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CHLORINE SOURCES, SINKS, AND IMPACTS IN WTE POWER PLANTS

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Abstract

The principal sources of chlorine in the MSW feed to WTE power plants are food wastes (e.g., wheat, green vegetables, melon, pineapple), yard wastes(leaves, grass, etc.), salt (NaCl), and chlorinated plastics (mostly polyvinyl chloride). Chlorine has important impacts on the WTE operation in terms of higher corrosion rate than in coal-fired power plants, formation of hydrochloric gas that must be controlled in the stack gas to less than the U.S. EPA standard (29 ppm by volume), and potential for formation of dioxins and furans. Past Columbia studies have shown that the chlorine content in MSW is in the order of 0.5%. In comparison, chlorine concentration in coal is about 0.1%; this results in much lower HCl concentration in the combustion gases and allows coal-fired power plants to be operated at higher superheater tube temperatures and thus higher thermal efficiencies. Most of the chlorine output from a WTE is in the fly ash collected in the fabric filter baghouse of the Air Pollution Control system. This study examined in detail the sources and sinks of chlorine in a WTE unit. It is concluded that on the average MSW contains about 0.5% chlorine, which results in hydrogen chloride concentration in the WTE combustion gases of up to 600 parts per million by volume. About 45% of the chlorine content in MSW derives from chlorinated plastics, mainly polyvinyl chloride (PVC), and 55% from salt (NaCl) and chlorine-containing food and yard wastes. An estimated 97-98% of the chlorine input is converted to calcium chloride in the dry scrubber of the Air Pollution Control (APC) system and captured in the fly ash collected in the baghouse; the remainder is in the stack gas at a concentration that is one half of the U.S. EPA standard. Reducing the input of PVC in the MSW stream would have no effect on dioxin formation but would reduce the corrosion rate in the WTE boiler.

Introduction

Chlorine is an important element in the feed to Waste-to-Energy (WTE) facilities because a) it accelerates waterwall and superheater tube corrosion, b) it is a chemical constituent of dioxins and furans, and c) hydrochloric gas (HCl) in the stack gases must be controlled below the EPA regulation level (29 ppm by volume or 95% removal of HCl from combustion gases). In this study, we examined the sources of chlorine in municipal solid wastes (MSW) and where this chlorine goes as the MSW is combusted in a WTE facility.

Sources of chlorine in MSW

Because of the presence of food and plant wastes and also some chlorinated plastics, such as polyvinyl chloride, the chlorine content in MSW varies somewhat from location to location. Table 1 (Albina, 2005) shows that chlorine content in three types of MSW varied from 0.47 to 0.72% Cl. In comparison, the chlorine concentration in coal is five to ten times lower, depending on the type of coal, and ranges from 0.05-0.1%Cl.

Table 1 is in good agreement with a detailed analysis of chlorine in the various constituents of MSW, using the chlorine concentrations of each material recommended by Rademakers (Table 2).

Table 1. Chlorine concentration in MSW and in coal (Albina, 2005)

	New York City MSW	**U.S. typical MSW**	**U.K. typical MSW**	**U.S. coals, average**
Total Cl, g/kg	4.71	7.26	4.53	0.4-1
%	0.471	0.726	0.453	0.04-0.1

Table 2. Chlorine concentration in various components of MSW (after Rademakers , 2002)

	% of component in MSW	Chlorine concentration in component, g/kg	Chlorine in MSW, g/kg
Paper	29.4	2	0.59
Plastics	10.4	25	2.60
Organics	34.7	3	1.04
Textiles	4.4	12.5	0.55
Wood	2.7	12.5	0.34
Miss. Combustible	5	12.5	0.63
Glass	4	0.6	0.02
Metals	4.7	0.6	0.03
Miss. Non-Combustible	4.7	0.6	0.03
Total	100		5.82 (0.58%)

On the basis of the data in Table 2, we can calculate the contribution of the various components of a typical MSW feed to its chlorine concentration (Table 3).

Table 3. Contribution of MSW components to its chlorine content

Material in MSW	Percent contribution to chlorine content
Paper	10.1%
Plastics	44.7
Organics	17.9
Textiles	9.4
Wood	5.8
Miss. Combustible	10.7
Glass	0.4
Metals	0.5
Miss. Non-combustible	0.5
Total	100.0%

Chlorine in plastics

Table 3 shows that plastics are a large contributor to the chlorine input to a WTE. The principal chlorinated plastic is polyvinyl chloride (PVC) that is a thermoplastic material formed by the polymerization of the chloroethene (CH_2=CHCl) monomer that contains 56.7% chlorine.

The monomer is formed by reacting chlorine gas, generated by the electrolysis of sodium chloride, with ethylene; this monomer is then polymerized and blended with other chemicals to derive the required properties of the final PVC product.

Polyvinyl chloride is one of the most useful and valuable organic products of the chemical industry. Various additives can be added to PVC. For example, it can be plasticized to produce flexible flooring or unplasticized (PVC-U) for use in piping, window frames and many other applications. More than half of the PVC produced globally is used in construction, such as piping and plumbing fixtures, vinyl siding, windows , doors, etc. It is also used in household items, toys and, in its soft form in clothing , upholstery, flooring, roofing, and cables some of which end up in the MSW stream to WTEs. PVC is a very durable material, easy to form, assemble and join.

According to American Plastics Council (2009) reports, in 2002 the total production of plastic resins in the U.S. and Canada was about 50 million short tons of which 39 million tons were thermoplastic and the rest thermosetting resins. The PVC component of thermoplastics was about 8 million short tons, i.e. 20% of the thermoplastics and 16% of the total plastics production. On the basis of the above facts regarding plastics production, the known concentration of chlorine in PVC and the estimated chlorine input of plastics in the MSW stream (Table2), it is possible to estimate the fraction of PVC products in MSW as follows:

$$0.567X_{PVC} = 0.104 \times 0.025 \quad (1)$$

and

$$X_{PVC} = 0.46\% \text{ of total MSW feed} \quad (2)$$

Thus, the fraction of PVC in a typical U.S. MSW can be as high is 0.5% of the total mass

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Summary of chlorine input to WTE facilities

Since about 29 million short tons of MSW are combusted in U.S. WTEs, the volume of PVC discarded as MSW to WTEs amounts to 133,000 tons annually (0.46% of the total MSW). The corresponding amount of PVC going to landfills is estimated at 1,050,000 tons (NJT, BioCycle-EEC national survey of waste generation). Therefore, of the total amount of 8 million tons of PVC produced annually, presently only 13% end up in the MSW stream to WTEs or landfills. This rough estimate reflects the fact that much of the PVC is used in long-life products such as piping, door and windows.

In summary, the total input of chlorine in U.S. WTE facilities amounts to 186,000 short tons (169,000 metric tons) of chlorine of which 75,000 short tons are in the form of PVC.

Fate of chlorine in a WTE facility

When MSW is combusted, the chlorinated organic compounds decompose producing either gaseous chlorine (Cl_2) or hydrochloric gas (HCl). However, chlorine gas reacts with water vapor to form hydrochloric gas as shown by the reversible reaction (1).

$$2HCl\,(g)+0.5O_2(g)=Cl_2(g)+H_2O(g) \quad (3)$$

This reaction has a molar free energy ranging from -26 to –6 kJ between 200 and 600^{o}C and from +7 to +27 kJ between 700 and 1000oC (HSC Chemistry). Therefore, the formation of chlorine gas is favored below 600^{o}C and the formation of HCl at temperatures above 600^{o}C. This fact is of importance because at the temperatures encountered on the surface of waterwall and superheater tubes, the HCl in the combustion gas tends to form Cl_2 which encourages the corrosion of metals to metal chlorides.

Effect of chlorine input on HCl concentration in combustion gases

During combustion, nearly all of the chlorine content in the various components of the MSW is volatilized and converted to HCl gas. Assuming that the MSW contains 0.5%Cl and considering that the volume of combustion gases is about 5,000 dry cubic meters per short ton of MSW, the concentration of HCl in the combustion gases can be calculated as follows:

This number is in good agreement with reported HCl concentrations in the combustion gases of several WTE facilities (HCl: 450-700 ppm by volume), before the gases pass through the Air Pollution Control (APC) system These values were collected by means of a corrosion effects study conducted by WTERT in 2005 and reported in the NAWTEC Proceedings.

It was mentioned earlier that chlorine concentration in coal is one fifth of that in MSW. However, the typical stack gas volume from a coal-fired boiler is about 10000 standard cubic meters per ton of coal, that is double the WTE volume, per ton of feedstock. Therefore, the concentration of HCl in coal combustion gases is 5 x 2.=10 times lower than in WTE combustion, i.e. of the order of only 25-30 ppm. This allows coal-fired power plants to operate at higher steam temperatures and thus achieve higher thermal efficiencies.

Removal of chlorine in Air Pollu tion Control (APC) system

In the APC system, most of the HCl in the combustion gases is removed in the "dry" scrubbing operation by injecting a slurry of calcium hydroxide that combines with HCl to form calcium chloride according to the following chemical equation:

$$Ca(OH)_2 + 2HCl(g) = CaCl_2 + 2H_2O(g) \quad (4)$$

This is an exothermic reaction that releases about 115 MJ of heat, which corresponds to about 1.5 MJ per kg of HCl and, stoichiometrically, requires the injection of about 5 kg of $Ca(OH)_2$ per ton of MSW combusted (HSC Chemistry). Calcium hydroxide is produced by reacting (slaking) calcium oxide, the main constituent of cement, with water. The amount of calcium oxide added in the APC is usually twice that required stoichiometrically and amounts to about 1% by weight of the MSW processed in the WTE. The calcium chloride ($CaCl_2$) formed in the dry scrubber is then collected along with fly ash particles in the fabric filter baghouse that follows the dry scrubber. Most U.S. WTEs report stack HCl concentrations that are 10-15 ppm by volume, that is one half or lower than the regulatory limit.

Chlorine sinks in a WTE

There are three possible sinks of the chlorine input in a Waste-to-Energy combustion chamber: Bottom ash, fly ash that is separated from the gas stream in the Air Pollution Control (APC) system, and stack gas. Most WTEs in the U.S. mix the fly ash with bottom ash and the mixture is called "combined" ash. One of the reasons for doing this is that the fly ash contains a relatively high amount of calcium which seems to act as a cementing agent that reduces leaching of heavy metals from the ash. Another reason is that "combined" ash can be used in landfills beneficially as the Alternative Daily Cover, in place of the six-inch (15-cm) soil cover that is required by EPA regulation for sanitary landfills. Table 4 shows representative analyses of some of the important elements in the three types of WTE ash, obtained at a large WTE (875,000 short tons per year) in the northeast U.S. (Szurgot).

Table 4. Distribution of various elements in three ash products of a WTE[1]

Element Bottom	ash		Fly ash		Combined ash	
	g/kg	%	g/kg	%	g/kg	%
Calcium	46.00	4.6	206.3	20.6	59.12	5.91
Sodium	4.01	0.4	18.87	1.89	5.18	0.52
Chlorine	ND	ND	165.0	16.5	22.12	2.21
Aluminum	16.53	1.65	19.43	1.94	13.40	1.34
Iron	18.17	1.82	3.45	0.35	19.75	1.98
Lead	0.8	0.08	3.55	0.36	0.83	0.08
Magnesium	5.52	0.55	5.27	0.53	6.60	0.66
Zinc	1.38	0.14	8.75	0.89	2.25	0.23

[1]A.M. Szurgot, 1992 International Public Works Congress and Exposition, Boston, Aug. 29, 1992 (data from 825,000 t/y WTE)

Some interesting observations from the above tabulation are:

a) Nearly all the chlorides appear in the fly ash. This is as would be expected from the above discussion of chlorine volatilization and subsequent capture of chlorine in the form of calcium chloride.

b) If it is assumed that the combustion gases contain 574 ppm by volume of chlorine (as per above calculation) and the stack gas 15 ppm v, then 97% of the chlorine input ends up in the fly ash. Assuming that the 16.5% of chlorine in the fly ash of Table 4 applies to this case, then a simple chlorine material balance indicates that the fly ash constitutes 3% of the MSW feed. This is reasonable since WTE facilities report that the combined ash generated amounts to 20-30% of the MSW feed and that the fly ash corresponds to about 10% of the combined ash.

c) A chlorine material balance based on the Cl concentrations of bottom, fly and combined ash results in the estimate that the fly ash represents 12 % of the combined ash, which is fairly close to the estimate of 10% made in (b).

d) A calcium balance for bottom, fly, and combined ash, based on the assumption that these two ashes are divided in the ratio of 90% to 10%, results in a calcium concentration in the combined ash of 6.2%Ca, which is fairly close to the 5.9%Ca figure of Table 4.

e) Although the concentrations of lead and zinc in the fly ash are about five times higher than in the fly ash, an estimated 67% of the input lead and 59% of the input zinc end up in the bottom ash. The material balances for lead and zinc in the three ash products are fairly consistent, based on the assumed 90% to 10% split of bottom ash to fly ash.

f) The above indications confirm the observation that the bottom ash represents about 90% of the total ash and the fly ash the other 10%.

Relation b etween chlorine inpu t to WTE and dioxin formation

The WTE facility represented in Table 4 (Szurgot) processes 875,000 short tons of MSW annually. At an assumed chlorine concentration in the feed of 0.5% Cl, the chlorine input to the WTE is 4,125 short tons per year. Following MACT implementation, the U.S. WTE facilities are required by EPA to emit less than 30 nanograms per dry standard cubic meter (dscm) of total dioxins, which is equivalent to about to 0.6 ng of toxic dioxins -TEQ). The European standar is much lower at 0.1 ng/Nm3 and, in fact, on the average the U.S. WTE facilities emit less than 0.1 ng TEQ per dscm. Thus the annual emissions of the entire WTE industry were reported by EPA in 2002 to be 12 grams TEQ, i.e. only 0.34 grams TEQ dioxins for the plant of Table 4.

It is obvious that there is no relation between the 4,125 short tons (i.e., 3.75 billion grams) of chlorine input to this plant and the 0.34 grams of TEQ dioxins emitted. Therefore, if chlorinated plastics in the MSW stream were to be eliminated altogether, as advocated by some environmental organizations, it would have no effect whatsoever, on the formation of dioxins since nearly 2,000 tons of chlorine would still be present in the feedstock, in the form of salt and chlorine- containing food and yard wastes. However, reducing the HCl concentration in the combustion gases by nearly one half would reduce the corrosion rate in WTE boilers.

Conclusions

This study examines in detail the sources and the sinks of chlorine in a WTE unit. It is concluded that on the average MSW contains about 0.5% chlorine, which results in hydrogen chloride concentration in the WTE combustion gases of up to 600 parts per million by volume. About 45% of the chlorine content in MSW derives from chlorinated plastics, mainly polyvinyl chloride (PVC), and 55% from salt (NaCl) and chlorine-containing food and yard wastes. An estimated 97-98% of the chlorine input is converted to calcium chloride in the dry scrubber of the Air Pollution Control (APC) system and captured in the fly ash collected in the baghouse. The other 2-3% are emitted to the atmosphere at a concentration of 10-15 ppm by volume, that is less than one half of the U.S. EPA standard.

The chlorine content of fly ash can be recovered by a simple leaching procedure, as is done in some European WTE facilities, such as trhe ones in Hamburug. Germany, and Amsterdam, The Netherlands. Because of the large volume of MSW landfilled in the U.S., the usual practice is to mix bottom and fly ash and use the resulting “combined ash” beneficially in landfills as Alternative Daily Cover in place of soil.

The input of chlorine in , e.g., a one million ton WTE amounts to about 5,000 tons per year. If the chlorinated plastic wastes were to be eliminated somehow from the feed stream to a WTE, the chlorine input would be reduced by 45%

but this would have no effect on the formation of dioxins, which for this particular plant amount to only 0.35 grams. However, lowering chlorine input by this amount would result to a significant decrease of the corrosive atmosphere in the WTE boiler.

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