Effect of plastics on the lignin results for MSW and the fate of lignin in laboratory solid waste reactors

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Effect of plastics on the lignin content of MSW and the fate of lignin in laboratory solid waste reactors

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Abstract

Cellulose to lignin ratio is one of the widely used indicators of degree of landfill stabilization. This ratio shows the amount of carbohydrate or cellulose consumed by anaerobes compared to relatively inert lignin. However, the method of lignin measurement contains an intrinsic error. Plastics are contained in the landfill samples and these are characterized as lignaceous materials due to their acid-insolubility. Lignin is typically measured as the organic residue that is acid insoluble but is combustible upon ignition. Additionally lignin may degrade under anaerobic, high temperature conditions associated with wet conditions in sediments and bioreactor landfills.

In this study, it has been found that the typical measure of lignin, a gravimetric measure, also includes plastics, leading to erroneous measures of both lignin and the cellulose/lignin (C/L) ratio. Typically, 100% of the plastic will be measured as lignin. Since plastic amounts to approximately 10% of landfill contents, lignin measurements will be 10% greater than actual amounts. Laboratory reactors were set up with known amounts of paper and plastic. The degradation of the cellulose and lignin in paper was measured and compared to plastics, which was collected by hand and weighed. Ratios of cellulose to plastics and lignin to plastics were obtained. It was found, based on the cellulose to plastic ratio and lignin to plastic ration that lignin degrades under anaerobic conditions although at a much slower rate than cellulose. These findings indicate that the cellulose to lignin ratio cannot be used as the sole indicator of stabilization in the landfills. The inclusion of the biochemical methane potential test data along with C/L is thought to provide a better indication of landfill stabilization.
I would like to thank to Dr. Novak for giving me a wonderful opportunity to experience solid waste and allowing me to work at my pace. I also thank to Dr. Douglas Goldsmith for showing his sincere interest in my work and providing samples and reactors. I want to thank to Dr. Clifford Randall for reviewing my thesis at the short notice and being a member on my committee. Special thanks to both of laboratory supervisors, Julie Petruska and Jody Smiley for all the sincere help with analytical equipment and keeping a great working environment. Thanks to my colleagues, Garret Bricker and Ayesha Irani for helping me with my work and being a good consultant. Thanks to all students in the environmental engineering department for tolerating what nuisance that may come with the trashes. Special thanks to Chul Park and Chris Muller for letting me borrow their ideas and answering my immature questions. I would like to thank Waste Management Inc. for the funding and making this study possible. I want to give my heartful gratitude to my parents who prayed for me all the time and ensured me that I got the best opportunities in life.
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Chapter 1. Introduction

Landfilling is one of the primary solid waste disposal methods and was responsible for the disposal of about 55.3% (USEPA, 2002) of the MSW generated in the United States in 2000. In spite of its importance, research on solid waste disposal has been limited. However, about two decades ago, bioreactor landfills were proposed as an improved way of landfilling and in recent years, increased attention has been focused on understanding and optimizing these systems.

The landfill bioreactor utilizes higher moisture content that traditional landfills to achieve higher temperatures and faster degradation rates. This method has been found to be very economical for the utilization of space, owing to accelerated degradation, efficient collection of gas, and reduced leachate volumes and improved leachate quality. Accelerated degradation also shortens the required monitoring time after closure, which otherwise lasts about 30 years. Because of these advantages, bioreactor landfills are now being widely studied and implemented at many landfill sites.

The end point for completion of landfill monitoring has not yet been clearly defined. Leachate COD and BOD, gas production rates, morphological judgment, and cellulose to lignin ratio are widely accepted as indices of landfill stabilization (Reinhart and Townsend, 1998). In this research, the focus will be in the validity of the lignin test and the solubilization and degradation of lignin in paper.

Paper or pulp-oriented products consist of 40% of the waste disposed to municipal landfills. Methane generated from degradation of this material is mainly responsible for greenhouse gas emission from landfills. The constituents of these products are mostly lignocelluloses, complex carbohydrates that can usually be found in papers and trees. It is widely believed that celluloses and hemicelluloses degrade in the landfill under anaerobic conditions with nutrients and moisture, but lignin is not susceptible to microbial attack under the same
conditions. Using this logic, the cellulose to lignin ratio was used as a landfill stabilization index in the field. That is, a landfill is considered stabilized when the C/L ratio reaches about 0.2.

However, MSW is not homogeneous and contains not only paper, but also many kinds of waste debris and industrial products. It is difficult to detect only lignin since acid insoluble and volatile materials such as plastics may also be measured as lignaceous material. Furthermore, many biological scientists have shown that lignaceous materials degrade under anaerobic condition and this was partially confirmed by Kelly (2002).

The purpose of this study was to evaluate the effect of plastics on the gravimetical lignin detection method and to monitor changes in cellulose and lignin content of paper samples under conditions that simulate landfill bioreactors, including leachate recirculation. Leachate was also collected and tested for additional evidence of lignin solubilization.
Chapter 2. Literature Review

1. Introduction.

Landfilling has been used as one of the primary solid waste disposal options throughout human history. This option was considered convenient and economical until people encountered adverse effects such as groundwater contamination, unpleasant odor, rodents and insects oriented diseases, etc. It was about decades ago when bioreactor landfills, using higher moisture contents and more strict controls of nutrients, pH, buffering, reduced particle sizes, lining enhancement, etc was suggested as an alternate landfilling method to the conventional way of digging and dumping. The bioreactor landfill has recently been the focus of research by several environmental scientists. These studies have considered the relationships between degradation rates and various factors including moisture content, pH, temperature, buffering, nutrients, different terminal electron acceptor (TEAP) and gas production.

2. MSW generation trends

The major components of Municipal Solid Waste (MSW) are paper, plastic, yard wastes and construction wastes. About 40 percent of total mass of MSW is paper or pulp-oriented products. (Barlaz et al., 1990; Kelly, 2002) Plastic and petroleum-related products comprised approximately 3 percent of MSW in the early 70s to 6.5 percent in 1986 (Barlaz et al., 1990; Kelly, 2002). If the increase of plastic contents in MSW follows a linear relation, plastics should be about 10.4 percent of MSW in 2004. This is close to the values reported by the EPA report for the year 2000 dealing with MSW generation, source reduction, recycling and disposal published in June 2002. According to the report, plastics comprised 10.7 percent of MSW generated in United States. Reinhart and Townsend (1998) also analyzed the trend of waste generation in United States. According to their summary, the population of United States increased by 16% and MSW generation rate increased by
28%. This jump was found to be mainly due to an increase in the number of households by about 34%, which caused an increase in yard waste, waste home furnishings and waste clothing. An increased office work force was responsible for increased waste paper generation. More packaging materials and less food waste was also found due to the change in packaging in grocery stores and the frequent use of convenient stores. The MSW generation trend of United States from 1960 to 2000 is depicted in Figure 2-1.

![Figure 2-1. MSW generation rates from 1960 to 2000 (USEPA, 2002)](This graph is redrawn from the Figure ES-1 in USEPA report, Municipal Solid Waste in The United States: 2000 Facts and Figures published June 2002)

It was recently reported that a decline in per capita refuse production and a reduction of the ratio of landfilled materials had occurred. This is due to the result of source reduction and recycling. (USEPA, 2002). Table 2-1 shows the amount of reduction of MSW via material recovery and composting from 1960 to 2000.
Table 2-1. Generation, materials recovery, composting and discards of municipal solid waste, 1960-2000 (In millions of tons)

(Table is prepared from the Table ES-1 in USEPA report, Municipal Solid Waste in The United States: 2000 Facts and Figures published June 2002)

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Generation</td>
<td>88.1</td>
<td>121.1</td>
<td>151.6</td>
<td>205.2</td>
<td>211.4</td>
<td>223.4</td>
<td>231.0</td>
<td>231.9</td>
</tr>
<tr>
<td>Recovery for recycling</td>
<td>5.6</td>
<td>8.0</td>
<td>14.5</td>
<td>29.0</td>
<td>45.3</td>
<td>48.0</td>
<td>50.1</td>
<td>53.4</td>
</tr>
<tr>
<td>Total Materials Recovery</td>
<td>5.6</td>
<td>8.0</td>
<td>14.5</td>
<td>33.2</td>
<td>54.9</td>
<td>61.1</td>
<td>64.8</td>
<td>69.9</td>
</tr>
<tr>
<td>Discards after Recovery</td>
<td>82.5</td>
<td>133.0</td>
<td>137.1</td>
<td>172.0</td>
<td>156.5</td>
<td>162.3</td>
<td>166.2</td>
<td>162.0</td>
</tr>
</tbody>
</table>

* Composting of yard trimming and food wastes. Does not include mixed MSE composting or backyard composting.

Details may not add to totals due to rounding.

Source: Franklin Associates, Ltd.

3. Control Parameters of Bioreactor Landfill

A bioreactor landfill is similar to a conventional landfill, but its moisture content is maintained at much higher level (about 40%, wet basis) through leachate recirculation and water addition. Other operational differences include higher temperatures, nutrients and buffer control, sludge addition, shredding, and lift design (Kelly, 2002). Extra moisture allows microbes to have a better chance to contact nutrients and waste material, which results in accelerated degradation. One method used to achieve this is through leachate recirculation and this has shown great success in both real landfill sites and in research. Pohland et al (2000) described this newly developed landfilling method as an anaerobic process with the capability to generate and consume organic substrate loading internally, if an external organic source is not added.

Hartz et al (1982) stated that the optimum temperature for methane production in landfills was 41 °C and the production decreased around 50 °C. As a matter of fact, a temperature in the range of 30 to 45 °C is usual in the landfill with moderate water control and increased
temperature is thought to be caused by microbial action and the insulation due to the waste itself. (Warith and Sharma, 1998)

The optimal ratio of nutrients was also reported by Warith and Sharma. (1998) Based on their research, ratio of organics (in COD), nitrogen, and phosphorus as 100:0.44:0.08 is the most appropriate for microbial activity.

Sludge may act as an inoculum for methanogens in spite of the presence of these organisms in refuse. Degraded refuse can also be applied as an inoculum for methanogenesis in fresh waste. Old trash may also dilute toxic compounds. (Barlaz et al., 1990) Cover soil that is used daily at the landfill is reported as a large source of anaerobes.

Leachate recirculation with buffer and nutrient control and sludge addition was reported to accelerate waste stabilization (Barlaz et al., 1989). Small and well-sorted waste size should increase waste degradation since this attributes to greater chance of contact between microbes and nutrients. However, Barlaz et al. (1990) reported that increased rate of hydrolysis and pH depression due to an accumulation of organic acids could result from the small particle size. The pH drop inhibits methanogenesis since a neutral pH range is optimum for the methane production.

4. Advantages and Disadvantages of Bioreactor Landfill

The advantages of the bioreactor landfill are reported in economical and environmental aspects. This advanced waste disposal method accelerates waste degradation, which makes more space available for refuse disposal and less time is required for the monitoring. In addition, the diminished amount of time for leachate and gas generation makes management easier and gas recovery may become commercially viable (Boda, 2002). Leachate recirculation reduces ex-situ leachate treatment requirements, as well as its strength. San et al. (2001) described leachate recirculation as a relatively controlled
anaerobic filter. Pohland and Al-Yousfi (1994) reported a cost saving of approximately $U.S.2500 per acre at landfills with leachate recirculation, due to reduced monitoring requirements, space recovery, and other potentials. (Reinhart and Al-Yousfi, 1996)

However, the disadvantages are also recognized. Energy, expertise and capital cost is higher than for conventional landfills (Boda, 2002). Increased leachate volumes and degradation rates require stronger liners and more strictly controlled operations. Current U.S. federal regulations for MSW landfills (Subtitle D, Resource Conservation and Recovery Act) specify the requirements as a double liner with the drainage layer in between (Reinhart and Townsend, 1998). This new method also imposes complicated siting, construction, and operation upon the engineers. Inclined water pressure due to the increased volume of leachate may cause layer failure and the effluent as a result can contaminate ground and surface water. Landfill gas can also create adverse environments such as odors, health hazards, explosions, and greenhouse gas production (Reinhart and Townsend, 1998). In case of excess leachate recirculation, landfill operators may face the problems such as saturation, ponding and acidic condition. (San and Onay, 2001) In spite of these risks, the U.S EPA announced that leachate recirculation is being applied to more than 200 landfills. (Reinhart and Carson, 1993).

5. Five Significant phases of degradation in Landfill

Five separate phases are thought to exist in landfill stabilization processes. The biochemical environments vary in each phase, which indicates that different biological and chemical reactions are taking place in the landfill. These environments, along with chemical changes, are shown in Figure 2-2.
The first or the initial adjustment phase represents the initial distribution of the waste and moisture. This adjustment period usually indicates the time required for building appropriate moisture content and consumption of oxygen that is not yet completely depleted. Aerobic degradation is most likely to happen and carbon dioxide can be detected as a byproduct.

The second or the transition phase indicates that the field capacity is fulfilled and a change in the environment from aerobic to anaerobic. Nitrate and sulfate are starting to be substituted for oxygen as an electron acceptor and this can be verified by observing the redox potential, which is expected to be negative. Chemical oxygen demand (COD) and volatile organic acids (VOA) become measurable in the leachate.

The third or the acid formation phase can be characterized by high amount of VOAs. These are the products from the hydrolysis of refuse and the biological conversion of their organic
intermediates into acids. The typical pH is between 5 and 6 and metal ions are released due to low pH.

The fourth or the methane fermentation phase can be described as conversion of the intermediate acids to methane and carbon dioxide by methanogenic microbes. Sulfide appears due to the reduction of sulfate and pH increase can be observed, which is induced from the consumption of the organic acids. Since methanogens prefer a neutral pH environment, this condition supports methanogenesis. Metals precipitate because of the increased pH. In bioreactor landfills, the time required for this phase is significantly reduced and this results in increased gas volumes that may enable better control over gas collection. This also means that it is possible to reduce the emission of the greenhouse gas that depletes ozone in the outer atmosphere. Since methane-producing organisms are very sensitive to substrates, temperature and pH, this leads to difficulties in controlling the system. For instance, methanogenesis can be inhibited in sulfate-rich environments since sulfate-reducing organisms have tendency to out-compete methanogens for electron donors such as hydrogen or acetate. Gurijala and Sulfita (1993) showed that extracts of papers or textiles contained more sulfate than other landfill components, which suggests that paper can be either cellulose and sugar reservoirs or inhibitors of methanogenesis. Considering 40% of landfilling materials are paper or pulp-related materials, their effects on methane producing reaction could be significant. Moreover, construction wastes such as gypsum are also good sulfate source (Gurijala and Sulfita, 1993).

The fifth or the maturation phase can be observed after most of available substrate is consumed and gas production becomes significantly lower. Leachate strength stays constant at low concentration and recalcitrant organics start to slowly degrade by contacting gas from the atmosphere that is permeated through the remaining wastes. This phase may last for several years or decades (Reinhart and Townsend, 1998).
6. Lignocellulose

The term, lignocellulose is the combination of cellulose, hemicellulose and lignin, which may comprise 89 to 98% of the dry weight of wood. (Conberg, 1988) Cellulose provides flexibility and strength to cell walls and hemicelluloses provide links or chemical bonding between cellulose and the lignin. Lignin protects cells from attack by various chemicals and enzymes due to its amorphous and hydrophobic characteristic. (Boda, 2002)

![Diagram of major components of wood and chemical structures of lignin, cellulose, and D-glucose](image)

Figure 2-3. Major components of wood, including the chemical structure of lignin (model), cellulose and its hydrolysis products, cellulose and D-glucose (Conberg, 1988).

Cellulose is the dominant natural organic compound on earth. This material can be usually found between the primary and secondary cell walls of plants. It is an unbranched polymer containing thousands of D-glucose units connected by a β-1, 4-glycosidic linkage (Conberg, 1988).
Hemicellulose is also a polysaccharide composed of various polymers such as xylose, arabinose, and mannose. The compound, with xylose or arabinose as a main building component, is referred to as xyloglucans or arabinoglucans, respectively. This natural building material of plant cell wall is abundant in primary walls but is also found in secondary walls. Hemicellulose molecules are often branched, very hydrophilic and transformed to gelatinous material in the presence of water.

(http://sunflower.bio.indiana.edu/~rhangart/courses/b373/lecturenotes/cellwall/cellwall.html)

Lignin, which is the second most abundant natural organic material, is relatively ill defined due to its structural variety. For this reason, lignin is usually described in average terms. The definition of lignin is morphologically summarized by Freudenberg (1955). According to his definition, lignin is a material that appears in the membranous polysaccharides and the spaces between the cells, accordingly giving strength to them. It can be found in physiologically dead tissue. Freudenberg (1955) also mentioned the chemical characters of coniferous lignin in an idealized way. In this sense, lignin is assumed to be a compound of thermoplastic 3-dimensional polymers consisted of coniferyl alcohol or other guaiacylpropane monomers. It is not soluble in water, most organic solvents, and strong sulfuric acid. However, it is readily oxidized and soluble in hot alkali. It also spontaneously condenses with alcohol and phenolic compounds. The lignin has most of the methoxyl content of the wood, contains a specific ultraviolet absorption spectrum and shows characteristic color reactions with a number of phenols and aromatic amines. It has many different basic compositions and methoxy content. (Pearl, 1967). Lignin can be broadly divided into three groups including softwood (gymnosperm), hardwood (dicotyledonous angiosperm), and grass or annual plant (monocotyledonous angiosperm) lignin. Softwood or coniferous lignin is very homogeneous group comprised of derivatives of coniferyl alcohol or similar guaiacylpropane (4-hydroxy-3-methoxylphenylpropane) monomers. This type of lignin is most widely studied. Hardwood contains derivatives of 3, 5-dimethoxy-4-hydroxyphenylpropane monomers as well as those of gaiaicylepropene polymers. Grass or
annual plant consist of polymers of both guaicylpropane and 3, 5-dimethoxy-4-hydroxyphenylpropane monomers and has 4-hydroxyphenylpropane. (Pearl, 1967)

The amount of lignin content is usually measured gravimetrically. The acid insoluble part of test material is ignited and the volatilized portion is considered lignin, which is also called Klason lignin (Baldwin et al., 1998; Kelly, 2002).

The MSW undergoes anaerobic decomposition, which mainly results in carbon dioxide and methane through the biodegradation of complex polymers. The constituents of these polymers are mainly cellulose (40 to 50 % by dry weight basis), hemicellulose (12% by dry weight basis) and lignin (10 to 15% by dry weight basis) (Wang et al., 1994; Boda, 2002).

7. Aerobic and Anaerobic degradation of lignocelluloses

Lignocelluloses degrade aerobically and anaerobically. The decomposition, however, occurs at different speeds. Aerobic degradation is much faster than anaerobic. Figure 2-4 shows the degradation pathways for lignocelluloses.

Aerobically, these natural organic reservoirs experience a humification process, which results in humus or humic substances being produced. These relatively inert materials are major storage products of organic carbon in soils and aquatic environments (Aiken et al., 1985; Tuomela et al., 1999). However, their definitive structure is not known because of their numerous groups with various chemical components (Tuomela et al., 1999).

Anaerobically, cellulose and hemicellose undergo hydrolysis and are broken down into simple sugars, which become acetate or formate through fermentation. These materials are readily degradable substrates that are converted to carbon dioxide or methane by methanogens. About 72% of anaerobic oxidation happens as a form of acetic acid oxidation.
However, lignin is considered relatively inert due to its intrinsic resistance against chemical and enzymatic attacks. Lignin is believed to be recalcitrant to anaerobic degradation. This originated from a study where no degradation of synthetic lignin was found in a number of oxygen-deficient conditions such as anoxic soil and sediments (Colberg, 1998). Recently it was found that polymeric lignin could degrade at a rate that can be considered environmentally significant in a certain aquatic environment (Colberg, 1998).

Figure 2-4. Lignocellulose carbon cycle (Brown, 1985; Colberg, 1998; Tuomela et al., 1999)
It was 1934 when the first evidence of anaerobic degradation of lignin was reported by Boruff and Buswell (1934). They found that 54% of the lignin in cornstalks was mineralized to carbon dioxide and methane after 600 days of incubation. Tarvin and Buswell (1934) provided more promising evidence at a later year. They simulated anaerobic digestion of four aromatic compounds (benzoic, phenylacetic, phenylpropionic, and cinnamic acids) with an inoculum of sewage sludge. These compounds were completely converted to carbon dioxide and methane. (Colberg, 1998) Young et al. (1987) summarized the recent reports about anaerobic degradation of synthetic lignin monomers, oligomers, and complex lignin polymers. Based on the summary, monomers can undergo complete metabolism and mineralization by providing their methoxyl content (-OCH$_3$) as a carbon substrate for acetogens. Oligomers or a polymer that consists of more than two monomers can be anaerobically depolymerized and available for the metabolism. Furthermore, the complex lignin polymers possibly experience small but consistent rate of degradation in various anaerobic conditions such as rumen isolates, sediment samples, etc.

8. Landfill stabilization indicators

The point at which a landfill can be considered stable is not clearly defined. Three categories of indicator are the most promising and these are leachate quality, gas quality and waste composition. It is widely accepted that near complete stabilization is reached when leachate strength is sustained at a COD below 1000mg/l and BOD below 100mg/l or BOD to COD ratio less than 0.1. Other indicators include the gas production ratio that reaches the value lower than 5 % of the peak, waste cellulose to lignin ratio less than 0.2 and biological methane potential less than 0.045m$^3$/kg volatile solids. Additionally, a dark-colored and sludge-like appearance is considered as an indicator of stabilization of solid waste in the landfill. (Reinhart and Townsend, 1998)

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Webpage sited
http://sunflower.bio.indiana.edu/~rhangart/courses/b373/lecturenotes/cellwall/cellwall.html
CHAPTER 3

Evaluation of the Effect of Plastics on Lignin content

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Abstract

MSW from several landfills was characterized to determine the effect of plastics on the measured lignin content of refuse. Pure plastics, hand removed from refuse were measured using the gravimetric lignin test and were found to be measured as lignin. When plastics were removed from refuse, the “lignin” content dropped in direct proportion to the amount of plastics removed. This suggests that the conventional gravimetric lignin measurement is incorrect and estimates of refuse stability, based on the cellulose to lignin (C/L) ratio, may not be appropriate.

Keywords

Cellulose/Lignin test, MSW, and Plastic.
**Introduction**

Plastics are intrinsic recalcitrant materials contained in refuse and they may remain undegraded in landfills over several decades to centuries. Due to their poor degradability, plastics have been considered very important materials in landfills with regard to space utilization. The amount of plastics buried in landfill increased about 14 times between 1960 and 1990. A recent report from the USEPA shows that plastics comprised 10.7% of MSW generated in 2000, which was equal to 23.2 million tons. This increasing trend will continue as long as manufacturers continue to substitute plastics for household products such as house furnishings, packaging, etc. The recovery of plastics for recycling is relatively small, accounting for only 5.4% or 1.3 million tons of plastics generated in 2000 (USEPA, 2002). Furthermore, plastics buried in the landfill or incinerated after recovery were rated 14.4% of total MSW discarded, which was estimated at 23.4 million tons. The long-term trend of plastic generation and recycling is provided in Figure 3-1.

![Figure 3-1. Trend of plastics generation and recovery (USEPA, 2002)](image-url)
The lignin content of MSW is usually quantified by a gravimetric method that is widely used for measuring the acid insoluble lignin content from solid waste, which, in turn, is one of the indicators of the stabilization level in a landfill. That is, landfills are considered stabilized when the waste cellulose to lignin ratio is less than 0.2 (Reinhart and Townsend, 1998). However, due to the complexity and heterogeneity of MSW, this method detects not only lignin, but may also measure other acid insoluble and volatile materials. The problem with the lignin test was also noted by Kelly (2002). Based on his research, the percent lignin content by weight is much larger in the MSW samples that contain plastics than samples without them. He suggested that acid insoluble lignin content cannot be used as a sole index but should be accompanied with other test values such as biochemical methane potential, or plastic content should be accounted for the calculations.

In this study, samples with and without plastics were tested for cellulose and lignin in order to determine the impact of plastics on the lignin content of refuse. This information will then be used to assess the value of the C/L ratio as a stabilization indicator for solid waste disposed in a landfill.

**Methods and Materials**

**Sample preparation**
A drill rig equipped with a 36-inch bucket auger was used to collect solid wastes from several landfills. These samples were taken from various depths and shipped to Virginia Tech, Blacksburg, VA. In order to keep the samples from unintended degradation, the samples were cooled during shipping and kept in 4°C refrigerator prior to analysis.

MSW from the King George landfill, King George County, VA was chosen for this research since this was readily available at the time. Samples were sent from 6 different locations in 15 gallon plastic buckets with sealable tops. Samples were collected from top, middle and bottom of the bucket and plastics were manually removed and stored in a
separate container. Mixtures of plastics (about 10% by weight) and non-plastics were prepared and dried at 105 °C for 2 days for the cellulose/lignin test.

**Grinding**
Dry samples were ground to a fine powder for the cellulose/lignin tests. These solids were shredded by the household electric blender and then ground by a Thomas Intermediate Wiley Mill with a 10-mesh screen. Non-grindable or big materials such as rocks, metals were removed by hand.

**Cellulose and Lignin tests**
AST Method E 1758-95 (1995) was adopted for the cellulose and lignin tests. A 300±10mg sample was dried and milled and then digested by 3.00 ±0.01ml of 72% sulfuric acid (H₂SO₄), first incubating the sample in a water bath at 35 °C for an hour followed by autoclaving for an hour at 121 °C and 15psi. Eighty-four ml of deionized water was added to each bottle before autoclaving. These samples were then filtered through a standard 55mm diameter microfibre filter and the solids remaining on the filter was incinerated at 550 °C for 20 minutes. The weight loss by incineration is considered to be the amount of lignin in the samples. This test was developed primarily for measuring the cellulose and acid insoluble lignin in wood but has been applied to MSW.

Calcium carbonate (CaCO₃) was added to neutralize the filtrate to a pH between 5 and 6. The supernatant was filtered through 0.45-micrometer pore size membrane and a reversed-phase cartridge. The cellulose contents of filtered liquid were quantified by using high performance liquid chromatography (HPLC) with a refractive index detector and HPX-87C column. The water flow was fixed to 0.5ml/min and synthetic dextrose powder was used for the standard.
Results and discussion

Cellulose and lignin tests were performed on a variety of MSW samples. These samples included those with the natural plastic content, with plastics removed by hand, and on the removed plastics. The results of these tests are summarized in Table 3-1. It can be easily seen that plastics are detected as pure lignin. This is also shown in Figure 3-2. In addition, the sum of % lignin of non-plastic samples and % plastic of mixtures is very similar to % lignin of mixture, which also indicates that plastics are detected as lignin using the gravimetric cellulose and lignin procedure.

Figure 3-2 shows the results of lignin analysis for samples that contained only plastics hand picked from the refuse from King George. The average lignin content by weight was 102%.

Table 3-1. Cellulose and Lignin analysis for Mixed Refuse (MR), Plastics removed from refuse (P) and Refuse with plastics removed (NP)
(Samples from King George, King George County, VA)

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Lignin</th>
<th>% Cellulose</th>
<th>% Plastic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A-P</td>
<td>102.52</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>1A-NP</td>
<td>10.90</td>
<td>9.60</td>
<td>0.00</td>
</tr>
<tr>
<td>1A-MR</td>
<td>24.20</td>
<td>28.95</td>
<td>11.79</td>
</tr>
<tr>
<td>2A-P</td>
<td>131.42</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>2A-NP</td>
<td>29.32</td>
<td>28.44</td>
<td>0.00</td>
</tr>
<tr>
<td>2A-MR</td>
<td>39.17</td>
<td>30.94</td>
<td>16.39</td>
</tr>
<tr>
<td>3A-P</td>
<td>96.63</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>3A-NP</td>
<td>27.10</td>
<td>33.42</td>
<td>0.00</td>
</tr>
<tr>
<td>3A-MR</td>
<td>37.73</td>
<td>24.73</td>
<td>12.91</td>
</tr>
<tr>
<td>4A-P</td>
<td>73.50</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>4A-NP</td>
<td>16.31</td>
<td>47.51</td>
<td>0.00</td>
</tr>
<tr>
<td>4A-MR</td>
<td>25.07</td>
<td>32.87</td>
<td>12.50</td>
</tr>
<tr>
<td>1B-P</td>
<td>105.40</td>
<td>0.00</td>
<td>100.00</td>
</tr>
<tr>
<td>1B-NP</td>
<td>31.38</td>
<td>44.28</td>
<td>0.00</td>
</tr>
<tr>
<td>1B-MR</td>
<td>22.22</td>
<td>28.62</td>
<td>17.08</td>
</tr>
<tr>
<td>4B-NP</td>
<td>25.89</td>
<td>38.76</td>
<td>0.00</td>
</tr>
<tr>
<td>4B-MR</td>
<td>33.92</td>
<td>18.54</td>
<td>14.39</td>
</tr>
</tbody>
</table>

% by weight.
All discussed above reveals the invalidity of cellulose to lignin ratio as an indicator of landfill stabilization. That is, it is clear that volatile, acid-insoluble materials are intrinsically measured as lignin and this may result in smaller cellulose to lignin ratio, which may lead to improper decision making about the degree of waste decomposition. Considering 0.2 is the ratio that indicates MSW is fully degraded and not significant amount of gas production and settlement are expected, this misjudgment may also cause early closure of landfill, if not accompanied with other judging devices.

**Conclusion**

Plastics are completely measured as 100% lignin. Since plastic is included in the gravimetrically measured lignin content, the use of the cellulose to lignin ratio as an indicator of refuse stability is of questionable validity.
References


CHAPTER 4

DEGRADATION OF LIGNIN FROM VARIOUS PAPERS UNDER ANAEROBIC CONDITION

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Abstract
Bioreactor landfill simulations using laboratory reactors with a mix of paper and plastic were performed for 186 and 361 days in order to evaluate the potential for lignin degradation under anaerobic condition similar to a landfill with leachate recirculation. Lignin degradation was detected from all the simulations and lignaceous materials were also measured in the leachate samples, which indicates that lignin degradation is occurring in paper samples.

Keywords
Anaerobic, Bioreactor landfill, Cellulose, Lignin, and Plastic.

Introduction
In the late seventies, bioreactor landfills were proposed as an alternate method for conventional landfilling for municipal solid waste (MSW). Bioreactor landfills provide a higher moisture content (about 40%, wet basis) through leachate recirculation and the addition of external moisture. The increased moisture is accompanied by increased
temperature and may include nutrient addition, buffers, sludge addition, shredding, and improved lift design to better distribute the moisture (Kelly, 2002). These alterations can all enhance anaerobic biological degradation in landfills. Accelerated decomposition enables landfill operators to spend less time monitoring, acquire more usable landfill space and reduce the uncontrolled emission of greenhouse gases.

Paper or pulp products account for about 40% of total MSW disposed in the landfill (Barlaz et al., 1990; Kelly, 2002). The MSW buried in the landfill undergoes anaerobic decomposition resulting in the production of methane and carbon dioxide from complex organic polymers. The constituents of these polymers are mainly cellulose (40 to 50 % by dry weight basis), hemicellulose (12% by dry weight basis) and lignin (10 to 15% by dry weight basis) (Wang et al.; 1994; Boda, 2002). Pickin et al. (2002) summarized the typical decay time of paper in landfills from a number of studies and his results are presented in Table 4-1.

Table 4-1. Estimation of typical decay times for landfilled paper. (Pickin et al., 2002)

<table>
<thead>
<tr>
<th>Source</th>
<th>Assumed decay time of paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bingemer and Crutzen (1987)</td>
<td>5-20yr</td>
</tr>
<tr>
<td>Barson and Gifford (1989: p.438)</td>
<td>Exponential decay function</td>
</tr>
<tr>
<td>Grierson et al. (1991: p.24)</td>
<td>a half life of 1year</td>
</tr>
<tr>
<td>NGGIC (1994)</td>
<td>1yr</td>
</tr>
<tr>
<td>NGGIC (1998)</td>
<td>25yr (all waste types)</td>
</tr>
</tbody>
</table>

Due to the rapid degradation of cellulose compared to lignin, a cellulose to lignin ratio under 0.2 is widely used as a value that indicates that biodegradable organic matter is nearly fully degraded and the landfill can be considered stabilized (Reinhart and Townsend, 1998). However, Kelly (2002) and Kim (2004) raised questions about the validity of this index. Based on their research, plastics are included in the lignin measurement and they
suggested that lignin itself degrades. As a result, there are questions about the validity of the cellulose to lignin ratio as a stability indicator.

The purpose of this research was to investigate the degradability of lignin in a simulated landfill. In order to account for the impact of plastics, a measured amount of plastics were added to paper from different sources and the plastic removed by hand and quantified separately from the lignin in paper. In this way, the ratio of cellulose to plastics and lignin to plastics could be used to assess lignin degradation since the plastics added to the paper do not degrade.

**Methods and Materials**

**Columns**
Polyvinyl chloride (PVC) pipe (4” diameter X 15” height) was used for the main reactor systems. For sampling, two male and female adapters (PVC, 4” inside-diameter) were attached at each end and small-sized male and female adapters (PVC, 1.5” inside-diameter) were installed at the mid points of the main column. The column design is shown in Figure 4-1. Male adapters at each end were equipped with an outlet (funnel type connector reducing 3-6mm) where leachate was collected during sampling. These leachate ports were also used for monitoring gas production by connecting rubber tubes and Tedlar bags. A plastic tube with a diffuser attached was installed at one female adapter for nitrogen purging.

Eight columns of this configuration were constructed for this study. Columns were turned over once or twice per a week to allow leachate to drain through the sample. A nitrogen purge was applied after each sampling in order to maintain anaerobic condition. Silicon heat tape with a controller (Thermolyne/Brisk heat) was wrapped around each reactor and temperature was maintained at 38°C. After opening, a standard thermometer was inserted to
check the temperature for each column. The temperatures of the individual reactors initially varied somewhat since there was time difference between the opening and checking.

![Configuration of Reactor Column](image)

**Figure 4-1. Configuration of Reactor Column**

**Materials used in the study**

Three different paper types were selected in order to determine degradation of different cellulose and lignin compositions under anaerobic conditions. These types were cardboard, newspaper, and office paper. Mixtures of these papers were used and mixing ratio was decided based on multiple cellulose/lignin tests. Pieces of overhead projector film (1/2 inch X 1 inch) were introduced to each column as a references material since this material is non-biodegradable. The amount of plastic was set at 10% of entire sample weight. Seeding was also applied to the columns to initiate microbial activity. A mixture of 90% of leachate (outer loop, Louisville, KY) and 10% of sludge (Cargill, Blair, NE) was used and the
amount of seed materials was measured by volume. In addition, nutrients were added to the broth and the nutrient list is shown in Table 4-2. This chemical list is same as that of biochemical methane potential test (Shearer, 2001; Boda, 2002) except the trace solution and thickened biomass were excluded.

Table 4-2. Nutrients added to Seeding

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH$_2$PO$_4$</td>
<td>0.27</td>
</tr>
<tr>
<td>K$_2$HPO$_4$</td>
<td>0.35</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>0.53</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>0.1</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>0.07</td>
</tr>
<tr>
<td>FeCl$_2$.4H$_2$O</td>
<td>0.02</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>1.2</td>
</tr>
<tr>
<td>Na$_2$S.9H$_2$O</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Per 1L

Sampling
Two kinds of samples were collected from each column for the periodic tests. These were solids and leachate. At the scheduled sampling time, solid samples (about 2.5g per each trial) were taken from the top, middle and bottom sampling ports and leachate (about 25ml per each trial) was collected from the outlet attached to one end of the column.

Moisture Content
The moisture content was determined according to standard method 2430-B (APHA et al., 1995). Five hundred to one thousand grams of wet and unshredded solid samples were taken and weighed in an aluminum pan. These samples were dried at 105°C for 2 days and weighed. The weight lost during the drying was divided by the initial weight of sample and the result was reported in percentage by weight as moisture content.

pH
The pH probe (Acumet electrode poly combo liquid, Ag/AgCl reference) was directly inserted into the leachate samples from each column while agitating the collected sample. The values were obtained from Acumet pH meter 910.
**Oxidation / Reduction Potential (ORP)**

ORP of leachate collected from each reactor was measured according to 2580-B method. (APHA et al., 1995) Silver/Silver Chloride electrode and Zobell’s solution were used for the references.

**Shredding and Grinding**

After the samples were dried at 105℃, the dried samples were used for VS, cellulose and lignin tests. The solids were ground in 2 stages, shredding by a commercially available electric blender and then grinding by Thomas Intermediate Wiley Mill with a 10-mesh screen. Hard particles such as rocks and metals were removed by hand before grinding.

**Cellulose and Lignin test**

Cellulose and hemicelluloses were measured by AST Method E 1758-95 (1995). A 300±10mg dried, milled sample was placed in a 16x100mm glass tube. In order to degrade polymers into sugar monomers, ground refuse samples were hydrolyzed to cellulose and hemicelluloses through two stages. The first stage was acid solubilization, which was performed by adding 3.00 ±0.01ml of 72% sulfuric acid (H₂SO₄) to the ground refuse and stirring. This was followed by incubation in a water bath at 35℃ for one hour. Second, these digested samples were transferred into 250ml septa bottles with 84ml of deionized water and the bottles were autoclaved for an hour at 121℃ and 15psi. After cooling at room temperature for about 20 minutes, the samples were filtered through a standard glass microfibre filter (diameter: 55mm) and the residue and filter were ignited at the 550℃ for 20 minutes. The weight loss of the filtered material was considered to be the amount of lignin in the samples. This method is also called as a gravimetric acid-insoluble lignin test.

The filtrate was neutralized to pH between 5 and 6 by adding calcium carbonate (CaCO₃). The precipitate was filtered through 0.45-micrometer membrane and a reversed-phase cartridge. The cellulose and hemicelluloses of the filtered liquid were quantified using high
performance liquid chromatography (HPLC) with a refractive index detector and HPX-87C column. The water flow was fixed to 0.5ml/min and synthetic dextrose powder was used for standard of cellulose. D (+) xylose, D (+) mannose, D (+) galactose, D (+) arabinose, and D (+) glucose were used as standards for hemicellulose.

Leachate samples were also processed for cellulose and lignin testing. Since the method described here was originally suggested for milled samples, the leachate was dried and the solids were collected for the test. A metal blade was used for scraping off dried leachate and the powder was stored in a plastic bag top. The same procedure for solids was used to determine the cellulose and lignin in the dried leachate.

**Results and discussion**

Three different papers were selected for the lignin degradation test. These were cardboard, newspaper, and office paper. These papers were chosen because they are common refuse constituents.

Multiple sets of cellulose and lignin tests were performed for cardboard, magazine and newspaper and the plan is summarized in Table 4-3. Cellulose and lignin contents were normalized based on 100 for the convenience of calculation. Ratios of cellulose to lignin to plastic were also selected based on the content ratio of cellulose and lignin of each paper. Columns numbered 4 and 5 were identical. Other ratios were different by 5%. The plastic content was fixed at 10% by weight.
Table 4- 3. Initial plan of paper mixture.

<table>
<thead>
<tr>
<th>Column Number</th>
<th>Cellulose % by weight</th>
<th>Lignin % by weight</th>
<th>Plastic % by weight</th>
<th>Newspaper (g) C: L=60:40</th>
<th>Cardboard (g) C: L=33:67</th>
<th>Office paper (g) C: L=69:31</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>30</td>
<td>10</td>
<td>0</td>
<td>6</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
<td>35</td>
<td>10</td>
<td>0</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>40</td>
<td>10</td>
<td>0</td>
<td>34</td>
<td>56</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>45</td>
<td>10</td>
<td>57</td>
<td>33</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>45</td>
<td>10</td>
<td>57</td>
<td>33</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>50</td>
<td>10</td>
<td>38</td>
<td>52</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>35</td>
<td>55</td>
<td>10</td>
<td>20</td>
<td>70</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>60</td>
<td>10</td>
<td>1</td>
<td>89</td>
<td>0</td>
</tr>
</tbody>
</table>

- C: Cellulose, L: Lignin

During the entire experimental period, the moisture content of samples was maintained at around 60%. Distilled water or leachate with nutrients was added to keep the samples wet and to make up for the liquid volume collected for leachate tests. Five columns including number 1, 2, 4, 5 and 8 were opened at day 186 and the others (Column #3, 6 and 7) were kept for an additional 175 days. Plastics were removed manually from the collected samples and weighed to calculate the percent ratio by weight. The ratio of plastic was used for each rate calculation as a reference since plastic is considered biologically inert. However, since the plastic became sticky in the presence of water and it was not distributed homogeneously in the columns, it was difficult to get a composite sample that reflected the overall composition of the columns. Even though the overall ratio declined, data points fluctuated and the variance was greater than one. For this reason, the data over time was not useful. The highly variable changes in the lignin to plastic ratio are shown in Figure 4-2.
Therefore the first and last samples, incubated for 186 days, were compared and these are provided in Figure 4-3, 4-4 and 4-5. Since the entire contents of the column were removed for sampling of the last set, the ratio was considered reliable. The highest percentage of lignin loss was from columns # 1 and 2 and these contained the highest cellulose among any of the columns. Columns # 4, 5 and 8 also showed loss of lignin. The cellulose content of each column dramatically declined over 6 months. Since column #1 and 2 contained the most cellulose, their cellulose degradation was greater than others.

Figure 4-6, 4-7 and 4-8 show the lignin to plastic and cellulose to plastic ratios of columns that were operated for an additional 175 days. These columns also showed similar trends, even though total operating time was almost doubled.
Figure 4-3. Changes of Lignin/Plastic Ratio after 186 days of incubation (Column # 1, 2, 4, 5, and 8)

Figure 4-4. Changes of Cellulose/Plastic Ratio after 186 days of incubation (Column# 1, 2, 4, 5, and 8)
Figure 4-5. Changes of Cellulose/Lignin Ratio after 186 days of incubation (Column# 1, 2, 4, 5, and 8)

Figure 4-6. Changes of Lignin/Plastic after 361 days of incubation (Column# 3, 6, and 7)
Figure 4-7. Changes of Cellulose/Plastic Ratio after 361 days of incubation (Column# 3, 6, and 7)

Figure 4-8. Changes of Cellulose/Lignin Ratio after 361 days of incubation (Column# 3, 6, and 7)
It appears that at least some of lignin is being degraded in an environment similar to landfills. However, it is not clear if the type of paper used influences cellulose or lignin degradation. It may be that lignin that is associated with certain types of paper is more easily degraded than other types of lignin. In order to show the relationship between a certain type of paper and the degradation, cardboard was selected as a reference material since this paper was the only one that was added to every column. Figure 4-9 shows the relationship between amount of cardboard and total weight loss from each column.

![Figure 4-9. Cardboard content vs. Weight Loss](image)

It seems obvious that higher weight loss was obtained from the column with smaller cardboard content. This indicates that cardboard is more difficult to degrade than office paper and newspaper.
Additionally, a leachate lignin analysis was used as an alternate way of checking the fate of lignin that was transformed from the solid form. The lignin content of dried leachate increased throughout the test period and this is shown in Figure 4-10. About 25ml of leachate samples were collected for the drying process but the amount of powdered samples from some columns were not enough for the test.

Since it is not clear if lignaceous materials detected from these dried leachate samples are real lignin derivatives or other chemicals, additional analysis is needed to identify their composition. Cellulose test were also conducted on leachate, but no cellulose was detected at any of the samples. As an alternate way of detecting these carbohydrates or their derivatives, hemicellulose tests were performed for these leachate samples and one set of data is shown in Figure 4-11. These data show the presence of hemicelluloses in the leachate as a proof of degradation of lignocelluloses. The hemicelluloses were not quantified.
Figure 4-10. Changes of leachate lignin from column#1 to column#8
Gas production was also monitored for about 7 months and the amount collected was rated by a number from 0 to 10, which represents no gas to a completely filled bag, respectively. Since the gasbags may not have been perfectly sealed, the rating was entirely subjective so the data are only suitable for learning about the trend of gas production. It can be easily seen that columns with lower numbers produced more gas at an earlier time and columns with higher numbers did so at a later stage. This may be caused by the availability of cellulose, which is a readily degradable source of gas production by microbes. It appears that celluloses comprised most of the gas producing materials in the column #1 to 5 but lignin-associated cellulose and hemicelluloses comprised the majority of gas producing material in column# 6 to 8. Additionally, the time for the sharp increase in gas production coincides with higher amounts of lignin detected in the leachate. This suggests that higher gas production is associated with lignin solubilization, which happens much later than cellulose degradation. Column #3 produced the largest amount of gas among 8 columns. The monitored values are summarized in Table 4-4 and depicted in Figure 4-12.
Table 4-4. Monitored gas production.

<table>
<thead>
<tr>
<th>Column #</th>
<th>05/07/03</th>
<th>05/08/03</th>
<th>05/09/03</th>
<th>05/11/03</th>
<th>05/16/03</th>
<th>05/19/03</th>
<th>05/20/03</th>
<th>05/23/03</th>
<th>05/27/03</th>
<th>06/01/03</th>
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<th>06/05/03</th>
<th>06/06/03</th>
<th>06/07/03</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>2</td>
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<td>0</td>
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<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>4</td>
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<td>0</td>
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<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
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- The number is rated according to visual inspection. 0 represents no gas observed and 10 means gasbag is completely filled with gas.
The amount of paper samples degradation during the experiments is summarized in Table 4-5. It seems clear that almost half of sample is liquefied or gasified from column #1 to 3, which contains cellulose at 60, 55 and 50% by weight, respectively. One tenth of sample weight disappeared from column# 4, which failed to maintain anaerobic conditions and a neutral pH. However, column#5 is identical to column #4 and 30% of the sample is missing from its original sample weight. Almost same amount of material (30% by weight) is lost from column#6 to 8.
Table 4-5. Weight of samples disappeared through gaseous or liquid form.

<table>
<thead>
<tr>
<th>Column Number</th>
<th>Total weight of sample used (g)</th>
<th>Initial weight (g)</th>
<th>Weight loss (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>52.31</td>
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<td>54.97</td>
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<td>70.90</td>
<td>100</td>
<td>29.10</td>
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<td>6</td>
<td>72.57</td>
<td>100</td>
<td>27.43</td>
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<td>8</td>
<td>66.70</td>
<td>100</td>
<td>33.30</td>
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- Weight of sample from set#2 is fixed at 2.5g in this table.
- The number of total set is 9

Loss of cellulose is also quantified in order to provide the alternate evidence of lignin degradation. These values are shown in Table 4-6. The differences between total weight loss and cellulose loss are shown about 10 to 20% in the columns with lower numbers where office paper was the majority of constituents. On the other hand, columns with higher numbers, which were filled primarily with cardboard, showed minute differences between weight and cellulose loss. These values imply that something other than cellulose was lost during the experiment and it is thought that lignaceous material as part of the material loss.

Table 4-6. Loss of cellulose and its difference from the total weight loss

<table>
<thead>
<tr>
<th>Column #</th>
<th>Initial Cellulose Content (g/100g)</th>
<th>Final Cellulose Content (g/100g)</th>
<th>Weight Loss (%)</th>
<th>Total Weight loss - Cellulose loss (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>60.05</td>
<td>40.40</td>
<td>32.73</td>
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- Total weight loss is taken from Table 4-5.
Figures 4-13 and 4-14 show the relationship between weight loss and cellulose content or lignin content. These graphs also show the ready availability of cellulose and relative inertness of lignin. That is, the cellulose content and the amount of degradation are proportional to each other but lignin content and its decomposition ratio shows the opposite relationship.

Figure 4-13. Initial Cellulose content (%) Vs. Weight loss (%)
Figure 4-14 shows the changes of mass content of plastic, lignin and cellulose over time. It is obvious that cellulose degrades and the plastic content increases due to its inertness to the biochemical reaction. However, lignin shows increase in the early phase and a small but clear decrease at the later time of experiment. Owing to its slower degradation, the lignin content, when calculated in percentage, increases and starts to decrease after cellulose degradation slows.
Figure 4-15. Percent changes of lignocellulose and plastic content.

Figure 4-16 depicts overall weight loss of cellulose and lignin. Every column shows cellulose and lignin degradation. Samples in the columns that had been maintained for an additional 175 days were similar in weight loss of cellulose to that of the columns that had been in operation for 186 days. It appears that cellulose loss greatly decreased after about 186 days.
A theoretical model is proposed from the findings from this research and it is presented in Figure 4-17. The cellulose content decreases dramatically since it is readily degradable. On the other hand, the plastics increase since other materials undergo degradation. Lignin also shows similar trend to plastic until the cellulose loss slows down. Lignin loss accelerates afterward.
Conclusion

- Lignin appears to degrade in the condition similar to landfill but at much slower rate than cellulose. Because of degradability of lignin in the landfill, it may not be feasible to use cellulose to lignin ratio as a sole landfill stability indicator.
- Dried leachate was processed for the cellulose and lignin test and lignin was detected from all samples. If these are real lignaceous materials, this implies the path of mobilization of lignin.
- Some types of paper such as cardboard may be associated with much slower degradation in the landfill.
- No cellulose was detected from the dried leachate but hemicelluloses were detected. This may be the pathway of solubilization of lignocelluloses.
- Plastic chip is not suitable for references in the laboratory landfill simulation in spite of its advantages such as availability, inertness in chemical and physical
conditions similar to landfill, etc because of its stickiness with liquid, which hinders homogeneous distribution.

- The lignin content, measured on a percent basis, increases until the cellulose degradation rate slows. Lignin degradation then begins.

References


Otieno, F. G., 1989, Leachate recirculation in landfills as a management technique, Proceedings of Sardinia `89: Second International Landfill Symposium, Galgari, Italy.


Shearer, Brad, 2001, Enhanced Biodegradation in Landfills, Master’s theses

VITA

Jongmin Kim was born on 19th January 1977, in Daegu South Korea. He completed his Bachelor’s degree in Civil Engineering in 2002 from Yonsei University, South Korea. Thereafter he started his master’s degree in Environmental Engineering in fall 2002 at Virginia Polytechnic and State University, USA. He worked as a research assistant during his school years. He has graduated in October 2004 and will work as an Environmental Engineer.