or air enriched with oxygen.

In the following discussion, changes in the combustor hardware and operation are described in the section called Combustor Development. The extent to which the complete combustion conditions defined above were achieved, as well as a summary of some features of the combustion runs, is given in Combustor Operation, which is the second part of Combustor Development. Combustion pellet preparation, ash preparation, cleaning procedures, and methods of analysis are described in Experimental Procedures. The discussion of results is given in Results of the Chlorine Mass Balance Study and is divided into five parts. The results of experiments with real RDF and real RDF with binders are described in the first four parts. The topics are: the composition of the RDF with binders, the distribution of the total chlorine in the combustion products of RDF, the total and water-soluble chlorine contents of the RDF and its ash, and the actual chlorine mass balance in terms of the total chlorine "in"/"out" ratios. The fifth part of the discussion of results is concerned with the results of experiments with synthetic RDF doped with an inorganic chlorine or an organic chlorine compound. A summary of the main results of the chlorine mass balance study is given in Summary and Conclusions.

COMBUSTOR DEVELOPMENT

Hardware Modifications

The components of the present combustion apparatus are those described in an earlier works [2, 3]. The following hardware changes were made:

(a) As shown in the cross section of Fig. 1, the combustor, C, and its enclosure, F, have been removed from the multikilogram-capacity flow calorimeter and are suspended vertically in a support frame, H, on a deck, G. The combustor enclosure is required to maintain a gas tight seal around the combustor which is operated at a positive pressure 7–21 kPa gauge (1–3 psig).

(b) The product gas flows out of the combustor to a 10-turn cooling coil and then to a water collector; both components are now submerged in a water bath rather than in the calorimeter vessel. The water bath is near room temperature. The product gas then flows through a cold trap submerged in a bath held below −5°C (23°F), a charcoal trap, and then to the laboratory exhaust. The water vapor from the combustion is condensed in the water collector and cold trap and is actually a dilute hydrochloric acid solution.

(c) To achieve the complete combustion conditions cited earlier, efforts were focused on increasing the combustion flame temperature. Electrical heaters were wound on the distribution tubes of all five of the horizontal tiers of nozzles in the combustor wall that supply oxidant gas below, around, and just above the sample.

(d) Radiative heat loss from the combustion zone was reduced by adding a baffle, D of Fig. 1, with a 150 mm (6 in.) port about 510 mm (20 in.) from the bottom of the combustor. The space between the combustor and its enclosure was packed with alumina and silica wool insulation, E, from the level of the baffle downwards to reduce heat transfer by radiation and convection.

(e) The product gas is monitored, as before [2, 3], for THC content as it leaves the combustor and the concentrations of CO_2, CO, H_2O, and trace components (down to ppm) as it leaves the cold trap. Oxygen detectors monitor the input oxidant gas supply and the product gas stream.

Combustor Operation

Complete combustion conditions were finally obtained for undoped synthetic RDF consisting of 80 mass % cellulose and 20 mass % sand by adjusting the oxidant gas supply so that it did not quench or starve the combustion. The combustion is quenched if the CO concentration increases when the flow rate is increased, and the combustion is starved when the CO increases when the flow rate is decreased. Complete combustion conditions were maintained for an hour by burning a 5 kg (11 lb) rather than a 2–3 kg (4–7

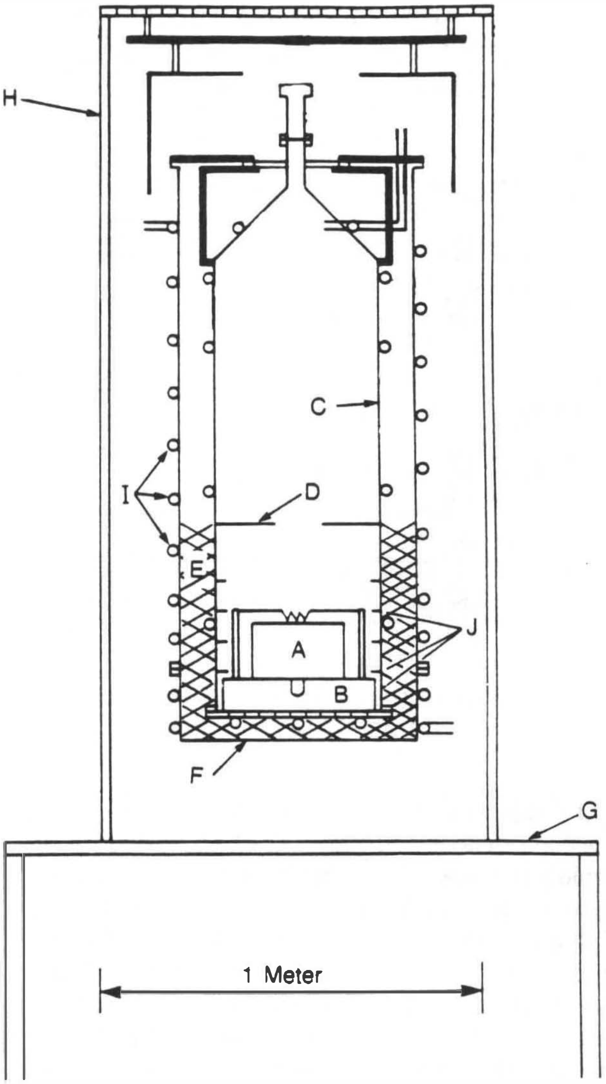

FIG. 1 NBS COMBUSTOR
(A) Sample; (B) Ash Pan With Sample Grate; (C) Combustor; (D) Baffle; (E) Insulation; (F) Combustor Enclosure; (G) Deck; (H) Support Frame; (I) Cooling-Water Coils; (J) Oxidant Gas Nozzles

lb) sample and by minor adjustments of the flow of gas to the various tiers.

CO concentrations of less than 100 ppm could be obtained in cellulose experiments but not with other types of synthetic RDF or real RDF. The lowest practical CO level was 1000 ppm and this level could only be obtained if the oxygen concentration was greater than 21 mol %. However, the THC content could be kept below 10 ppm (as methane) and the carbon content of the ash less than 0.1 mass %.

In a typical combustion run, the sample pellet is ignited and burned in 50 mol % oxygen for about 10–15 min, called the ignition period. The oxygen concentration is then changed over a period of 2–5 min to the minimum oxygen concentration needed to keep the CO concentration below 1000 ppm, and is held constant for the rest of the run. The burn period begins after the oxygen concentration is constant. Flow rates to the various tiers of nozzles are adjusted to maintain the CO concentration less than 1000 ppm. The burn period ends when the CO concentration begins to rise, which occurs approximately 45 min prior to the end of combustion. The CO concentration rises to a peak of 1000 to 10,000 ppm while the CO_2 concentration decays. During this time, referred to as burnout, the THC content remains constant and less than 10 ppm. The CO peak during burnout cannot be eliminated or substantially reduced by either a change in flow rates or oxygen concentration.

About 30% of the combustible fraction of the sample is burned in the ignition period, 60% in the burn period, and about 10% during burnout. The CO and THC concentrations usually peak when the oxygen concentration is changed at the beginning of the burn period. For a run with cellulose/sand, the peak is of the order of 1000 ppm CO and 170 ppm THC content. After the oxygen concentration is adjusted to the minimum level needed to keep the CO concentration less than 1000 ppm in the burn period, the THC content remains less than 10 ppm. The CO_2 production decreases about 50% (e.g., from 40 to 20 mol %) during the burn period for cellulose/sand mixtures but only about 25% for RDF.

A summary of the sample compositions of the various materials studied in the chlorine balance work is given in Table 1. The first column contains the number of the experiment for use with other tables. The second and third columns describe the composition of the samples[2]. The fourth column lists the mass % of the ash and the fifth column describes the nature of the ash.

Some of the combustion characteristics of the materials in Table 1 are summarized in Table 2. The first and second columns correspond to those of Table 1. The third column lists the pellet mass and the fourth column contains the oxygen concentration used after the ignition period. The fifth column contains the length of the burn period. For "atypical" combustions,

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[2] Compositions and ash contents for runs 6 through 16 are given in more detail in the section on results of the chlorine mass balance study.

TABLE 1 SAMPLE CHARACTERISTICS

(1)	(2)	(3)	(4)	(5)
Run	--------- Initial Sample ----------- Type	Composition[a] (mass%)	-------Ash------ Amount[b] (mass%)	Type
	Synthetic RDF:			
1	Cellulose/Sand	80/20	20	loose[c]
2	Cellulose/Sand/PVC	79.9/20/0.1	20	loose
3	Newsprint/Sand	86/14	15	loose
4	Newsprint/Sand/PVC	84.3/14/1.7	15	loose
5	Newsprint/sand/NaCl	84.5/13.9/1.6	15	loose
6	Mag print/water	96.6/3.5	22	cake[d]
7	Mag print/water/PVC	94.9/3.5/1.7	22	cake
8	Mag print/water/NaCl	94.4/4.0/1.6	23	cake
	Real RDF:			
9	Ames RDF	100	19	clinker[e]
10	Ames dRDF	100	20	clinker
11	Ames dRDF	100	21	clinker
12	Ames dRDF	100	19	clinker
13	Ames RDF/com. lime[f]	99/2	22	part cake[g]
14	Ames RDF/mixture[h]	95/5	24	part cake
15	Ames RDF/com. lime	93/7	28	cake
16	Ames RDF/ar lime[i]	77/23	38	cake

[a] As received or prepared; dRDF/RDF with binder on dry basis.
[b] Dry basis.
[c] Ash fragmented and in ash pan.
[d] All ash remains on grate in the shape and size of the original pellet.
[e] About 1/4 of ash forms a clinker on the sample grate.
[f] Commercial lime, assume 98% calcium hydroxide.
[g] Some ash remains on grate, similar to shape of original pellet.
[h] Mixture of 36.1% Portland cement, 39.5% $CaCO_3$, and 24.4% commercial lime.
[i] Analytical reagent, 99% calcium hydroxide.

TABLE 2 COMBUSTION CHARACTERISTICS

(1)	(2)	(3)	(4)	(5)	(6)
Run	------- Initial Sample ------- Type	Pellet Mass (kg) (lb)	Inlet O_2 (mol%)	Burn Time (min)	Outlet CO (ppm)[a]
Synthetic RDF:					
1	Cellulose/Sand	5.3 (11.7)	21	60	$\lesssim$ 100
2	Cellulose/Sand/PVC	3.7 (8.1)	21	45	1000-3000
3	Newsprint/Sand	4.8 (10.6)	21	80	1000-3000
4	Newsprint/Sand/PVC	4.6 (10.1)	35	70	$\lesssim$1000
5	Newsprint/sand/NaCl	4.5 (9.9)	35	60	$\lesssim$1000
6	Mag print/water	4.2 (9.3)	75	200,28[b]	$\lesssim$1000
7	Mag print/water/PVC	4.0 (8.8)	80	100,20	$\lesssim$1000
8	Mag print/water/NaCl	4.1 (9.0)	70	250,34	$\lesssim$1000
Real RDF:					
9	Ames RDF	4.4 (9.7)	31	65	200-2000
10	Ames dRDF	3.2 (7.0)	31	100	2000-3000
11	Ames dRDF	3.9 (8.6)	35	45	500-1500
12	Ames dRDF	5.0 (11.0)	31	28	200-100,000
13	Ames RDF/com. lime[c]	3.2 (7.0)	40	60	700-4000
14	Ames RDF/mixture[d]	3.8 (8.4)	40	90	600-2000
15	Ames RDF/com. lime	4.4 (9.7)	45	160,13	$\lesssim$1000
16	Ames RDF/ar lime[e]	3.9 (8.6)	50	195,0	$\lesssim$1000

[a] by volume, dry gas.
[b] Percent of the burn time immediately following ignition that CO concentration is greater than 1000 ppm; burn time is time from ignition to no CO_2 detection.
[c] Commercial lime, assume 98% calcium hydroxide.
[d] Mixture of 36.1% Portland Cement, 39.5% $CaCO_3$, and 24.4% commercial lime.
[e] Analytical reagent, 99% calcium hydroxide

the fifth column is the time from ignition to the end of the CO_2 production and, after the comma, the percent of the time following ignition during which the CO concentration is greater than 1000 ppm. The sixth column contains the range of the CO concentration in the product gas during the burn period that was obtained with the oxygen concentration in the fourth column. The "atypical" combustions are runs 6, 7, and 8, in which magazine print is burned, and runs 15 and 16, in which RDF with large amounts of binder is burned. These combustions are discussed below.

In Table 2, run 1 is the last of the seven experiments made with cellulose/sand mixtures during the course of the modification of the combustor hardware and operation. Doping this mixture with PVC to a level of only 0.1 mass %, run 2, resulted in a tenfold increase in CO concentration during the burn period. Presumably this is due to the tendency we have observed of plastics to melt, vaporize, and burn rapidly. Replacement of the cellulose by newsprint in run 3 also resulted in a tenfold increase in the CO concentration. The newsprint has an ash content of 1 mass %. The large CO concentration may be due to the printer's ink, lignins in newspaper, or both.

The ash in the three runs with synthetic RDF containing glossy magazine print, runs 6, 7, and 8, closely resembled the original pellet both in shape, original dimensions, and color (off-white). Both the CO_2 and CO production differed from that of a typical combustion run described above. The CO_2 production rises rapidly to a peak a few minutes after ignition and then decays exponentially thereafter. The CO concentration follows the same pattern. At the end of the CO_2 production, the CO level is well under 100 ppm. There is no broad rise of the CO production corresponding to burnout in the "typical" combustion. Our preliminary interpretation is that the reaction zone moves inward leaving behind a porous "ash pellet." As the ash layer increases, the flow of the oxidant gas to the enclosed reaction zone decreases. CO production is small, even though CO_2 production (and, hence, heat production) is low, because the ash layer, being a good insulator, maintains the temperature of the combustion zone.

The RDF and dRDF with and without binder studied in this work were supplied by North Texas State University/Argonne National Laboratory (NTSU/ANL). Details of the combustion pellet preparation are given in the next section in the description of the chlorine balance studies. All dRDF and RDF, with the exception discussed below, was milled to −3 mm (−⅛ in.) particle size[3] prior to pressing a combustion pellet.

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[3] In this work, the particle size means 95 mass % passes through a square mesh of the designated size.

About one-quarter of the ash from runs 9, 10, and 11 remained on the sample grate. Fused soft glass was present but the amount was much less than that produced in previous combustions in this laboratory in 100 mol % oxygen using different RDF.

Run 12 provided an assessment of the chlorine balance procedures under incomplete combustion conditions. The combustion pellet was prepared by compressing 5 kg (11 lb) of the dRDF pellets; the surface of the resulting large combustion pellet was porous. The CO_2 production was about double that of the previous three runs and the CO concentration rose to 100,000 ppm at 6 min. after ignition in spite of the use of the maximum flow (300 slm, 140 scfh) of oxidant gas. The CO concentration was less than 100 ppm for the last 10 min of the burn period; burnout started 45 min after ignition. An appreciable fraction of the ash remained on the sample grate. What was remarkable was that all of the ash had the form of pellets similar to those of the original dRDF. This was particularly surprising to us because the dRDF contained no binder. The dRDF pellets retained their general shape under the force of 534 kN (120,000 lbf), which was used to form all the combustion pellets.

The combustion of the dRDF/RDF with binder produced ash that was progressively more cohesive as the binder content increased. The fraction of the ash remaining on the sample grate increased from about one-third of the total ash in run 13 to nearly all the ash in run 16. The ash of runs 15 and 16 had the same shape as the original pellet. In contrast to runs 13 and 14, runs 15 and 16 were "atypical" combustions similar to runs 6, 7, and 8, as mentioned above.

Our general observations concerning the combustion control aspect of the experiments were as follows:

(a) The CO and THC concentrations are not always coupled. They are not coupled during burnout but they appear to be coupled during "upsets" caused by changes in oxygen concentration and, sometimes, with changes in flow rates.

(b) When burned in the form of a pellet, newsprint produces more CO than cellulose when each is mixed with sand. Magazine print does not burn as rapidly as cellulose mixed with sand, because the ash from magazine print is cohesive and impedes the access of oxidant gas to the reaction zone. Also, sand is not fused (fusion at about 1700°C, 3100°F) in a cellulose combustion and falls away from the unburned cellulose into the ash pan below the sample grate.

(c) The CO production in the combustion of RDF is greater than the CO production in cellulose/sand mixtures for the same oxidant gas. This may be due to the presence of plastics in the RDF and the fusion of some of the glassy components of the ash in the RDF.

EXPERIMENTAL PROCEDURES FOR CHLORINE MASS BALANCE STUDY

Combustion Pellet Preparation

Synthetic RDF mixtures were prepared by first milling the separate components, if required, to a particle size of −3 mm (−⅛ in.). The cellulose, sand, powdered PVC, and NaCl were used as-received. The newsprint was the "Washington Post" with the exclusion of colored and glossy print. The newsprint was reduced using a Williams Hammer Mill (Model GP-1512, Williams Patent and Crusher and Pulverizer Co.)[4] with a 3 mm (⅛ in.) screen. The glossy magazine print was obtained by using "Waste Age" magazine. It was first processed with a document shredder and then with a Wiley Mill (No. 4, Model S-60982, Sargent-Welch Co.) having a 2 mm (0.080 in.). screen.

Mixtures were prepared by first homogenizing a known mass of the main combustible component (cellulose, newsprint, or magazine print) in a large vee-blender having an intensifier. A grab sample of about 100 g (0.2 lb) was removed for later analysis and weighed. Known masses of the remaining minor[5] components were then added, the mixture was blended, and a 100–200 g (0.2–0.4 lb) grab sample of the mixture was removed for later analysis. The remainder was poured into a die and pressed into a pellet using equipment described earlier [3]. Grab samples of the pure minor (by mass) components were also used for analysis.

Five dRDF samples, two without binder and three with binders, and one sample of the Ames RDF used (by NTSU) to prepare the dRDF were supplied by NTSU in the fall of 1985 shortly after the dRDF was prepared. The dRDF consisted of pellets 20 mm (¾ in.) in diameter and 25–50 mm (1–2 in.) in length. The RDF was −150 mm (−6 in.) particle size and was obtained by NTSU from Ames, Iowa, in mid July, 1985. The samples were stored in a walk-in refrigerator until one or two days before the combustion pellets were prepared.

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[4] The commercial sources cited in this paper are included to adequately describe the experimental procedures. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.

[5] Water in the amount of 3.5–4% of the mass of the milled magazine print was added to prepare pellets without cleavage planes.

All the RDF and dRDF samples were reduced to -3 mm ($-\frac{1}{8}$ in.) particle size or less using the Williams Hammer Mill with a 3 mm ($\frac{1}{8}$ in.) screen except for the dRDF of run 12, as discussed in the previous section. The milled materials were homogenized in the vee-blender, a 100–200 g (0.2–0.4 lb) grab sample was removed for analysis, and pellets were pressed as for the synthetic RDF. An analysis sample for run 12 was obtained by selecting pellets of dRDF at random, and the pellet was formed by placing the material directly into the combustion pellet die. The material for run 16 was prepared by adding a known mass of analytical grade calcium hydroxide to the milled and blended RDF in the vee-blender and then proceeding as with the synthetic RDF.

Ash Preparation

The ash from the synthetic RDF containing cellulose and newsprint and the ash from the dRDF runs was reduced in particle size using a ZM-1 mill (Model ZM-1, Brinkmann Co.) and homogenized by stirring. The ash from the runs with magazine print and the lime-RDF mixture was reduced in particle size and homogenized using a mullite ball mill. The ash from the RDF and dRDF without binder had appreciable amounts of fused soft glass, etc. Grab samples of the ash were used for laboratory analysis.

Cleaning Procedures

The inside of the combustor, cooling-coil, collector, and cold trap were washed with tap water at 46°C (115°F). The chlorine content of the washings of the combustor and cooling-coil were necessary for the chlorine balance measurements; they contained from 6% to 28% of the total chlorine of the combustion products.

Analysis

Samples of the components and the final mixture of each synthetic RDF, the components and the final mixture of the lime-RDF, and the other dRDF and RDF materials were analyzed for total chlorine, water-soluble chlorine, residual moisture, and ash (where needed). The chlorine was determined according to ASTM standard method E 776-81, "Forms of Chlorine in Refuse-Derived Fuel", except that the titration method used for water-soluble chlorine was that used in EPA method 325.3 [4]. Moisture and ash were determined by ASTM standard methods E 790-81, "Residual Moisture in a Refuse-Derived Fuel Analysis Sample," and E 830-81 "Ash in the Analysis Sample of Refuse-Derived Fuel," respectively. Chloride was determined in aliquots of the collector condensate, coldtrap condensate, and the washings from the combustor and cooling coil from each experiment using EPA method 325.3. All chemical analyses were performed by Gascoyne Laboratories, Inc., Baltimore, Maryland.

Checks on the total and water-soluble chlorine analyses of selected ash samples were carried out by Spots, Stevens, and McCoy, Inc., Reading, Pennsylvania in conjunction with determination of the carbon and hydrogen content of these ash samples. (The chlorine measurements of the two laboratories were in agreement.) Chlorine was determined according to ASTM standard method E 776-81; carbon and hydrogen were determined by ASTM standard method E 777-81, "Carbon and Hydrogen in the Analysis Sample of Refuse Derived Fuel."

RESULTS OF CHLORINE MASS BALANCE STUDY

Composition of RDF with Binders

Compositions of the combustion pellets of Ames RDF without and with binders are given in Table 3. The first column identifies the run number. In the second column, d indicates that the material for the combustion sample was obtained from densified RDF pellets prepared by NTSU; the NTSU run number in Ref. [1] is in the parentheses. The letter f indicates that the material was obtained from RDF fluff, -150 mm (-6 in.) particle size, that had not been densified. The third column contains the measured moisture content of the milled material, and the fourth column is its ash content on a dry basis.

The fifth column contains the type of binder. The sixth column indicates the % of binder present on a dry basis according to the composition at preparation prior to densifying the RDF by NTSU or, in run 16, prior to pressing the combustion pellet. The seventh column is the amount of binder calculated from the ash content, as discussed below. The eighth column contains the calculated mass percent of calcium hydroxide present assuming that the commercial lime contains 98% calcium hydroxide, that the calcium oxide in the cement was inactive, and that the $CaCO_3$ in the mixture was active (i.e., it calcines under combustion conditions).

The calculated binder content in the seventh column of Table 3 serves as a check to indicate that gross

TABLE 3 COMPOSITION OF AMES RDF WITHOUT AND WITH BINDERS

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Run	RDF Type	Water	Ash	Binder type	Binder amount prep.[a]	Binder amount calc.[b]	$Ca(OH)_2$ calc.[c]
		(m%,ar[d])	(m%,d[e])		(m%,d)	(m%,d)	
Ames RDF without Binder:							
9	f[f]	6.50	18.61	--------	0	0	0
10	d(38)[g]	8.27	20.41	--------	0	0	0
11	d(37)	5.34	21.34	--------	0	0	0
12	d(38)	9.79	19.11	--------	0	0	0
Average			19.87				
Std. Dev.			1.24				
Ames RDF with Binders:							
13	d(31)	6.78	22.03	com. lime[h]	2.2	2.7±2.4	2.2
14	d(53)	4.79	24.31	mixture[i]	4.8	5.5±2.3	2.6
15	d(34)	5.64	27.76	com. lime	7.1	9.9±2.2	7.0
16	f	2.04	38.43	ar lime[j]	22.8	23.2±1.9	22.8

[a] As given by preparation.
[b] Calculated from $B=A-(19.87 \pm 1.97)x(1-B/100)$ where B is the mass % binder and A is the mass % ash, both on a dry basis.
[c] As calculated from preparation.
[d] Mass %, as-received basis.
[e] Mass %, dry basis.
[f] RDF, -150 mm(-6 inch) size.
[g] dRDF, (xx) is NTSU run number.
[h] Commercial lime, assume 98% calcium hydroxide.
[i] Mixture of 38.1% Portland cement, 39.5% $CaCO_3$, and 24.4% commercial lime.
[j] Analytical reagent, 99% calcium hydroxide.

TABLE 4 CHLORINE DISTRIBUTION IN PRODUCTS AMES RDF AND AMES RDF WITH BINDER

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Run	Sample RDF Type	Binder type	Binder amount prep.[a]	$Ca(OH)_2$ calc.[b]	Total Cl "out"	Percent of Chlorine in Ash	Condensate	Wash
			(m%,d)	(m%,d)	(m%,d)	(%)	(%)	(%)
Ames RDF without Binder:								
9	f[c]	--------	-----	--	0.39	11	80	9
10	d[d]	--------	-----	--	0.43	8	78	14
11	d	--------	-----	--	0.40	17	75	8
12	d	--------	-----	--	0.47	13	59	28
Average					0.42	12	73	15
Std. Dev.					0.04	4	10	9
Ames RDF with Binders:								
13	d	com. lime[e]	2.2	2.2	0.28	26	66	8
14	d	mixture[f]	4.8	2.6	0.40	35	57	8
15	d	com. lime	7.1	7.0	0.39	48	46	6
16	f	com. lime[g]	22.8	22.8	0.31	72	22	6

[a] As given by preparation.
[b] As calculated from binder preparation.
[c] RDF, -150 mm (-6 inch) particle size.
[d] dRDF.
[e] Commercial lime, assume 98% calcium hydroxide.
[f] Mixture of 36.1% Portland cement, 39.5% $CaCO_3$, and 24.4% commercial lime.
[g] Analytical reagent, 99% calcium hydroxide.

changes in binder content (i.e., in excess of 2 mass %) have not occurred between preparation of the dRDF by NTSU and the pressing of a combustion pellet at NBS. It is the measured ash content minus the average ash contributed by the RDF without binder. It is assumed that the combustion reaction does not alter the total mass of the lime and ash of the RDF by, for example, volatilization of binder, increased binding of chlorine, or chemical interaction between the binder and RDF ash. The average ash in the RDF without binder is 19.87%, and the standard deviation is 1.24%. The corresponding imprecision at the 95% confidence level in the calculated binder content is given after ± in the seventh column. The calculated and preparation binder contents agree within the imprecision limits except for run 15; the disagreement in this case is not thought to be significant.

Chlorine Distribution in Products

The distribution of the chlorine in the products in the chlorine balance study of the Ames RDF without and with binder is given in Table 4. The first through fifth columns are the first, second, fifth, sixth, and eighth columns, respectively, in Table 3. The sixth column is the total chlorine "out" concentration which is the total chlorine "out" divided by the dry mass of the pellet. The total chlorine "out" is the sum of the total chlorine in the ash, the chloride in the condensate in the collector, the chloride in the condensate in the coldtrap, and the chloride in the washings from the combustor and the cooling coil. The percent of the total chlorine in the ash, in the combined condensate of the collector and the cold trap, and in the washings are given in the seventh, eighth, and ninth columns, respectively. For example, in run 13, the sum of the total chlorine in the ash, condensate (from collector and coldtrap), and washings divided by the dry pellet mass was 0.28 mass %. The ash contributed 26% of this total chlorine "out" concentration, the condensate contributed 66%, and the washings contributed 8%. The total chlorine "out" concentration is obtained from combustion of the sample in the NBS flow combustor and analysis of the total chlorine of the products.

The total chlorine "in" concentration, which is listed in column 4 of Table 5 and is discussed below, is obtained from combustion of a representative gram-size sample (removed from the parent material) in a bomb calorimeter and analysis of the products. The comparison of the "out" and "in" values is given in the section Total Chlorine "In" and "Out".

The average and standard deviation of the distribution of the percentages of chlorine in the combustion products of the RDF without binder are given in the fifth and sixth rows of data in Table 4, respectively. The percentages for the ash, condensate, and washings

TABLE 5 CHLORINE DISTRIBUTION IN SAMPLE AND ASH AMES RDF AND AMES RDF WITH BINDER

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Run	Binder		Sample			Ash			Chlorine Balance
	Type	Ca(OH)$_2$ (m%,d)[a]	Total Cl "In" (m%,d)	Water Sol Cl (m%,d)	WS Cl / Total Cl (%)	Total Cl (m%,d)	Water Sol Cl (m%,d)	WS Cl / Total Cl (%)	Total Cl "In"/"Out"
			Ames RDF without Binder						
9	------	--	0.60	0.25	42	0.24	0.12	50	1.54
10	------	--	0.80	0.19	24	0.18	0.14	78	1.86
11	------	--	0.40	0.22	55	0.32	0.10	31	1.00
12	------	--	0.40	0.25	63	0.33	0.23	71	0.85
Average			0.55	0.23	46	0.27	0.15	58	1.31
Std. Dev.			0.19	0.03	17	0.07	0.06	21	0.47
			Ames RDF with Lime Binders						
13	lime	2.2	0.32	0.18	56	0.34	0.34	100	1.14
14	mixture	2.6	0.55	0.16	29	0.58	0.46	79	1.38
15	lime	7.0	0.52	0.33	63	0.69	0.47	68	1.33
16	lime	22.8	0.20	0.16	80	0.54	0.60	111[b]	0.65
Average					57			87	1.13
Std. Dev.					21			16	0.33

[a] Mass % on a dry basis.
[b] A value of 100 was assigned to calculate the average and standard deviation

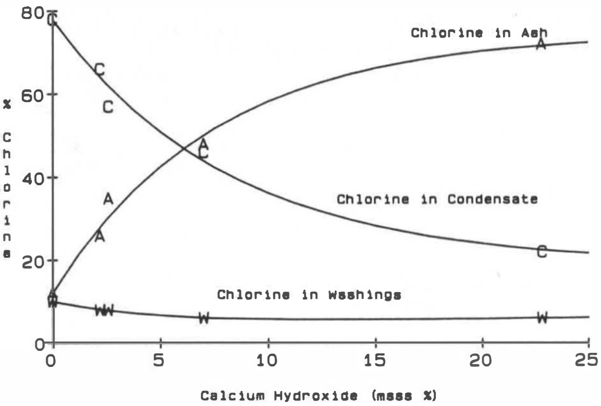

FIG. 2 CHLORINE DISTRIBUTION IN PRODUCTS FROM COMBUSTION OF RDF WITH LIME

of the individual runs agree with the average within one standard deviation except for the percentages for chlorine in the condensates and washings of run 12. Run 12 differed from the other three in that combustion conditions were poor (i.e. Run 12 had a CO concentration much greater than 1000 ppm and a THC content greater than 100 ppm). If run 12 is excluded, the averages of the chlorine distribution with standard deviations are 12 ± 5% for the ash, 78 ± 3% for the condensate, and 10 ± 3% for the washings.

As the lime content of the RDF increases, the percentage of the total chlorine transferred to the ash increases and the percentage of the chloride in the condensate correspondingly decreases. The percent of chlorine retained on the walls of the combustor and the cooling coil is small and varies little with changing lime content. A plot of the values is given in Fig. 2.

Total and Water-Soluble Chlorine

The remaining results of the chlorine mass balance study for the Ames RDF with and without binder are given in Table 5. The fourth and fifth columns contains the total chlorine "In" and water soluble-chlorine content of the combustion sample. The ratios of the water-soluble to the total chlorine of the sample were calculated from the values in the fourth and fifth columns and are listed in the sixth column. The seventh and eighth columns list the total and water soluble-chlorine content of the ash. The corresponding ratios for the ash, which are given in the ninth column, were calculated from the seventh and eighth columns. The ratio of the total chlorine "in" values, given in the fourth column of Table 5, divided by the total chlorine "out" values, given in the sixth column of Table 4, are listed in the tenth column of Table 5.

Comparison of the values of the total chlorine content of the ash of the RDF with binder with those of the RDF without binder in the seventh column indicates that the binding capacity of the ash for the chlorine per unit mass of ash increases as the lime content increases to a limiting value of double that of the ash from the RDF without binder.

Examination of the ratios of the water-soluble to total chlorine (referred to as WS Cl/Total Cl) of the combustion sample and ash in the sixth and ninth columns shows that the ratio for the ash is greater than for the corresponding initial combustion sample for RDF, both with and without binder, except for run 11. The average WS Cl/Total Cl for the ash for RDF with binder is quite high, 87%. There seems to be no noticeable trend in the WS Cl/Total Cl for either the sample or the ash as the lime content increases. The average WS Cl/Total Cl values for the initial sample and ash, either with or without binder, do not differ significantly, at the 95% confidence level, from each other because of large standard deviations, which range from 16% to 21%.

Total Chlorine "In" and "Out"

The ratio of the total chlorine "in" divided by the total chlorine "out" (referred to as In/Out), given in the tenth column of Table 4, is not significantly different from one at the 95% confidence level for the

RDF with or without binder. We attribute the large standard deviation of the In/Out values to the larger variability in the total chlorine "in" values as compared to the total chlorine "out" values. The average and standard deviation of the chlorine "in" values for the RDF without binder are 0.55% and 0.19%. The corresponding values for chlorine "out" are 0.42% and 0.04% from Table 4. That is, the actual total chlorine content values for the material in the different runs are actually quite constant; the chlorine "in" values do not reflect this constancy. Correction of the total chlorine "in" and "out" values for the RDF with binder to a binder free basis (to eliminate variability and bias associated with varying binder content) also shows the same larger variability in the chlorine "in" as compared to chlorine "out" values[6].

We attribute the greater standard deviation in the chlorine "in" values as compared to the chlorine "out" values to the failure to obtain a representative sample of the material in the combustion pellet for chlorine analysis. It is not clear whether this failure occurred primarily in taking the main analysis sample, obtained by a grab, or in taking the individual measurement samples, also obtained through a grab by the chemical analyst. In run 15, the particle size of the remainder of the primary grab sample, left after the first set of analyses, was further reduced in the Wiley mill. Single measurement samples were then obtained using a Brinkmann rotary riffler and supplied to the chemical analyst. This eliminated the sampling ambiguity associated with the chemical analyst taking grab samples. Reanalysis gave total chlorine "in" results with a standard deviation of 0.09%. This is comparable with the smaller standard deviation of the chlorine "out" values, 0.07%, cited above for the RDF with binder (after converting chlorine contents to a binder free basis). Further tests are needed to confirm that riffling will produce a more representative sample and, thus, reduce the variability in the In/Out ratios.

Inorganic Chlorine and Organic Chlorine

Table 6, Inorganic Chlorine versus Organic Chlorine, contains the chlorine mass balance study carried out with magazine print doped with PVC and NaCl. The sample composition is given in the first four rows.

TABLE 6 INORGANIC VERSUS ORGANIC CHLORINE

Run	6	8	7
Sample composition			
Additive, type	None	NaCl	PVC
Additive, mass %, ar[a]	0.00	1.58	1.68
Magazine print, mass %, ar	96.55	94.38	94.86
Added water, mass %, ar	3.45	4.04	3.46
Magazine print Cl content			
Total Cl, mass %[b]	<0.01	0.03 ±0.01	0.01 ±0.01
WS Cl, mass %	0.013±0.001	0.009±0.001	0.01 ±0.01
Residual moisture, mass %, ar	7.09	2.21	2.69
Composite sample Cl content			
Total Cl, in, meas., mass %	-----	1.27 ±0.07[c]	0.91 ±0.02
Total Cl, in, calc., mass %	-----	1.04 ±0.01	1.01 ±0.01
Total Cl, out, mass %	-----	1.04	1.06
WS Cl, meas. mass %	-----	1.33 ±0.01	0.04 ±0.01
WS Cl. calc., mass %	-----	1.01 ±0.01	0.01 ±0.01
Residual moisture, mass %, ar	-----	4.96	4.40
Ash			
Total Cl, mass %	0.15	0.10	0.27
WS Cl, mass %	0.0008	0.0055	0.0058
Chlorine Distribution			
Percent chlorine in			
ash	43	2	6
condensate	49	82	87
washings	8	16	7
Chlorine Mass Balance			
WS Cl/Total Cl, sample[d], %	100	98	1
WS Cl/Total Cl, ash, %	1	1	2
Total Cl, In[d] Total Cl, Out	0.17	1.00	0.95

[a] As received basis.
[b] Dry basis.
[c] Standard deviation.
[d] Based on calculated total chlorine "in".

The total and water-soluble chlorine for the magazine print alone, which are given in the next set of rows, are small which indicates that this magazine print should be an acceptable combustible material for use in a synthetic RDF in future work. The measured and calculated values of the total and water-soluble chlorine contents for the composite sample are given in the third set of rows. The calculated values are computed from composition and data on pure components. The standard deviations of the measured and calculated values are given after the ± sign. All measurements on the composite samples were made using measurement samples prepared from the main analysis sample with a rotary riffler.

We find that essentially all the chlorine from the NaCl was volatilized and, like the chlorine from the PVC, was trapped in the condensate. In addition, the ratio of water-soluble to total chlorine of the ash is small, 1–2% (next to last row, Table 6).

The same result, that water-soluble chlorides are trapped in the condensate, applies to RDF without a binder. From the fifth row of Table 5, one obtains the result that, on the average, the total chlorine content of the ash from the RDF without binder (average of 0.27 mass %) is about the same as the water-soluble

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[6] The average and standard deviation for the chlorine "in" for runs 13 through 16 on a binder free basis are 0.43% and 0.16%, respectively. The average and the standard deviation of the chlorine "out" for runs 13 through 16 on a binder free basis are 0.39% and 0.07%, respectively. (These values are not listed in the tables.)

chlorine content of the corresponding combustion sample (average of 0.23 mass %). This means that between 80% and 90% of the water-soluble chlorine of the original RDF is volatilized (i.e., does not remain in the ash)! This is true whether it is organic or inorganic chlorine. The lower bound of 80% follows from the fact that the mass of the ash is only 20% of the sample mass. The upper bound of 90% would be the result if only the water-soluble chlorine in the original material contributes to the water-soluble chlorine in the ash. In this case, the difference between the total and the water-soluble chlorine would have to be an organic chlorine compound due to incomplete combustion. This seems unlikely because the carbon content of the ash is $\leq 0.05\%$ for run 10 of Table 5 and similar small carbon contents are expected for the ash of runs 9, 11, and 12 of Table 5 and run 7 of Table 6.

SUMMARY AND CONCLUSIONS

The following conclusions were drawn from the chlorine mass balance study:

(a) The total chlorine in the combustion products of RDF is about 12% in the ash, 78% in the condensate, and 10% is trapped on the combustor and cooling coil walls. The total chlorine in the condensate is that which would normally stay in the flue gas.

(b) There is no gross difference in the fraction of water-soluble or total chlorine originally in the RDF that is trapped by the ash. The chlorine from inorganic water-soluble chlorine or organic water-insoluble chlorine compounds ends up almost completely in the condensate.

(c) The lime traps chlorine. The addition of lime to RDF increases the percent of the total chlorine that is trapped by the ash at the expense of the total chlorine trapped in the condensate. The fraction of the total chlorine in the ash that is water-soluble also increases as the lime content increases.

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REFERENCES

[1] Daugherty, K. E., et al. "Densified Refuse Derived Fuel — An Alternative Energy Source." *Proceedings of American Power Conference* 48 (1986): 930.

[2] Domalski, E. S., et al. "Monitoring the Fate of Chlorine from MSW sampling through Combustion. Part II: Combustion Studies." *Chemosphere* 15 (1986): 1355.

[3] Churney, K. L. et al. "A Multikilogram-capacity Calorimeter for Heterogeneous Materials." *J. Res. Nat. Bur. Stds.* 15 (1986): 1339.

[4] Kopp, J. F. and McKee, G. D. "Methods of Chemical Analysis for Water and Wastes." Third Edition. EPA Report No.: EPA-600/4-79-020. NTIS order no. PB84-128677. Springfield, Virginia: U.S. Department of Commerce, National Technical Information Service, March 1983, method 325.3.