

**Incineration, Waste-to-energy and Catalytic Gasification:
the Past, Present and Future of Medical Waste Management**

Kimberly Llewellyn

Advisor: Prof. Marco Castaldi

Earth Engineering Center

At the Henry Krumb School of Mines

**Submitted in partial fulfillment of the requirements for the
M.S. degree in Earth Resources Engineering**

**Department of Earth and Environmental Engineering
Fu Foundation School of Engineering and Applied Science
Columbia University
New York, NY 10027
May 2006**

TABLE OF CONTENTS

List of Table	3
List of Figures	4
Executive Summary	5
Acknowledgements	6
Introduction	7
Analysis of Medical Waste	12
Characterization of Sample	15
Heating Value Determination	17
Chlorine Content Determination	19
Discussion of M.W. Disposal/Use Options	
Incineration	25
Waste-to-Energy	28
Gasification	29
Waste-to-Energy Ash Research	31
Dioxins	35
Discussion of Gasification/Catalytic Alternative	36
GCMS Setup and Valving Design	38
References	41
Appendix	
Table 1: Heating Value Determination Data	44
Table 2: Chlorination Determination Data	45
Figure 1: Atomic Absorption Lead Data Sample	46
Figure 2: Atomic Absorption Copper Data Sample	47
Figure 3: Atomic Absorption Cadmium Data Sample	48
Method 1: Parr Instruments Chlorine Determination	49
Method 2: EPA TCLP Method 1311	51

LIST OF TABLES		Page
Table 1: Mass distribution of MW categories		14
Table 2: Heat Content of MW categories		16
Table 3: Percent moisture content by mass of MW		19
Table 4: Average % chlorine and average range in categories		21
Table 5: Total % chlorine in the mixture		24
Table 6: Comparison of energy and chlorine content of MSW and MW		33
Table 7: % chlorine by mass and heat content for a theoretical MW sample containing no hard plastics		21
Table 8: Summary of average concentrations and pH values for samples		31

LIST OF FIGURES

	Page
Figure 1: Separation of sample into 8 categories	13
Figure 2: Parr Bomb Calorimeter used in analysis	15
Figure 3: (Graph) Btu/g content based on the plastic sample category	16
Figure 4: Moisture Determination- Sample TGA Result for Category #3	18
Figure 5: (Graph) % Moisture by mass for each of the plastic sample types	18
Figure 6: (Graph) Mass based calculation of average % chlorine in each sample category	20
Figure 7: Typical air-controlled incinerator	27
Figure 8: BGL gasification reactor	30
Figure 9: Agitator and hazardous waste filtration unit used in ash analysis	32
Figure 10: Copper calibration curve for concentration determination by flame AA	33
Figures 11 & 12: Summaries of cadmium and lead concentrations in ash leachate	33
Figure 13: 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)	35
Figure 14: Conceptual schematic of catalytic gasification reactor	37
Figures 15 & 16: Initial flow configuration and flow configuration at injection of 6 and 10 port valving system for GC/MS and TCD	40

EXECUTIVE SUMMARY

Waste disposal poses a problem which is increasingly difficult to ignore. While the increasing volumes of generated waste are a problem, the types of waste being generated further complicate the challenge of disposal. Medical waste produced by hospitals and medical facilities falls into this category and amounts to a significant volume of waste requiring special handling. The issue of medical waste treatment and disposal is gaining the attention of organizations, including the World Health Organization, worldwide. While incineration remains the most common method for treatment of medical waste, the high environmental impacts associated with incinerators produce a need for viable alternatives. Waste-to-energy is an obvious replacement for medical waste incinerators whose numbers are likely to decline due to more stringent emission standards. The high plastic content of medical waste is looked at as a potential feedstock for a novel catalytic gasification reactor. With the number of operational incinerators on the decline, waste-to-energy offering a functioning alternative and innovative possibilities awaiting further investigation incineration, waste-to-energy and catalytic gasification could be considered the past, present and future of medical waste management.

Acknowledgements

I would like to thank my advisor Marco Castaldi for giving me the opportunity, the resources and the guidance needed to succeed in achieving my goals while in this program. I would never have found my way to this department if it were not for professor Themelis who will always be an inspiration to me for his dedication to making this world a better place. The support and love of my husband, family and friends have made this and all parts of my life's journey possible.

Dedication

This thesis is dedicated to Marco Castaldi for the generosity with which he shared his time and knowledge and for unknowingly convincing me that the mind of an engineer is not so different from that of an artist.

Incineration, Waste-to-energy and Catalytic Gasification: the Past, Present and Future of Medical Waste Management

Introduction

As waste volumes grow in tandem with development and population growth, the question of how and where to dispose of our trash is fast becoming an issue that needs attention. The United States Environmental Protection Agency (U.S. EPA) estimates an increase in waste generation in the U.S. of about 1% from 1990 to 2000 while another study conducted by the Earth Engineering Center at Columbia University found an increase of approximately 4% over the same time period¹. While the increasing volumes of generated waste are a problem, the types of waste being generated further complicate the challenge of disposal. Biomedical waste produced by hospitals and medical facilities falls into this category and amounts to a significant volume of waste requiring special handling².

Traditionally, landfilling and incineration have been the most common treatment and disposal methods for municipal solid waste,³ however there are major drawbacks to both. Land and air are increasingly viewed as precious resources warranting protection. Landfilling requires the digging up of U.S. soil to accommodate over 200 million tons of waste per year¹. Land is widely considered more valuable when used for housing, development, recreation and agriculture. Public concern for the odors and off-gases associated with landfills as well as environmental impacts of leachate and runoff from landfills has raised much resistance to new zoning of landfills from communities and environmental organizations²⁰.

Incinerators gained attention in the late 1980's due to increasing levels of airborne toxins like mercury, lead, dioxins and sulfur dioxides resulting from unregulated emissions⁴. In response, the U.S. Congress passed amendments

to the Clean Air Act in 1990 requiring closure of many incinerators if compliance with emission standards could not be met. Though widely phased out for disposal of municipal solid waste (MSW), incinerators are the most commonly used treatment for medical waste (MW)⁵.

There are an estimated 2,400 medical waste incinerators (MWI) in the U.S. according to the EPA (1996)⁶. They have been identified as the largest contributors of the most toxic and potentially harmful pollutants, namely dioxins and mercury⁷. While compliance with stricter standards issued by the U.S. EPA would dramatically decrease emission levels from incineration plants (95% for mercury and 96% for dioxins and furans)⁸, many facilities are expected to fall short in their capability to pay for the cost of retrofit installations of required air pollution control technologies by 2000. In contrast to incinerators, waste-to-energy plants recover energy from the combustion of waste. Unlike MWI's they have been regulated since the mid 1990's. Having already been outfitted with advanced air pollution controls, WTE should be considered as a more environmentally friendly treatment for the growing volumes of disinfected medical waste.

The magnitude of medical waste disposal is bound to increase as developing nations advance the state of their infrastructures including health-care systems. For this reason medical waste and the issues surrounding its handling and disposal are gaining the attention of regulatory bodies and organizations worldwide. The World Health Organization (WHO) in recognition of this universal problem proposes to work with developing countries to follow short, medium and long-term strategies, which include the use of common plastics for the production of all syringe parts to facilitate recycling, research and promotion of new technology and risk assessment to compare the health risks associated with incineration and exposure to health waste⁹.

A group from the National Environmental Engineering Research Institute in Nehru Marg, India estimates medical waste generation to be approximately 0.5-2.0 kg/bed/day and 0.33 million tons a year¹⁰. The corresponding U.S. estimates are 9 kg/bed/day and 22 million tons a year¹¹. It is likely that waste production

will follow trends similar to energy and resource consumption. As developing nations like India proceed, it is critical that well-established alternatives to landfill and incineration be developed. If left unchecked a serious disposal issue will quickly develop. By providing feasible alternatives to incineration and landfilling in the earlier stages of advancement, fighting ineffective infrastructures at a later date can be avoided. At the same time it is important for developed countries including the U.S. to focus on reduction and recycling of their massive medical waste stream.

One of the challenges of effective medical waste management is born from the heterogeneous nature of the waste generated in the medical community. This makes it difficult to clarify which types of waste require special handling and treatment and additionally how facilities can effectively go about executing segregation of these wastes. Definitions of medical waste vary between regulatory agencies as well as from state to state. The U.S. EPA's Resource Conservation and Recovery Act (RCRA), Part 259 (1989) uses the following definition:

“Medical waste is defined as any solid waste which is generated in diagnosis, treatment, or immunization of human beings or animals, in related research, biologicals production or testing.”¹²

The RCRA, an amendment made in 1979 to the Solid Waste Disposal Act (1965), was passed by Congress in response to syringes and other waste items washing up on East coast beaches¹³. It specifies medical waste as solid waste and so subjugates it to regulation under the amendment. If medical waste is determined to be hazardous then it is subject to tracking and handling regulations under subtitle C, subpart 264 and 265 of that same act. In addition, transportation of hazardous waste is regulated under the RCRA by the Department of Transportation. In response to this potentially confusing web of regulations, some states such as New York have made attempts to clarify which items do and which do not need to be added to the regulated waste stream. A publication of compliance guidelines claims that many items are currently

assumed to be regulated waste simply because they looked “medical”, as opposed to actually being hazardous or infectious waste¹³.

According to studies conducted in Korea and India mismanagement of MW is a major problem^{14,10}. These studies point to the same problem as many U.S. based analyses of the issues surrounding MW including one study conducted for the National Association of Physicians for the Environment, and that is a common failure to segregate biomedical and regulated waste from non-regulated waste¹⁵. While infectious or “red bag” waste typically contributes 15% of hospital waste some facilities treat as much as 90% as specialized waste requiring sterilization². Part of the reason for this failure, at least in the U.S., is due to a lack of clear guidelines for the handling of MW. Many components of medical waste streams could be recycled, paper products in particular⁵. However, they generally are not, due to a lack of organization or of understanding as to what, in fact, medical waste is according to regulations.

This thesis focuses on a part of the waste stream that has a particularly high impact: plastics, and more specifically medical plastics. Plastics make up approximately 9% of the MSW waste stream¹⁶ and 20-25% of the medical waste stream¹⁷ though values as high as 30% have been reported¹⁸. As plastics are generally non-biodegradable and contain many potentially harmful and conversely useful chemical compounds, it is important to develop optimum methods for treatment, disposal and reuse.

In the case of medical plastics, there is a high potential for recycling of certain components. Recycling is being looked at as a key component of any integrated waste management program^{16,19,20}. One study which analyzed the plastic waste streams of eight U.S. hospitals²¹ found that 30% of the medical waste stream was plastic by weight and that 67% of the plastics fell into one of the following categories: cafeteria plastics, sharps (plastic-bodied syringes), medical packaging, blood and IV bags or tubing. As a result, they concluded that the first three of these items should be considered first as the best candidates for recycling. The latter three have the potential to infect personnel during use and handling and so must be controlled as regulated waste. Recycling and disposal

of non-regulated waste is easier and less energy intensive in that it does not need to be treated by autoclaving or other means for disinfection².

Plastic recycling is most efficient only when the waste streams are homogenized. To this end hospitals are being encouraged to buy syringes that are made out of the same plastic⁸. In addition, because of the chlorine in polyvinylchloride (PVC) and the high temperatures to which materials are exposed during recycling processes it is also recommended that PVC alternatives, like polyolefin, be sought out¹⁹.

Though recycling is certainly an important option to consider in the handling of all waste types, this thesis considers three alternatives: traditional incineration, waste-to-energy and a novel, catalytic gasification process. As discussed, incineration is no longer considered an acceptable method of disposal for waste though it remains the most common treatment for biohazardous material. Typical incineration systems will be described because it is important to understand how they differ from modern waste-to-energy plants. Some of the advantages and disadvantages of accepting MW at WTE facilities are investigated using results of an analysis carried out in the EEAE department of Columbia University. Additionally, experiments using the EPA's Toxic Leaching Characteristic Procedure (TCLP) aid in the determination of leaching characteristics of WTE ash residues, which are generally sent to landfill. Finally, a catalytic gasification process intended specifically for the treatment of plastics is discussed as a viable alternative to the latter two options. This novel technique could allow for realization of the potential to reuse the chemical building blocks of plastics for useful and valuable products like fuels. The setup of a GC equipped with a mass spectrometer, TCD and valving system is described as the instrument intended to supply critical information in the development and performance evaluation of the gasification reactor.

Analysis of Medical Waste

The following analysis of a sample of medical waste produced a good point of reference for comparing varying results of components and other characterization criteria for medical waste. It also provides a starting point to make some reasonable projections in relation to the gasification technology discussed later in the paper.

Four stages of analysis were carried out in this project: separation and categorization of the medical waste, determination of Btu value, determination of moisture content and determination of chlorine content. Where possible, we compare our results to data in published studies as points of reference. Control runs were carried out to ensure that observed variations in values came from the samples themselves and not from the analytical methods used.

The initial stage was carried out by first thoroughly mixing the bucket of medical (MW) and then manually separating the mixture into 8 categories:

- 1. Light weight or soft plastic**
- 2. Hard plastics** (including syringe bodies or containers)
- 3. Plastic lined paper and cotton**
- 4. Paper and cloth bandages**
- 5. Plastic bags**
- 6. Gloves** (both latex and non-latex)
- 7. Random mix of non-combustibles**
- 8. Finely shredded mixture of categories 1-6**

The two major components by mass of the MW sample delivered to our lab are **hard plastics** (including syringe bodies and containers) at 31.5% and **paper and cloth bandages** at with 24.1%. The % plastics content is in line with the results of a study performed by B.K. Lee et al of the Dept of Work Environment,

University of Massachusetts who had a finding 29.9% average plastics content from 8 medical centers, hospitals and animal hospitals³.

Light-weight or soft plastic and **plastic bags** had the highest heat of combustion with 36-39 Btu/g. The overall heating value of the MW was determined to be 27.45 Btu/g or 25 million Btu/ton MW. The U.S. EPA quotes a value of 22 Btu/g or higher for MW with a high plastics content²². A study commissioned by the World Health Organization (WHO) found an average value of 23.79 Btu/g²³. The components with the highest moisture content were **plastic lined paper and cotton** and **the finely shredded mixture of categories 1-6** with 2.4% and 2.7% moisture content by mass, respectively. This translates into a total moisture content of approximately 1%. The WHO study had a value of 0% for moisture content for medical plastic waste. The chlorine content of **hard plastics** and **gloves** were the highest at 12.6% and 15.5% chlorine by mass, respectively. A weighted summation showed 6.3% chlorine by mass of the MW.

CHARACTERIZATION OF SAMPLE



Figure 1: Separation of sample into 8 categories

The medical plastics as delivered were in a 5 gallon bucket. A one liter sub-sample was taken from the 5 gallon sample of medical plastic waste after being thoroughly mixed. The sub-sample is taken to be representative of the entire 5 gallon sample. The total weight of the sub-sample was 101.5 grams. The sub-sample was then separated into 8 different categories, which were subsequently weighed:

CATEGORY	% MASS
1. Light weight plastic wrap	12.3
2. Hard plastics: syringe bodies, lids	31.5
3. Plastic lined cotton and paper	5.4
4. Paper and cloth bandages	24.1
5. Plastic bags	2.5
6. Gloves	10.3
7. Random: glass, screen, metal	4.4
8. Finely shredded mix of 1-6	9.4

Table 1: Mass distribution of MW categories

The majority of the mass of the medical plastics consist of hard plastics, including syringe bodies and bottles, (#2= 31.5%) and paper and cloth, (#4= 24.1%). Gloves, both latex and non-latex (#6), and plastic wrap (#4) contributed another 10.3% and 12.3% respectively. Category #7, comprising approximately 4% of the total mass is not analyzed as it primarily consisted of metals and glass. Category #8 included the finely shredded component of the whole sample. Pieces of syringes, bags, paper, etc. which were less than ~0.6 cm in diameter fell into this category. It appears to be an even mixture of categories 1-6.

HEATING VALUE DETERMINATION

The next stage of the analysis involved the determination of the heat content of the medical plastics. This analysis was performed using a Parr Oxygen Bomb Calorimeter, model #1341.



Figure 2: Parr Bomb Calorimeter used in analysis

Each sample type was handled according to a method specified by Parr for this model and the evaluation was repeated twice on each sample type. In summary, each sample was weighed and then combusted in an oxygen bomb which is submerged in water. The heat of combustion is calculated by measuring the difference in temperature of the water and then using the following equation:

$$\Delta H_{\text{rxn}} = \text{Mass}_{\text{H}_2\text{O}} * C_{\text{pH}_2\text{O}} * \Delta T + K \Delta T$$

Where $C_{\text{pH}_2\text{O}}$ is the heat capacity of water, K is a constant for the calorimeter and ΔT is the change in temperature. The following graph is representative of the found results.

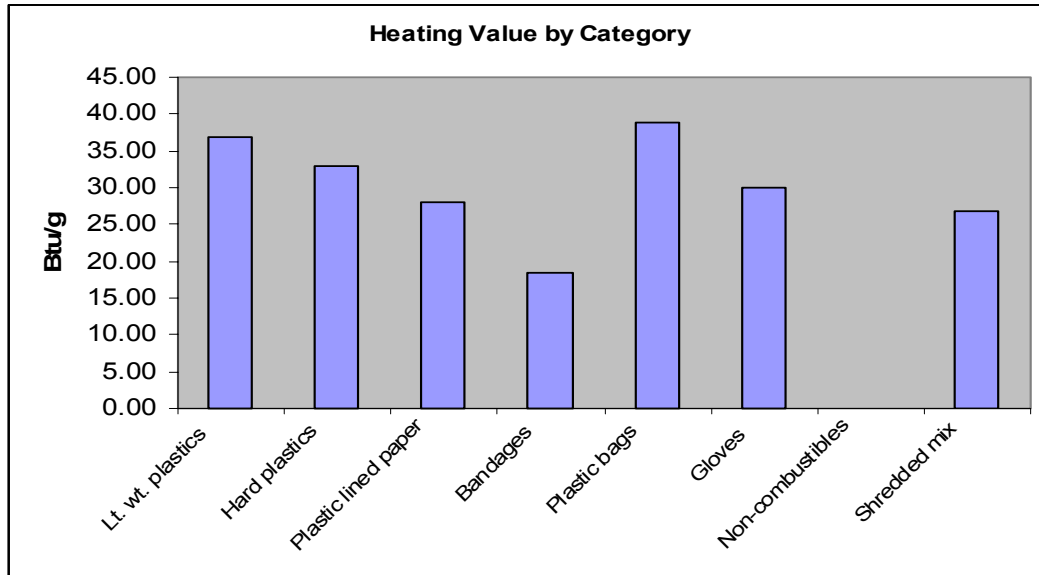


Figure 3: Btu/g content based on the plastic sample category. Category #7 is not included since it consists of non-combustibles.

Table 1 of the appendix can be referred to for a complete data table. The samples were found to have the heating values and variation ranges:

CATEGORY	Heat Content		%Variation
	(cal/g)	(Btu/g)	
1. Light weight plastic wrap	9293	36.89	2.4
2. Hard plastics: syringe bodies, containers	8274	32.85	7.4
3. Plastic lined cotton and paper	7078	28.10	16.0
4. Paper and cloth bandages	4656	18.48	4.1
5. Plastic bags	9784	38.84	6.8
6. Gloves	7580	30.09	7.1
7. Random: glass, screen, metal	ND	ND	ND
8. Finely shredded mix of 1-6	6740	26.76	16.0

Table 2: Heat Content of MW categories

The observed variation is due to the lack of homogeneity in the samples. Though the samples were made to be as like to one another as possible even within the categories there is considerable variation. Runs were performed using

standards of known heating values to ensure that the variation in fact came from the plastic samples and not from the method.

Weighted summation of total sample gives a heating value of 6914 (cal/g), 27.45 (Btu/g) or 25 million Btu/ton MW. It's possible that there is a good correlation between the heating value of the finely shredded mixture (category #8) with 26.76 (Btu/g) and the overall heating value. Further tests may be used to determine if the mixture of categories 1-6 consistently had a similar heating value to the weighted summation of the MW batch. If this were the case then it would be simpler to sift a representative batch for the finely shredded components and test that portion only for future heating value determinations.

MOISTURE CONTENT DETERMINATION

In the determination of the moisture content, we assume that medical wastes at American Ref fuel facilities are exposed to the air and are not burned directly from a closed container. Based on this assumption the samples were allowed to reach equilibrium with ambient air before being evaluated to simulate that field environment. The moisture content was determined using a Netzch TGA Model # STA409. TGA, thermal gravimetric analysis, is an instrument which measures mass changes as a sample is heated.

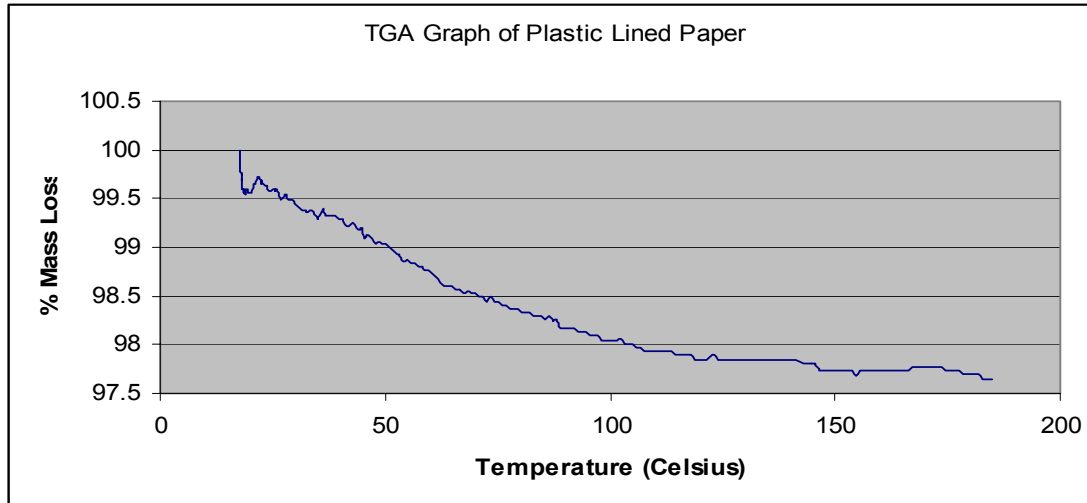


Figure 4: % Moisture Determination- Sample TGA Result for Category #3. Shows mass loss of 2.4% over a temperature range from room temperature (~18°C) to ~180°C.

The samples were heated up to ~180 °C at a rate of 20C/min. The observed mass change occurring over this temperature range was attributed to loss of water content. See figure 4 above for a sample graph of a TGA run.

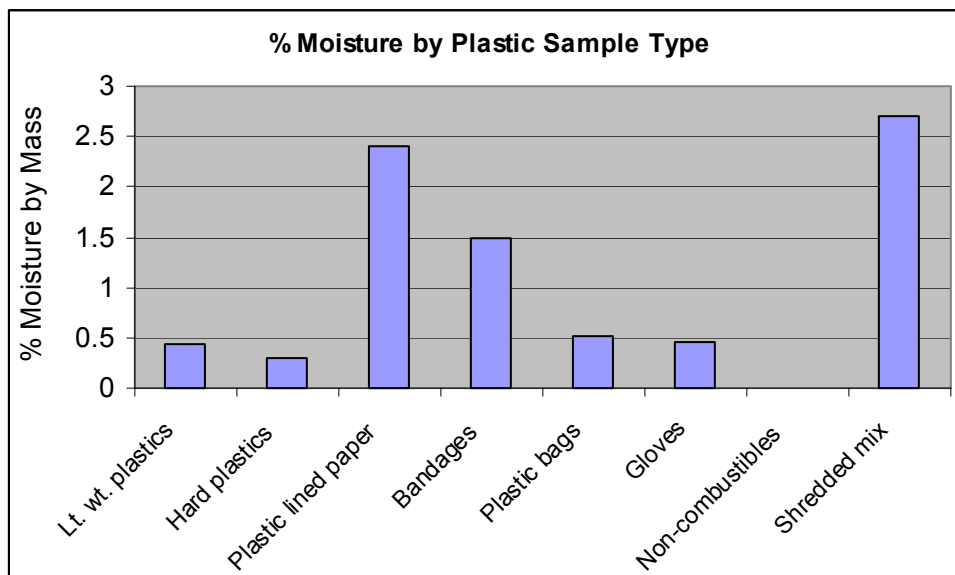


Figure 5: % Moisture by mass for each of the plastic sample types. Category #7 was excluded from the analysis. The total moisture content was found to be 0.95%.

As expected, the paper and cloth containing samples hold more moisture. The higher moisture content of the shredded mix (category #8), which also contains

paper and bandages, is likely due to the increased surface area of the pieces of sample included in the mixture.

CATEGORY	% Moisture	% Moisture of Category in Total	Total % Moisture Content
1. Light weight plastic wrap	0.44	0.05	
2. Hard plastics: syringe bodies, lids	0.29	0.09	
3. Plastic lined cotton and paper	2.4	0.13	
4. Paper and cloth bandages	1.5	0.36	
5. Red plastic bags	0.52	0.01	
6. Gloves	0.46	0.05	
7. Random: glass, screen, metal	ND	ND	
8. Finely shredded mix of 1-6	2.7	0.25	
TOTAL			0.95

Table 3: Percent moisture content by mass of MW.

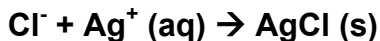
The calculations required for this stage of the analysis were minimal since only an initial mass and a final mass were needed to find the mass of water present in the original sample. Of the samples tested, the moisture content does not exceed 2.7%. A weighted summation of the categories shows 0.95% moisture content for the total medical plastic waste sample.

CHLORINE CONTENT DETERMINATION

% Chlorine by Category

The % of chlorine by mass in the medical waste was determined using a method adapted by Parr Instruments from ASTM methods 5050 and 9253 (method 1 in the appendix). The method involves combusting a test sample in a bomb calorimeter (same as the Btu determination) and rinsing it with distilled water to obtain a solution containing chloride ions which are reacted with silver nitrate to form silver chloride and then recovered using a precipitation technique.

Below is the equation of the governing reaction in the precipitation.



Nitrate and metal cations are spectator ions and do not appear in the net ionic equation.

Analyses were performed on samples from each category up to four times in order to find an average which was representative of that category. Hard plastics (category #2) and gloves (category #6) were found to have the highest chlorine contents. While the following graph represents the found results, Table 2 of the appendix can be referred to for data used in these calculations.

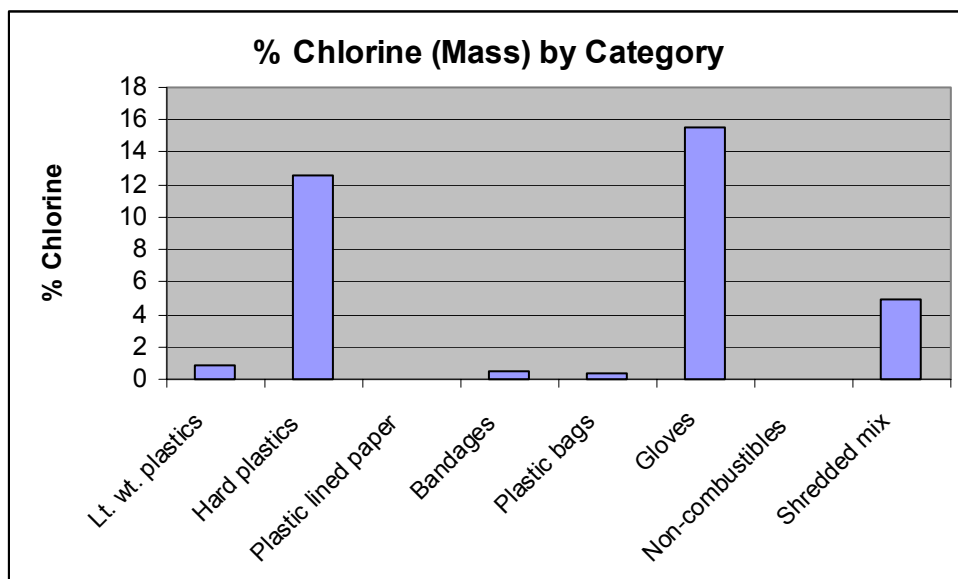


Figure 6: Mass based calculation of average % chlorine in each sample category. Category #3 which included plastic-lined paper yielded no precipitate.

The average values of the % chlorine and the range of the readings are represented in the following table. The ranges shown in the following table are reflective of the variety of plastic types within the sample categories. The categories themselves, while more uniform than the entire mixture, still have many different components, so this variation is to be expected. For example, category #1 (light plastic wrap) which includes all kinds of soft plastics of very thin to medium thicknesses and category #6 (gloves) which includes both latex

and non-latex gloves would be expected to have variation in chlorine content since they are not homogeneous.

CATEGORY	Average % Chlorine In sample (by mass)	Range of % Chlorine
1. Light weight plastic wrap	0.92	.07-1.89
2. Hard plastics: syringe bodies, lids	12.61	12.14-13.07
3. Plastic lined cotton and paper	ND	NA
4. Paper and cloth bandages	0.45	0.24-0.66
5. Red plastic bags	0.38	0.36-0.40
6. Gloves	15.48	13.75-17.20
7. Random: glass, screen, metal	NA	NA
8. Finely shredded mix of 1-6	4.87	3.81-5.93

Table 4: Average % chlorine and average range in categories

Category #3 which included plastic-lined paper typically used on examination tables and in dental offices repeatedly did not yield a precipitate. In addition, category #7 was not tested for the reason that it consisted of non-combustibles.

% Chlorine in Medical Plastic Mixture

The % chlorine by mass in the total mixture was determined using the contribution of mass of each category to the total mixture of medical plastics. The product of the two numbers gives the % of that category in the mixture and the sum of the product for each category gives the total amount of chlorine by mass of the total medical plastic mixture.

Or, in equation form:

$$[(\% \text{Mass cat. \#1})(\% \text{ Cl in cat.\#1}) + (\% \text{Mass cat. \#2})(\% \text{ Cl in cat.\#2}) + \dots + (\% \text{Mass cat. \#8})(\% \text{ Cl in cat.\#8})]/100 = \text{Total \% Chlorine}$$

CATEGORY	% Mass of Category in Total Mixture	Avg % Chlorine (by mass) in category	% Chlorine in Mixture
1. Light weight plastic wrap	12.3	0.97	0.12
2. Hard plastics: syringe bodies, lids	31.5	12.61	3.97
3. Plastic lined cotton and paper	5.41	ND	0.00
4. Paper and cloth bandages	24.1	0.45	0.11
5. Red plastic bags	2.5	0.38	0.01
6. Gloves	10.3	15.48	1.59
7. Random: glass, screen, metal	4.4	NA	0.00
8. Finely shredded mix of 1-6	9.4	4.87	0.46
TOTAL % CHLORINE			6.26

Table 5: Total % chlorine in the mixture. ND- non-detectable indicates that no measurable amount of precipitate was formed in the reaction between silver nitrate and chloride ions. NA- not applicable due to the non-combustible nature of most category #7 components.

From Table 5 it is evident that hard plastics and gloves make up the bulk of the 6.3% chlorine found in the MW stream. This is not only because the average % chlorine (by mass) is high, but also because the % mass of category in the total mixture is high. The light weight plastic wrap contributed significantly to the % mass but contained very little chlorine, therefore does not contribute significantly to the % chlorine in the mixture. It is likely that the plastic wrap is made up of polyethylene or polypropylene which are common plastics that do not contain chlorine.

Combining the experimental observations (or values) with the above equation for total % chlorine, the weight percent of chlorine was determined to be 6.3%. Approximately 80% of the chlorine content in MW comes from polyvinylchloride (PVC)²⁴ products. These products include intravenous (IV) and blood bags, tubing, gloves and packaging plastics. The products are likely distributed among the plastic containing categories, i.e. #1, 2, 5, 6 and 8. Considering the molecular formula of the monomer from which PVC is made, (-C₂H₆Cl-), chlorine accounts for 57% of the compound's mass. Therefore, the following formula was developed and allows for the estimation of PVC in the MW stream.

1. (Mass PVC in MW) (% Cl in PVC) = (Mass Cl in MW) (% Cl in MW from PVC)

2. (Mass PVC in MW(%)) = (6.26(%)) (80%)/(57%)

3. (Mass PVC in MW) = 8.8%

These estimates are consistent with results from a study conducted by Marrack et al. (1988) who found 9.4% of MW to be PVC²⁵. Other studies have shown PVC content to range from 5-18% of MW content(20). If efforts in the medical community could succeed in replacing PVC products with chlorine-free plastics, it could significantly reduce the amount of chlorine found in the MW stream.

This analysis was intended to aid in the determination of whether or not combusting MW at waste-to-energy plants was worth the expected cost of increased corrosion due to the higher chlorine content than typically found in MSW. This is an important point since corrosion due to chlorides represents a major cost of operation²⁶. A good place to start is with the question: is the energy content the same or similar in the MW stream on a percent mass basis of chlorine present compared to a typical MSW stream? The table below shows that this is not the case because the Btu/ % chlorine ratio is over three times higher for MSW. In other words, using MW instead of MSW, you would have to expose a WTE facility to three times the amount of chlorine for the same energy output. If, the PVC content in MW were lowered from 8.8% to 1% (still twice the avg PVC content in MSW) then the Btu/ % chlorine ratio would get close in value. This scenario assumes that the heating value of the PVC and its replacement will be similar.

	MSW	MW	MW (1% PVC by mass)
Energy Content	10.96 Btu/g	27.45 Btu/g	27.45 Btu/g
Chlorine Content	0.71 %	6.26%	1.9%
Btu/ % chlorine	15.4	4.4	14.4

Table 6: Comparison of energy and chlorine content of MSW and MW.

Another possible scenario considers source reduction of the high chlorine content category, namely hard plastics. This could be achieved some level through an aggressive segregation campaign in the medical community. Taking an extreme value case of 100% reduction of hard plastics is useful to illustrate the viability of creating a waste stream with low chlorine content but high Btu value. This requires recalculating mass percentages minus the mass of category #2. Additionally, the amounts of chlorine and heat content of the total mixture must be recalculated. The results of these calculations are shown in Table 8.

CATEGORY	% Mass of Category in Total Mixture (original values)	% Mass of Category in Mixture (excluding cat. #2)	% Chlorine in Mixture	Average Heat Content (Btu/g)
1. Light weight plastic wrap	12.3	18.0	0.17	6.64
2. Hard plastics: syringe bodies, lids	31.5	0	0.00	0.00
3. Plastic lined cotton and paper	5.41	7.9	0.00	2.22
4. Paper and cloth bandages	24.1	35.2	0.16	6.50
5. Red plastic bags	2.5	3.7	0.01	1.44
6. Gloves	10.3	15.1	2.34	4.54
7. Random: glass, screen, metal	4.4	6.4	0.00	0.00
8. Finely shredded mix of 1-6	9.4	13.7	0.67	3.67
TOTAL % CHLORINE			3.35	
TOTAL HEAT CONTENT				25.01

Table 7: % chlorine by mass and heat content for a theoretical MW sample containing no hard plastics.

The heating value is lower and the chlorine content higher for theoretical MW sample with no plastics from category #2 as compared with the proposed sample with reduced PVC content. It is also likely to be more difficult to attain this sort of source reduction which involves the active participation of many personnel as opposed to a PVC replacement program involving only a few management employees.

This is not to conclude that the high energy and chlorine content in MW make it worth it or not for WTE facilities to take on this specialized waste. There are other factors to be considered. One of those being that the high plastics content in MW could help maintain higher combustion temperatures. Since energy content is consistently high and moisture content is consistently low in plastics, MW could be mixed in regularly with the MSW stream to improve combustion conditions. At the same time, higher combustion temperatures may mean lower amounts of dioxin formation but higher levels of thermal NOx. Another consideration is that because energy content in the MW is about 2.5 times higher than MSW, some of the costs resulting from corrosion due to chlorine maybe offset by lower volumes of combustion gases requiring treatment by air pollution controls. The weighing out of these various factors requires further investigation which is not in the scope of this analysis.

Discussion of M.W. disposal/use options

INCINERATION

According to the US EPA, there were an estimated 2,400 incineration plants in the U.S. used for medical waste disposal in 1997 with an additional 700 incinerators being installed over five years through 2002²². Incinerators are the most popular choice of disposal with over 90% of medical wastes being treated in this way²⁷. As a process, incineration is the combustion or burning of materials particularly those that are carbon based. The advantages of incineration include up to 95% reduction of waste volume to ash residues²⁸. Reducing the volume of waste to this extent has the obvious implication of lowering impacts of both transportation and landfilling. If properly maintained it is a very reliable treatment technique for pathological and infectious wastes as most items are rendered unrecognizable (i.e. body parts, sharps) and pathogenic organisms can't withstand combustion temperatures. At the same time, medical waste

incinerators are known to be the largest producers of dioxins⁷, the reasons for which will be discussed in a later section.

Proper operating conditions become even more important when potentially dangerous pathogens are being destroyed. There are several factors which are critical to the proper function of any combustion system. Maintaining a somewhat steady temperature is important for consistent, complete combustion. This can be difficult because of the heterogeneity of composition in medical waste streams where heat contents can vary anywhere from 1,000 Btu/lb to over 10,000 Btu/lb²². Unlike the MW samples tested in the previous analysis which had already been disinfected by autoclave, waste streams going to MW incinerators can include high moisture content items like body parts and IV and blood bags. An abundance of these items result in the more extreme lower values. Waste with large percentages of plastics can have heat contents considerably over 10,000 Btu/lb.

Waste loads of this type can cause a sudden increase in furnace temperatures potentially causing damage to walls and burners. If, however heating values in a load are not high enough, insufficient temperatures may result in incomplete combustion²⁹. To safe-guard against this happening many incinerators have auxiliary fuel burners which are engaged when temperatures drop below about 800°C.

Another key to ensuring complete combustion is having a sufficiently long residence time and creating enough turbulence. The two are related in increasing the turbulence generally increases the time that gases remain in the reaction zones. This can be achieved by slowing the exiting gases with the aid of baffles or other obstacles near the entrance of the secondary chamber. Increased turbulence has the effect of improving mixing of reacting gases and so promotes more complete combustion.

The three most common types of incinerators are controlled air, excess air and rotary kiln with controlled air being the most popular for medical waste treatment.³⁰ All three designs have a primary and secondary combustion

chamber. The primary chamber serves to dry, heat and volatilize the waste while combustion is completed in the secondary chamber with excess air being added.

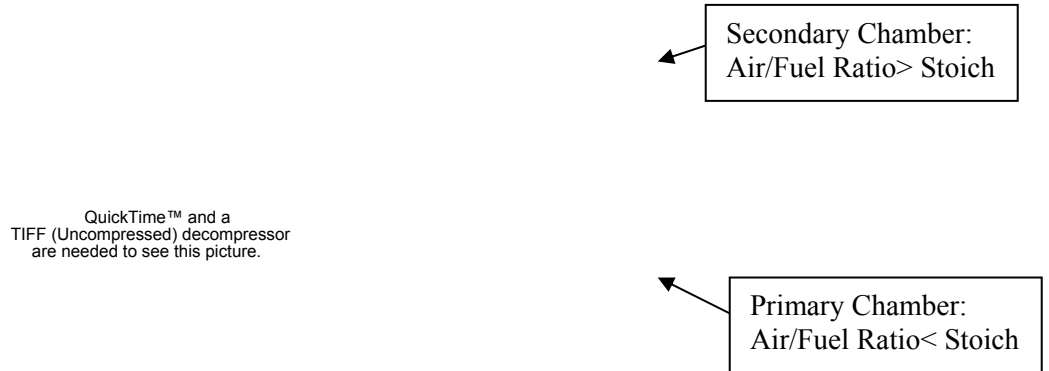


Figure 7: Typical air-controlled incinerator showing the predominant reactions in primary and secondary chambers³¹.

The air-controlled incinerators have the an advantage in that low added air flow rates in the primary chamber mean lower exit (flue) gas turbulence. This corresponds to less particulate matter entering the secondary chamber and cleaner complete combustion products as an end result. It is common for this type of incinerator to be able to meet emissions guidelines without additional APC devices³⁰. Typical operating conditions for an air-controlled incinerator include residence times of 1-2 seconds, combustion temperatures of 760-980 C in the primary chamber and 980-1095 C for the secondary chamber, waste feed rates which can vary from 75 to 6,500 lb/hr and heat release rates of 15,000-25,000 Btu/hr-ft³.

The advantage of incineration of medical waste in addition to significantly reducing landfill volumes is that it reliably destroys biohazardous agents. There

are several alternative medical waste treatment options currently in use. One of these options, ozonation, involves grinding waste in a sealed system which is then flooded with ozone gas³². Ozone gas works as a disinfectant by oxidizing biohazardous materials. Another of these processes requiring a high-energy input is microwave disinfection. The high frequency of microwaves is adsorbed by water molecules and in turn produces heat. The water in the waste is turned to steam³³, which acts as a disinfectant much like the commonly used autoclave systems. While there are options that effectively disinfect waste and in some cases reduce waste volumes, they tend to be very energy intensive and still result in large volumes of waste being sent to landfills.

WASTE-TO-ENERGY

Waste-to-energy differs from traditional incineration of municipal solid waste in that thermal energy produced by the combustion of waste is used to generate steam which is directed to an electricity generating turbine. Some plants, though very few domestically, additionally use the steam to provide industrial and residential heating³⁴. According to 2002 data, an average of 8% of U.S. MSW is combusted in domestic waste-to-energy (WTE) plants²⁵. As an alternative to landfilling, WTE regards MSW as a potential fuel. The burning of 1 ton of MSW at a waste-to-energy facility can produce the same amount of electricity as 1 barrel of oil³⁵. With MSW volume reductions of about 90%, WTE is advocated by some as a partial solution to the growing problems surrounding landfilling. Additionally, the U.S. EPA describes waste-to-energy as a “clean, reliable, renewable source of energy”.³⁶

The WTE design most commonly in use is the mass burn system favored for its operational and mechanical simplicity as well as its low capital costs. The alternative to mass burn is a refuse derived fuel (RDF) facility. In contrast to mass burn plants where waste is loaded directly into the combustion chamber with RDF waste is first carried on conveyors to a materials recovery facility (MRF). In the MRF large items and metal and glass recyclables are removed prior to combustion.³⁷

In the late 1980's the U.S. EPA named WTE plants as a significant contributor to mercury and dioxin emissions in the U.S.. In response to these findings, the EPA passed a final rule in 1995, specifying emission guidelines for Municipal Waste Combustors. These regulations required the implementation of the maximum available control technologies (MACT)³⁸. As a result, WTE plants have been retrofitted with some of the most advanced air pollution control technologies including dry and wet scrubbers for neutralizing acidic gases, bag houses for controlling particulates, carbon injection to control dioxin formation and mercury absorption and selective non-catalytic reduction (SNCR) for NO_x reduction³⁶.

In addition to emissions, combustion residues are another concern with WTE. There are primarily two categories of ash resulting from MSW combustion: bottom and fly. Bottom ash consists of unburned portions of waste from the main combustion chamber. It typically has a high metal oxide content and is not found to be toxic according to EPA leaching procedures. Fly ash on the other hand, comprises flue gases and filter dust from the APC's and usually has high levels of toxic heavy metals including Cd and Pb (see TCLP results). In the U.S. fly and bottom ashes are mixed to dilute the potency of the fly ash toxics. The combined ash can then be used for landfill coverage, road fill or disposed of as non-regulated waste. It should be noted that in Europe the ashes are not combined. Fly ash is often disposed of in salt mines while bottom ash is used in a variety of ways including for building materials.

GASIFICATION

Gasification is a process by which solid waste (or fuel) is heated under closely controlled conditions to produce gases. The resultant gases are mainly carbon monoxide (CO) and hydrogen, commonly referred to as "syngas". Syngas is a desirable product because of its versatility. Both carbon monoxide and hydrogen can be used in a number of ways to produce heat and electricity and can also be compressed for later use. Additionally, syngas can be used to produce methanol using a Fischer-Tropsch process³⁹. Figure 8 shows a BGL (British Gas- Lurgi)

gasifier, designed to process pretreated solid waste⁴¹. Another advantage of the process is that these gaseous products can be scrubbed before they are fully combusted, which means lower volumes of gases need to be treated.

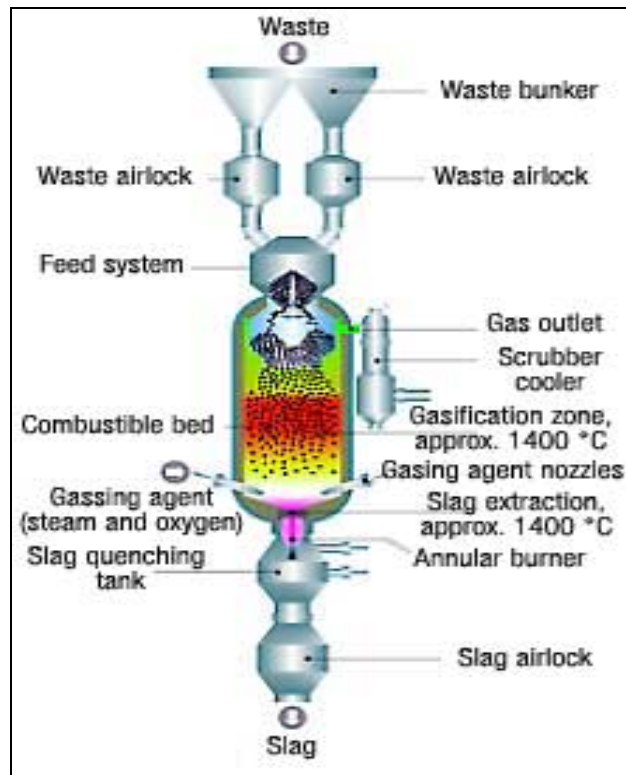


Figure 8: BGL gasification reactor.

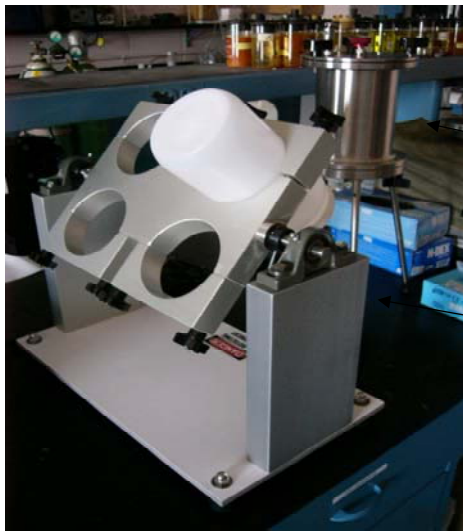
Gasification differs from incineration in that a good incineration system completely combusts the waste being burned with the intended products being carbon dioxide and water. The goal is to convert all of the chemical energy of the waste to thermal energy. By contrast gasification aims to produce carbon monoxide and hydrogen which are intermediate products of combustion. The process uses steam and small amounts of oxygen or air⁴⁰. In addition, the operating conditions during gasification must be properly maintained in order to prevent combustion from going to completion. To this end, the gasification

chamber is pressurized to about 25 atms and oxygen levels are kept low⁴¹. Because the requirements for operation are energy intensive, using gasification for electricity production doesn't make as much sense as utilizing syngas for future synthesis or fuel use.

Regardless of the system used, gasification or WTE, any time solids are involved, including coal, there is a certain amount of noncombustible material that leads to ash formation. Typically the ash content ranges from 3% to 20% depending on the source. For example, low quality coal tailings used as fuel would be in the upper range, whereas food wastes would be in the lower range. Typically the ash is made up of various minerals and metals that either oxidize or react out of the original matrix and remain as residuals. The ash does not yield any appreciable energy when oxidized and generally results in a loss reduction of the overall energy content of the fuel.

WASTE-TO-ENERGY ASH RESEARCH

As previously mentioned, ash residuals result from the combustion of MSW in waste-to-energy facilities. Fly ash in particular is associated at times with high levels of heavy metals. While bottom ash tends to have very low levels of these toxic salts. An analysis of ash residuals was performed using EPA Method 1311 which is the Toxic Characteristic Leaching Procedure (TCLP) in order to analyze ash samples obtained from two different WTE facilities. (See method 2 of the appendix for the first two pages of this method.) This is the standard method used to evaluate leaching characteristics of solids. A variety of compounds in a leachate can be tested. In this study, the heavy metals lead, cadmium and copper were analyzed using atomic absorption.



**Hazardous Waste Filtration Unit:
3750-LHWF**

**Agitator/Rotation Device:
Model #3740-4-BRE**

Figure 9: Agitator and hazardous waste filtration unit used in ash analysis.

The procedure involves obtaining a 100g solid sample and grinding it, if necessary, to a diameter of 1cm or less. When necessary, the ash samples were crushed using a mortar and pestle. A dilute acetic acid solution of pH 2.88 was prepared using ASTM type II de-ionized water to which the solid sample was added in a 20:1 liquid to solid by mass ratio. The mixture was then agitated for 18 (+/-2) hrs using a rotation device made by Associated Design and Manufacturing Company, Alexandria, VA model # 3740-4-BRE and separated using a hazardous waste filtration unit made by the same company model #3750-LHWF. The resultant liquid (leachate) was then nitrified with nitric acid to a pH of <2.

In this state the samples were ready for analysis. The technique used to test for lead, cadmium and copper is atomic absorption. The equipment used was a Buck Scientific Model #220A Flame Ionization Atomic Absorption unit with an air/acetylene flame. Solutions are drawn into the unit through a small tube at a rate of approximately 6mL/minute. The solution is then atomized and injected into the flame. Atomic absorption works using the principle that each metal to be tested has a characteristic absorption pattern when light of a specific wave-length is shined on it. Once the metal specific lamp is in place, the AA unit is calibrated

to read zero absorption for a blank solution.

The method of analysis involves generating a calibration curve from standard solutions with known concentrations of the metals being tested. The range of concentrations used in the plot should cover the approximate expected value of the samples to be tested. Below is an example of one of the calibration curves used for the analysis of copper. (Calibration curves and data samples for Cd, Cu and Pb can be found in the appendix figures 1-3.)

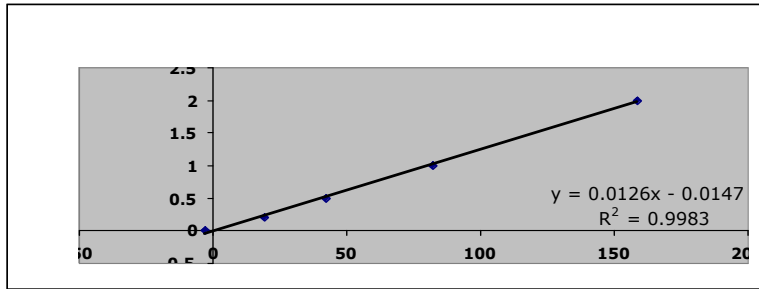
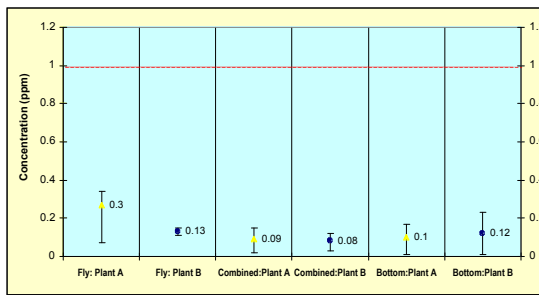


Figure 10: Copper calibration curve used in concentration determination by flame AA.

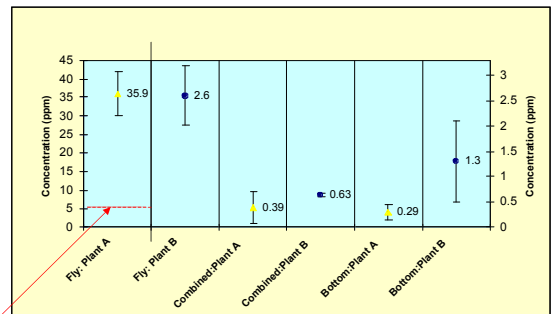
The following graphs show the results for cadmium and lead. The cadmium levels were well below the EPA allowable limits for all ash samples, while the lead levels in the fly ash from plant A greatly exceeded the EPA limit.

Cadmium Summary



EPA Allowable Limit: 1.0 (ppm)

Lead Summary



EPA Allowable Limit: 5 (ppm)

Figures 11 & 12: Summaries of cadmium and lead concentrations in ash leachate.

Following is a table summarizing the results of the ash analysis. Results from a study conducted by the National Research Energy Lab (1997) are used for comparison for the data points of combined ash.

ASH TYPE	BOTTOM		FLY		COMBINED		NREL Results* COMBINED	EPA Limits
	A	B	A	B	A	B		
PLANT	A	B	A	B	A	B		
Pb (ppm)	0.29	.83	35.87	2.64	0.39	.63	.30- .60	5.0
Cd (ppm)	0.10	.12	0.27	.13	0.09	.08	.13- .45	1.0
Cu (ppm)	0.28	.07	0.18	.07	0.51	.06	NA	STATE DEPENDENT
pH	7.58	5.93	11.93	11.63	8.58	9.77	NA	

Table 8: Summary of average concentrations and pH values for samples. Results from National Energy Resource Lab study conducted on samples from a WTE Plant from 1990-1997⁴².

On examination of the results a major question presents itself regarding the extreme difference in values of lead (Pb) concentration in fly ash. Since the pH of the solutions extracted from both plant A and plant B are almost the same this difference cannot be explained by an influence of pH on leachability. It is possible that a difference in the combustion or air pollution control process accounts for the variability between plants. Another explanation could be the inherent changeability of the MSW composition from day to day as well as from location to location.

DIOXIN DISCUSSION

“Dioxin” refers to polychlorinated dibenzodioxins (PCDDs) and to polychlorinated dibenzofurans (PCDFs), the most toxic of which is considered to be 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD)⁴³. The U.S. EPA acknowledges dioxins as carcinogens as well as likely to cause damage to the human reproductive system with extended low level exposure⁴⁴. For this reason a cursory explanation of dioxins is appropriate to this thesis in the context of investigating potential emissions that require precautionary measures.

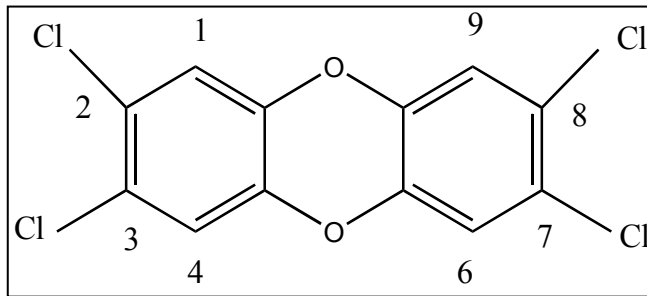


Figure 13: 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD).

It is generally accepted that temperatures must be maintained above 1200K in order to prevent dioxin formation⁴⁵. Maximum formation of PCDDs and PCDFs occurs in a temperature range of 300-400 °C⁴⁶. Since no combustion system is ideal, these temperatures are often found as cool zones due to inadequate mixing of waste and lack of turbulence in the chamber⁽⁴³⁾. Lower combustion temperatures can also result from batches of waste with high moisture content. As previously discussed high levels of moisture can be found in medical waste due to IV and blood bags as well as other biologicals. Other operating conditions, which should be maintained in order to minimize dioxin levels are sufficient turbulence (Reynolds number > 50,000), residence times of 1s or longer and adequate amounts of oxygen to ensure complete combustion. Though these are the factors commonly used to design combustion systems they are relevant to gasification systems also and so should be considered in the design of the gasification reactor discussed in the next section.

DISCUSSION OF CATALYTIC GASIFICATION ALTERNATIVE

The estimated 20 million tons of waste plastics being sent to landfill in the U.S. annually begs a viable alternative¹. As previously discussed, combustion of these products in Waste-to-Energy facilities at least makes use of the energy stored in the compounds by converting it to electricity and heat. However, it only delays the ultimate consumption of fossil fuels from which the plastics were made. It also does little to mitigate the production of CO₂, a known greenhouse gas. Gasification of plastic wastes could potentially allow for the recycling of hydrocarbons and concurrent avoidance of significant CO₂ production. While there are established waste gasification technologies already in operation, they tend to be energy intensive and costly due to the need for pure O₂ and dechlorination steps.

In response to these issues, a novel two stage catalytic, gasification reactor is being proposed for further consideration and investigation. A schematic of the reactor is shown below in figure 14. The stages of reaction can be broken into three stages: gasification of plastics, catalytic reduction of syngas and oxidative coupling of reduction products.

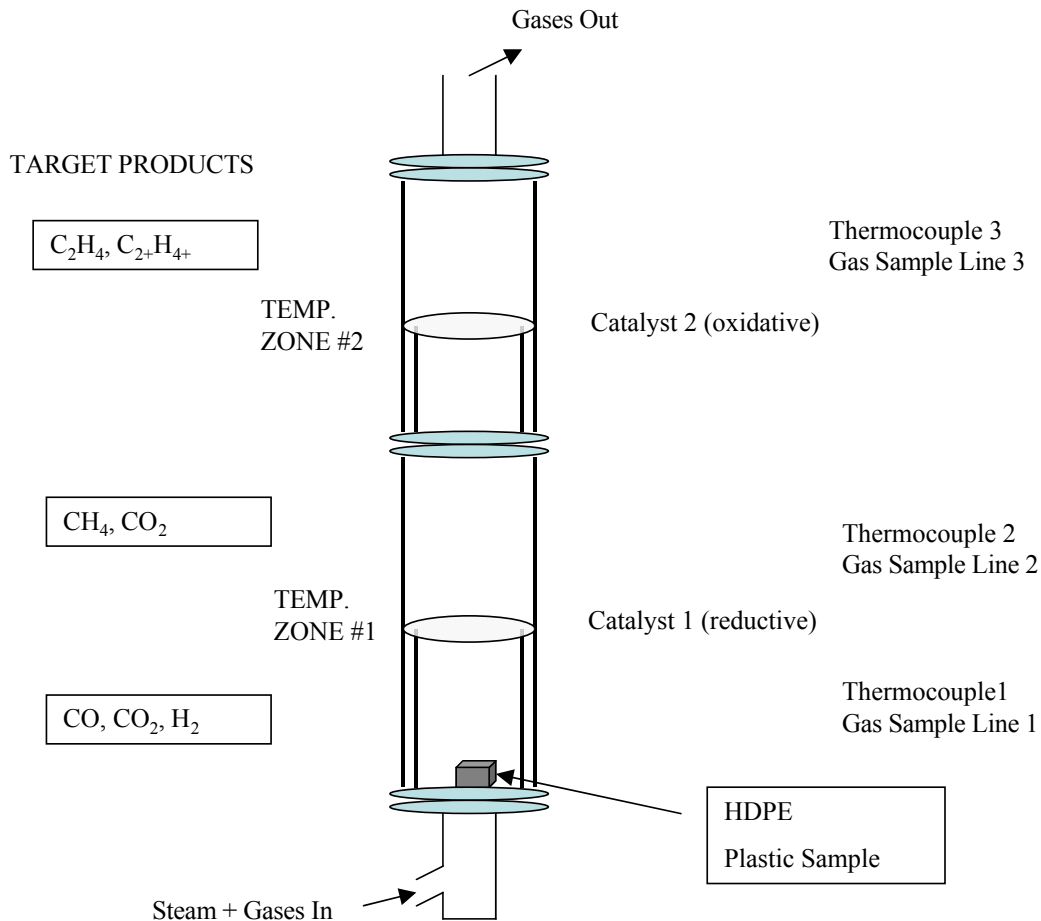


Figure 14: Conceptual schematic of catalytic gasification reactor.

A considerable amount of work has been done regarding many aspects of gasification using various plastics types as starting materials. The more fundamental studies have been conducted on high-density polyethylene (HDPE) to determine the parameters that affect product distribution for gasification and pyrolysis systems. Gasification experiments have shown that reactor temperatures near 730 °C increase the yield of ethylene⁴⁷. As the temperature increases, the production of gaseous products increases for both pyrolysis and gasification processes. At the same time, a decrease in the amount of heavy hydrocarbons, such as oil and wax, is observed. The ethylene/ethane ratio increases with temperature and is generally higher for gasification as compared to pyrolysis. The presence of oxygen appeared to result in more effective cracking and C₃ and C₄ compounds had a maximum concentration near 730°C.

There are several points which will set the proposed system apart from others. While the use of catalysts in a packed bed system has been investigated⁴⁸, we cannot find any evidence in the literature of gasification systems coupled with short contact time catalysts. We will also investigate the possibility of recycling O₂ produced in the oxidative coupling stage for the gasification process in order to cut down on operational costs. Another line of investigation will consider the potential of chlorine constituents in waste plastics to promote the desired catalytic reactions.

GCMS SETUP AND VALVING DESIGN

To aid in the development and performance evaluation of the gasification reactor and other research projects taking place in our group, gas analysis would obviously be necessary. Fortunately, there was a gas chromatography and mass spectrometer (GCMS) instrument boxed and unassembled in our lab. GCMS instruments are used to separate, identify and quantify the individual compounds which make up a given sample. Purchased by professor Schlosser but not needed by their group, professor Castaldi obtained permission to assemble and use the instrument. The GC model 6890 and MS 5973, both made by Hewlett Packard, now Agilent.

With the guidance of professor Castaldi and some help from Eilhann Kwon and Karsten Millrath, the GCMS was assembled and tested. In order to do this successfully it was necessary to read many of the instruments' manuals. The assembly involved connecting up the MS to the GC, which meant setting up the necessary gas carrier and vent line as well as downloading the accompanying software used for operating, monitoring and analyzing results of samples. The column that had been purchased with the instrument also needed to be installed.

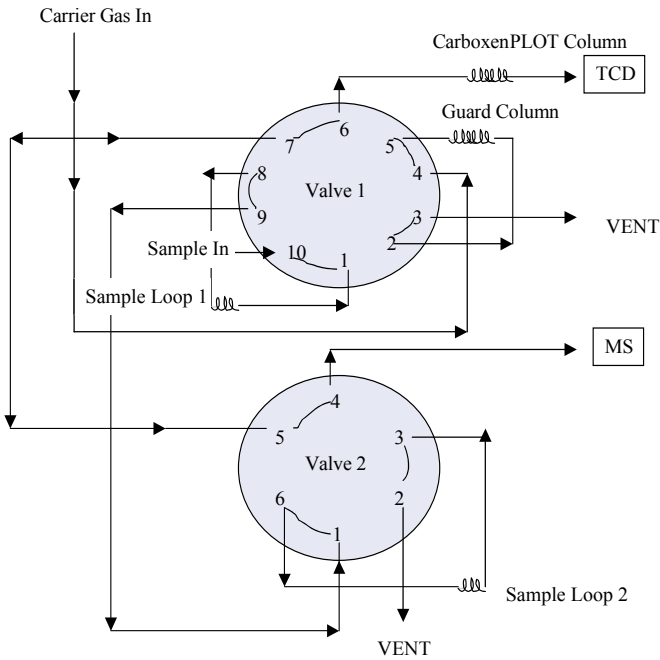
Once the instruments were together, the whole set up needed to be tested. With the column in place, it was possible to check air flow rates using a bubble meter. All gas lines were checked for leaks using Snoop at joints. The mass spec has an “Auto-tune” function which used internally housed chemical, PFTBA, to calibrate the instrument’s mass reading. This function should be performed periodically to compensate for drift which is inherent in the MS. The drift is primarily due to contamination of the ion source.

There is another function called an “Air and Water Check” that is part of the regular maintenance routine for the GCMS. A sample of ambient air is taken in and analyzed using PFTBA as a comparison. The instrument passes this check if the detected percentages of H₂O, N₂, O₂ and CO₂, relative to PFTBA match the inherent percentages of these compounds in air.

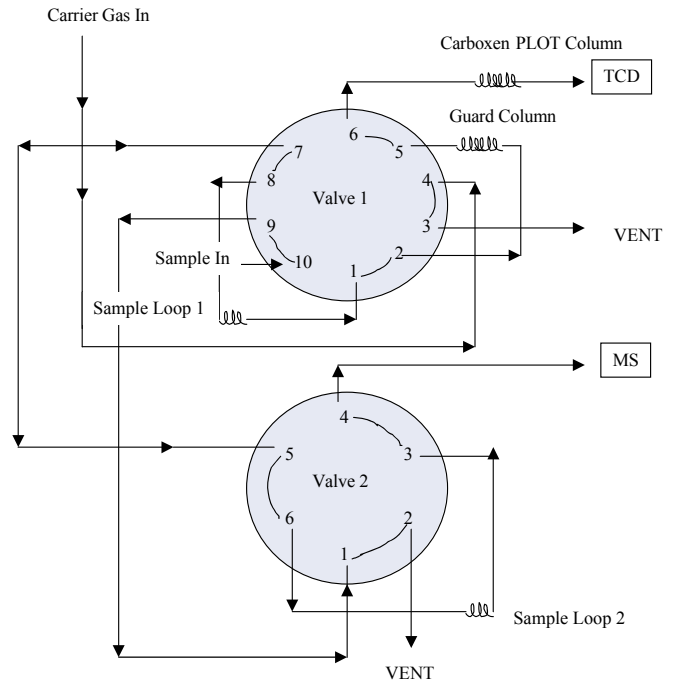
It was anticipated that a more complex set up would be necessary for the intended gasification research as well as for other projects to be undertaken by our group. To this end I designed, again with guidance from professor Castaldi, a combined six and ten port valving system which was purchased from Agilent Technologies and installed along with a thermal conductivity detector (TCD). A third detector, an electron capture device (ECD), was also installed per professor Schlosser’s request. Figures 15 & 16 portray the valving system in an initial flow configuration and then in the configuration after injection. While in the initial position, the columns are being charged.

When the valves are switched, the carrier gas flushes the sample out of sample loops 1 & 2 to the TCD and MS, respectively. Prior to reaching the TCD, the sample passes through the guard column as shown. This guard column protects the TCD by cleaning out heavier hydrocarbon compounds from the sample gas stream. These heavier compounds can be destructive to the sensitivity of the TCD.

INITIAL FLOW CONFIGURATION



FLOW CONFIGURATION AT INJECTION



Figures 15 & 16: Initial flow configuration and flow configuration at injection of 6 and 10 port valving system for GC/MS and TCD.

The anticipated analysis of permanent gases which included CH₄, O₂, N₂, CO₂, C₂H₆ required a different column. Literature research and consultation with GC experts resulted in the purchase of a Supelco Carboxen-1010 Plot column. One of the distinguishing and required characteristics of this column is a capability to separate O₂ and N₂ without the assistance of cryogenics. Once the instruments were assembled with the necessary detectors and were passing calibration tests, the first analysis was performed. Samples of jet fuels JP7 and JP8 required characterization. I aided Sophia Kozlova who was working with professor Castaldi on this project, the separation and analysis of the samples.

References:

- ¹ N.J. Themelis, S. Kaufman (2004) Waste in a Land of Plenty. Waste Management World. Sept.-Oct. 2004: 24-25.
- ² Committee on Health Effects of Waste Incineration Board on Environmental Studies & Toxicology Commission on Life Sciences National Research Council. Waste Incineration and Public Health. National Academy of Sciences (1999). <http://www.nap.edu/openbook/030906371X/html/24.html>
- ³ P. O'Leary, P. Walsh (2002). Landfilling as a Cornerstone of an Integrated Waste System. Solid and Hazardous Waste Center, University of Wisconsin-Madison.
- ⁴ J. Fuller (2000). Clean Air Act Amendments Provide the Muscle to Fight Pollution. <http://usinfo.state.gov/journals/itgic/0300/ijge/gj-07.htm>
- ⁵ B.K. Lee, M. J. Ellenbecker, R. Moure-Eraso (2001). Analyses of the recycling potential of medical plastic wastes. Waste Management 22(2002) 461-470.
- ⁶ U.S.EPA (1996). Standards of Performance for New Stationary Sources and Emission Guidelines for Existing Sources: Medical Waste Incinerators. Federal Register: June 20, 1996 (Volume 61, Number 120).
- ⁷ Center for Health Environment and Justice (1999). American People's Dioxin Report. <http://www.safealternatives.org/peoplesreport.html>
- ⁸ B. Weinholt (2001). Making Health Care Healthier: A Prescription for Change. Environmental Health Perspectives. EHP 109-8, 2001.
- ⁹ WHO. Safe Health-care Waste Management (Policy Paper). Department of Protection of the Human Environment, Water, Sanitation and Health. <http://www.healthcarewaste.org>
- ¹⁰ A.D.Patil, A.V.Shekdar (2001). Health-care waste management in India. Journal of Environmental Management. 2001 Oct: 63(2):211-20.
- ¹¹ M.L. Garvin (1999). Medical waste management: the problem and solutions. Handbook of modern hospital safety. Boca Raton, FL: Lewis Publishers, 1999.
- ¹² U.S. EPA (1989). Resource Conservation and Recovery Act, Part 259. <http://www.epa.gov/compliance/civil/rcra/medwastereq.html>
- ¹³ U.S.EPA <http://www.epa.gov/epaoswer/other/medical/mwfaqs.htm>
- ¹⁴ Y. Jang, C. Lee, O. Yoon, H. Kim (2005). Medical Waste Management in Korea. Journal of Environmental Management. 2005 Aug.
- ¹⁵ E. Rau, et al. (2000). Minimization and Management of Wastes from Biomedical Research (2000). Environmental Health Perspectives 108(suppl 6):953-977 (2000).
- ¹⁶ Franklin Associates service of McLarenHart for U.S.EPA Municipal and Industrial Solid Waste Division (1999). Characterization of Municipal Solid Waste in the United States: 1998 Update. Report No. EPA 530.
- ¹⁷ D. Marrack, D. Meyers (1994). PP/PE medical syringe recycling system: sharps away. 87th Annual Mtg and Exhibition, Air and Waste Management Association. Paper No. 94-RP-23B.01. Cincinnati, OH, June 19-24. <http://www.healthstate.ny.us/nydoh/>

-
- ¹⁸ B.K. Lee, M.J. Ellenbecker (1995) A Study of Disposal and Recycling of Hospital and Medical Wastes. Center for Environmentally Appropriate Materials (Final Report). University of Massachusetts, MA.
- ¹⁹ B. Kaiser, P.D. Eagan, H. Shaner (2001). Solutions to Health Care Waste: Life-Cycle Thinking and "Green" Purchasing. Environmental Health Perspectives 109:205-207 (2001).
- ²⁰ California Integrated Waste Management Board (2003).
<http://www.ciwmb.ca.gov/BIZWASTE/factsheets/hospital.htm>
- ²¹ K. Shapiro, M. Stoughton, R. Graff, L. Feng (2000). Healthy Hospitals: Environmental Improvements Through Environmental Accounting. Submitted to U.S. EPA, Office of Prevention, Pesticides and Toxic Substances, July 2000, pp.1.
- ²² U.S. EPA (1994). Medical Waste Incinerators- Background Information for Proposed Guidelines, Office for Air Quality Planning and Standards. EPA-453/R-94-043.
- ²³ World Health Organization.
http://www.who.int/water_sanitation_health/medicalwaste/002to019.pdf
- ²⁴ J.Thornton. Environmental Impacts of PVC Building Materials for U.S. Green Building Council, pp49.
- ²⁵ Marrack (1988). Hospital Red Bag Waste. JAPCA 38:1305-1311.
- ²⁶ D.Albina, K. Millrath, N.J. Themelis (2004). Effects of Feed Composition on Boiler Corrosion in Waste-to-Energy Plants. 12th North American Waste To Energy Conference (NAWTEC 12).
- ²⁷ U.S.EPA. Frequently Asked Questions, Medical Waste Home Page
<http://wwepa.gov/epaoswer/other/medical/mwfaqs.htm>
- ²⁸ NIIR Board of Consultants & Engineers. Medical, Municipal & Plastic Waste Management Handbook. Chp.3.
- ²⁹ National Academy of Sciences (1999). Waste Incineration and Public Health. Chp.2 pp37-40. <http://www.nap.edu/openbook/030906371X/html/37.html>
- ³⁰ U.S. EPA. Medical Waste Incineration. A.P.-42 Vol.I, Chp. 2.3.
www.epa.gov/ttn/chief/ap42/ch02/final/c0203.pdf
- ³¹ www.consutech.com/incineratorsection.jpg
- ³² Ozonator Industries, Canada. The Ozonator.
<http://www.ozonatorindustries.ca/ozonator.html>
- ³³ L.F.Diaz, G.M.Savage, L.L.Eggerth (2005). Alternatives for the treatment and disposal of healthcare wastes in developing countries. Waste Management 25 (2005) 629-630.
- ³⁴ N.J. Themelis (2003). An overview of the global waste to energy industry. Waste Management World, Review Issue, July-August 003, pp 40-47.
- ³⁵ N.J.Themelis, K.Millrath (2004). The Case for WTE as a Renewable Source of Energy. 12th North American Waste To Energy Conference (NAWTEC 12), 2004.
- ³⁶ International Solid Waste Association (2004). WASTE-TO-ENERGY:Clean, Reliable, Renewable Power, Fact Sheet. <http://www.wte.org>
- ³⁷ <http://wte.cbll.net/methods/incineration>

³⁸ U.S.EPA (1995). Standards of Performance for New Stationary Sources and Emission Guidelines for Existing Sources: Municipal Waste Combustors. 40 CFR Part 60[AD-FRL-5327-5]. Federal Register/ Vol.60, No. 243/ Tuesday, December 19,1995/ Rules and Regulations.

³⁹ Wikipedia contributors, "Gasification," *Wikipedia, The Free Encyclopedia*, <http://en.wikipedia.org/w/index.php?title=Gasification&oldid=46438636>

⁴⁰ A. Klein, K. Whiting, E. Archer, J. Schwager (2004). Gasification and Pyrolysis. Waste Management World, September-October, pp 73.

⁴¹ SVZ GmbH. Waste Utilization: BGL gasifier. <http://www.svz-gmbh.de/GB/Seiten/rahmttec.html>

⁴² Wheelabrator Environmental Systems, Inc. (1997). Beneficial Use and Recycling of Municipal Waste Combustion Residues. National Resource Energy Labs (NREL).

⁴³ T. Paddock (1989) Dioxins and Furans: Where They Come From. Academy of Natural Sciences.

http://www.newmoa.org/prevention/topic/sub/107/dioxins_and_furans-where_they_come_from.htm

⁴⁴ U.S.EPA (2003). <http://www.epa.gov/ncea/dioxinqa.htm#g2>

⁴⁵ V.I. Babushok, W.Tsang (2001). Gas-phase mechanism for dioxin formation. *Chemosphere* 51 (2003) 1023-1029.

⁴⁶ G. McKay (2001). Dioxin characterization, formation and minimization during municipal solid waste (MSW) incineration: review. *Chemical Engineering Journal* 86 (2002) 343-368.

⁴⁷ F.J. Mastral, E. Esperanza, C. Berrueco, M. Juste and J. Ceamanos (2003). Fluidized bed thermal degradation products of HDPE in an inert atmosphere and in air-nitrogen mixtures. *J. Anal. Appl. Pyrolysis*, 70, 1-17.

⁴⁸ J. Nishino, M. Itoh, T. Ishinomori, N. Kubota, Y. Uemichi (2003). *J. Material Cycles Waste Management*, 5, pp.89-93.

APPENDIX

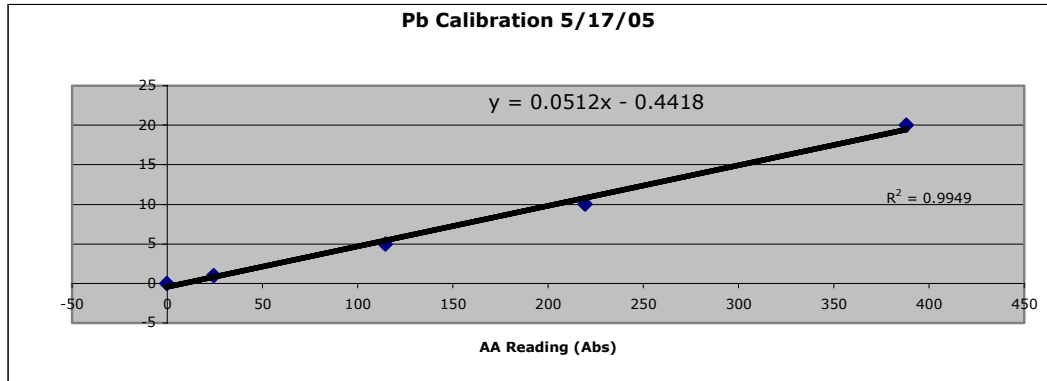
Table 1.: HEATING VALUE DETERMINATION DATA

Plastic Sample (category)	Change in Temperature (Celsius)	Mass of Sample (g)	Heat of Reaction (cal)	Heat of Combustion (cal/g)	AVG Heat of Combustion (cal/g)	Heating Content (Btu/g)	% Variation
Light weight plastic wrap (#1)							
sample 1	1.71	0.4255	4001	9,404	9293	36.89	2.4
sample 2	1.73	0.4409	4048	9,182			
Hard plastics: syringe bodies, lids (#2)							
sample 1	1.73	0.4718	4048	8,580	8274	32.85	7.4
sample 2	1.58	0.4640	3697	7,968			
Plastic lined cotton and paper (#3)							
sample 1	1.13	0.4060	2644	6,513	7078	28.10	16.0
sample 2	1.34	0.4103	3136	7,642			
Paper and cloth bandages (#4)							
sample 1	0.97	0.4976	2270	4,561	4656	18.48	4.1
sample 2	1.01	0.4975	2363	4,751			
Red plastic bags (#5)							
sample 1	1.13	0.2798	2644	9,450	9784	38.84	6.8
sample 2	1.17	0.2706	2738	10,118			
Gloves (#6)							
sample 1	1.42	0.4545	3323	7,311	7580	30.09	7.1
sample 2	1.53	0.4561	3580	7,850			
Finely shredded mix of 1-6 (#8)							
sample 1	1.41	0.4532	3299	7,280	6740	26.76	16.0
sample 2	1.23	0.4643	2878	6,199			
Random: glass, screen, metal (#7)	ND	ND	ND	ND	ND	ND	ND
Weighted Summation (Btu/g)							
27.45							

Table 2.: % CHLORINE DETERMINATION DATA

Sample	Sample (mass in grams)	AgCl Blank	AgCl Yield (mass in grams)	
Blank (Oil)	0.7924		0.0004	% of Chlorine Recovery
NaCl	0.0551	0.0004	0.1325	0.98
Plastic Sample (category)	Plastic Sample (mass in grams)	AgCl Blank	AgCl Yield (mass in grams)	% Mass of Cl of Plastic Sample
Light weight plastic wrap (#1)	0.2156	0.0004	btw 0.0102 and 0.0235	1.12-2.65
	0.2015	0.0004	no precipitate	ND
	0.3005	0.0004	0.0012	0.07
	0.2020	0.0004	0.0613	7.46
	0.2160	0.0004	0.0074	0.80
Hard plastics: syringe bodies, lids (#2)	0.2399	0.0004	0.1271	13.07
	0.2174	0.0004	0.0385	4.34
	0.2442	0.0004	0.1202	12.14
Plastic lined cotton and paper (#3)	0.2831	0.0004	no precipitate	NA
	0.3973	0.0004	no precipitate	NA
Paper and cloth bandages (#4)	0.2147	0.0004	0.0025	0.24
	0.2053	0.0004	0.0059	0.66
Red plastic bags (#5)	0.2120	0.0004	0.0035	0.36
	0.2091	0.0004	0.0038	0.40
Gloves (#6)	0.3042	0.0004	0.2119	17.20
	0.3014	0.0004	0.1679	13.75
Finely shredded mix of 1-6 (#8)	0.3929	0.0004	0.0256	1.59
	0.3996	0.0004	0.0094	0.56
	0.4061	0.0004	0.063	3.81
	0.4112	0.0004	0.099	5.93

FIGURE 1.: ATOMIC ABSORPTION LEAD DATA SAMPLE



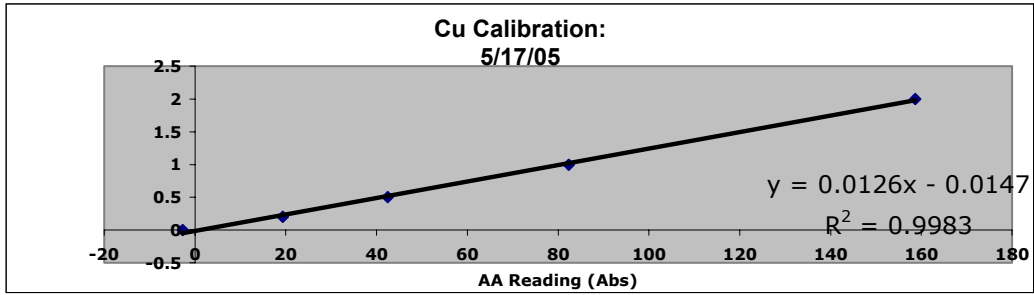
Pb (ppm)	Blank	AA reading			Blank	AA
0		0	0	-1		0
1	0	24	24	25	0	24
5	0	113	116	116	1	115
10	0	221	219	221	2	219
20	1	390	390	389	2	388

Pb-Trial #1	Blank	AA reading			Blank	Average	ppm
1-N: Bottom	1	22	20	20	2	19	0.54
1-N: Combined	2	23	24	24	2	22	0.67
1-N: Fly	2	74	73	72	2	71	3.19
1-N: Extr. Fluid	2	3	4	3	2	1	-0.37

Pb-Test	Blank	AA reading			Blank	Average	ppm
2-N: Combined	2	51	52	52	1	50	2.13
2-N: Combined	2	22	22	22	2	20	0.58
2-N: Bottom	2	51	52	51	2	49	2.08

Pb-Trial #2	Blank	AA reading			Blank	Average	ppm
2-A: Bottom	2	10	9	10	2	8	-0.05
2-B: Combined	2	13	12	13	3	10	0.08
2-C: Fly	2	552	553	553	3	550	27.73

FIGURE 2.: ATOMIC ABSORPTION COPPER DATA SAMPLE



Cu (ppm)	Blank	AA Reading			Blank	AA
0		-2	-3	-3		-3
0.2	-2	18	17	17	-2	19
0.5	0	42	42	42	-1	43
1	-1	81	80	80	-3	82
2	-2	156	157	157	-2	159

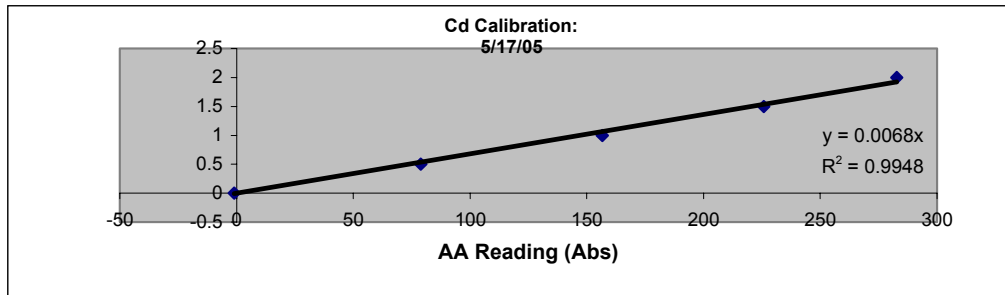
Cal. A

Cu-Trial New#1	Blank	AA reading			Blank	Average	ppm
1-N: Bottom	-2	131	128	127	-2	131	1.63
1-N: Combined	-2	0	0	2	-5	4	0.04
1-N: Fly	-3	6	5	5	0	7	0.07
1-N: Extr. Fluid	0	19	19	20	-1	20	0.24

Cu-New#2	Blank	AA reading			Blank	Average	ppm
2-N: Bottom	-1	401	404	397	-2	402	5.05
2-N: Combined	-4	5	5	5	-2	8	0.09
2-N: Fly	-2	3	3	3	0	4	0.04

Cu-Test	Blank	AA reading			Blank	Average	ppm
2-A: Bottom	-2	21	20	20	-2	22	0.27
2-B: Combined	-3	34	34	33	-2	36	0.44
2-C: Fly	-3	8	9	9	0	10	0.11

FIGURE 3.: ATOMIC ABSORPTION CADMIUM DATA SAMPLE



<i>Cd (ppm)</i>	<i>Blank</i>	<i>AA reading</i>			<i>Blank</i>	<i>Average</i>
0		-1	-1	-1		-1
0.5	-3	75	76	77	-3	79
1	-4	151	154	153	-4	157
1.5	-4	220	222	222	-5	226
2	-4	279	280	280	-2	283

<i>Cd-Trial #1</i>	<i>Blank</i>	<i>AA reading</i>			<i>Blank</i>	<i>Average</i>	<i>ppm</i>
1-N: Bottom	-4	31	31	32	-1	34	0.23
1-N: Combined	-3	16	15	18	1	17	0.12
1-N: Fly	-3	22	22	22	2	23	0.15
1-N: Extr. Fluid	0	0	-1	-1	-2	0	0.00

<i>Cd-Trial #2</i>	<i>Blank</i>	<i>AA reading</i>			<i>Blank</i>	<i>Average</i>	<i>ppm</i>
2-N: Bottom	-1	3	2	1	1	2	0.01
2-N: Combined	0	4	4	4	-1	5	0.03
2-N: Fly	-2	15	15	15	1	16	0.11

<i>Cd-Old Trial #2</i>	<i>Blank</i>	<i>AA reading</i>			<i>Blank</i>	<i>Average</i>	<i>ppm</i>
2-A: Bottom	-1	3	2	2	-2	4	0.03
2-B: Combined	-3	6	5	5	-3	8	0.06
2-C: Fly	-3	25	27	26	-2	29	0.19

METHOD 1: USED FOR CHLORINE DETERMINATION

Analytical Methods for Oxygen Bombs

No. 207M

2

with the addition of alcohol. Herrig²⁰ back titrates with Tritiplex III using phthalein purple as an indicator. A conductometric method has been suggested by Barthel⁶. Nephelometric methods for trace amounts of sulfate have been suggested by Toennies⁴³ and Bailey⁵.

Chlorine in Combustible Solids and Liquids.

Platinum combustion capsules and platinum ignition wire are recommended for these tests because of the extremely corrosive nature of chlorine and its compounds. After repeated use with such samples, the inner surfaces of the bomb will become etched to the point where appreciable amounts of metal salts will be introduced during each combustion. The ability of the bomb to withstand such corrosion can be improved by keeping the inner surfaces highly polished. Any bomb which is being used for chlorine determinations should be repolished at regular intervals to prevent the development of deep pits. The alternative to this procedure is to use an 1108CL bomb which offers much better resistance to chlorine than the standard 1108 bomb. Or for ultimate protection, use an 1105C or 1106C bomb with a platinum liner.

Samples containing more than 2% chlorine by weight should be diluted with U.S.P. white oil or some other non-volatile, chlorine-free diluent. The suggested amounts of sample and diluent are shown in the following table, but the user is cautioned that the combined weight of the charge **must not** exceed 1.0 gram.

% Chlorine in Sample	Grams of Sample	Grams of White Oil
Below 2	0.8	0.0
2 to 5	0.4	0.4
5 to 10	0.2	0.6
10 to 20	0.1	0.7
20 to 50	0.05	0.7

Place about 5 ml of a 5% sodium carbonate solution (135g Na₂CO₃·10H₂O per liter) in the bomb, assemble and fill with oxygen to a pressure of 35 atmospheres. Immerse the bomb in a bath through which cold

water is circulating. Attach the ignition wire to the bomb terminal, then stand at least six feet from the bath when firing the charge. Keep the bomb in the bath at least five minutes before removal. Release the residual gas slowly and at an even rate so that the pressure is reduced to atmospheric in not less than one minute. Open the bomb and examine for traces of unburned sample or sooty deposits. If found, discard the determination and clean the bomb thoroughly before using it again.

If the combustion was satisfactory, wash the sample cup and all interior surfaces of the bomb with a fine stream of distilled water, collecting the washings in a 600 ml beaker. Scrub the interior of the cylinder and the underside of the head with a rubber policeman. Continue washing until no acid reaction is observed on any bomb parts or passages, which will normally require at least 300 ml of wash water.

Acidify the solution by adding 1:1 nitric acid dropwise until the methyl red endpoint is observed; then add 2 ml excess acid. Filter through a qualitative paper and collect the filtrate in a 600 ml beaker. Heat to about 60 °C; protect from strong light and slowly add 5 ml of silver nitrate solution (50 g per liter) while stirring. Heat almost to boiling and hold at this temperature until the supernatant liquid becomes clear. Add a few drop of silver nitrate solution to test for complete precipitation. If cloudiness appears, repeat the above operation.

Allow the beaker to stand in a dark place for at least one hour. Filter the precipitate by suction onto a weighed fritted glass filter. Wash with distilled water containing 2 ml of 1:1 nitric acid per liter. Dry the precipitate and crucible at 110 °C for one hour. Cool in a desiccator and weigh.

Make a blank determination with 0.7 to 0.8 gram of white oil, omitting the sample; then calculate the chlorine content of the sample by substituting in the following equation:

Chlorine, % by wt. = $(P-B) 24.74 m$

where,

P = grams AgCl obtained from sample

B = grams AgCl obtained from blank

m = mass of sample in grams

PARR INSTRUMENT COMPANY

211 Fifty Third Street Moline, Illinois 61265

Phone 800 872 7720 Fax 309 762 9453

www.parrinst.com email parr@parrinst.com

Printed 07/04

METHOD 2: TCLP USED IN ASH CHARACTERIZATION

CD-ROM 1311- 1 Revision 0

July 1992

METHOD 1311

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the TCLP need not be run.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 SUMMARY OF METHOD

2.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

VITON is a trademark of Du Pont. 1 ®

CD-ROM 1311- 2 Revision 0

July 1992

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 + 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Section 4.3.1). The vessels shall have an internal volume of 500-600 mL, and be equipped to accommodate a 90-110 mm filter. The devices contain VITON O-rings which should be replaced frequently. Suitable ZHE®1 devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Section 7.3) refers to pounds per square inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.
