WASTE CONTAINMENT TECHOLOGY – LIFETIME PREDICTION OF THE LANDFILL LINER

Yick Hsuan,
Civil and Architectural Engineering

INTRODUCTION

Landfill implies disposal of waste in the ground. This method has been practiced for centuries, and still is the primary method use in nowadays. Each year more than 70% of the waste is disposed in landfill, according to the United States Environmental Protection Agency (U.S. EPA). Between 1960 and 1990, EPA's data indicated a linear increase in the amount of waste with time, as shown in Figure 1. Note that the data did not include construction demolition debris, incinerator ash, sludge and non-hazardous industrial waste, which usually dispose with municipal waste and approximately, double the quantities ("Characterization of", 1992). Thus, a large number of landfills are required to contain the waste, particularly in the highly populated area. The largest landfill "Fresh Kills", which covers 3,000 acres of land, is located on the Staten Island, New York. The landfill holds 2.4 billion cubic feet of waste, and is 25 times the volume of the Great Pyramid at Giza, as shown in Figure 2 (Rathje, 1991).
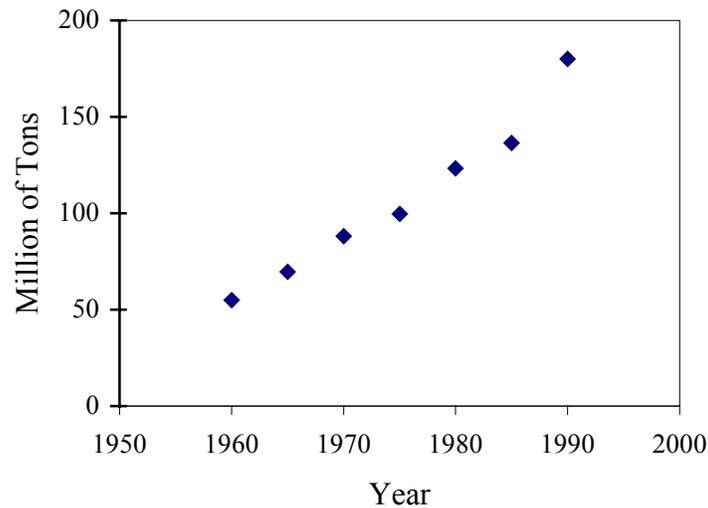

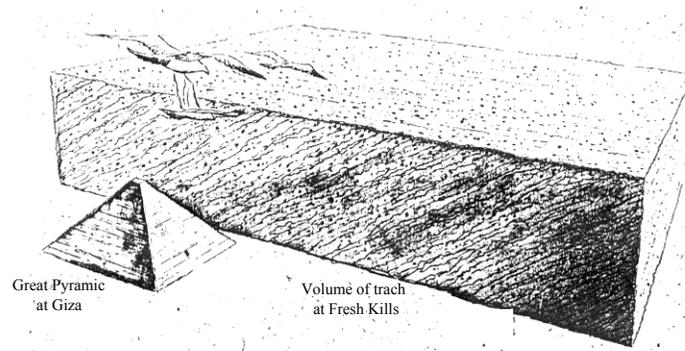Figure 1 – Amount of municipal solid waste from 1960 to 1990

Figure 2 – Size comparison between the Grate Pyramid and Fresh Kills Landfill

The most critical environmental concern to waste containment facilities (i.e., landfill) is ground-water pollution by the leachate. Leachate, which is generated by the interaction between water and waste, contains a high concentration of contaminants. In order to protect the ground-water leachate must be contained, removed and treated. From early 1980s, all landfills required a low permeability liner to restrict leachate from percolating through the base and sides of the landfill. At the same time, the waste containment technology has been evolved from the simply open pits approach to sophisticated engineering design.

In addition, new engineering materials have been introduced and used in the landfill liner and cover systems to enhance their functions as well as to reduce the cost. *Geosynthetic* is a group of new engineering products that was developed in late 1980s to serve the waste containment industry, since then they have become the critical components of the landfill system. Many landfills utilized multiple layers of different types of geosynthetics in both cover and liner systems, as shown in Figure 3. In all of the geosynthetics, geomembranes play the most significant role in landfill liner systems; they function as a liquid barrier so that leachate can be contained and removed from the landfill.

Since the integrity of landfill has direct impact on the safety of the environment, a confident engineering design and quality construction are the fundamental requirements. However, the durability of the materials that are used in the liner system is also crucial to ensure the long-term performance of the landfill. The focus of this paper is to present the basic theory, laboratory methodology and test data for predicting the lifetime of high-density polyethylene (HDPE) geomembranes, the most widely use geomembrane in the landfill liner system.

The paper begins with an overview on the waste management, describing various management methods as well as the waste classification. The second section of the paper focuses on the landfill design and related regulations. In addition, the function and usage of geosynthetics in the landfill system are explained. The evaluation of the lifetime of HDPE geomembranes is presented in the subsequent sections, starting with the composition of HDPE geomembranes, the function of antioxidants, experimental design, data analysis and results. Finally a section on the future of waste containment management describes the future trend of landfill management methodology. A series of questions are included at the end of this paper for student to practice.
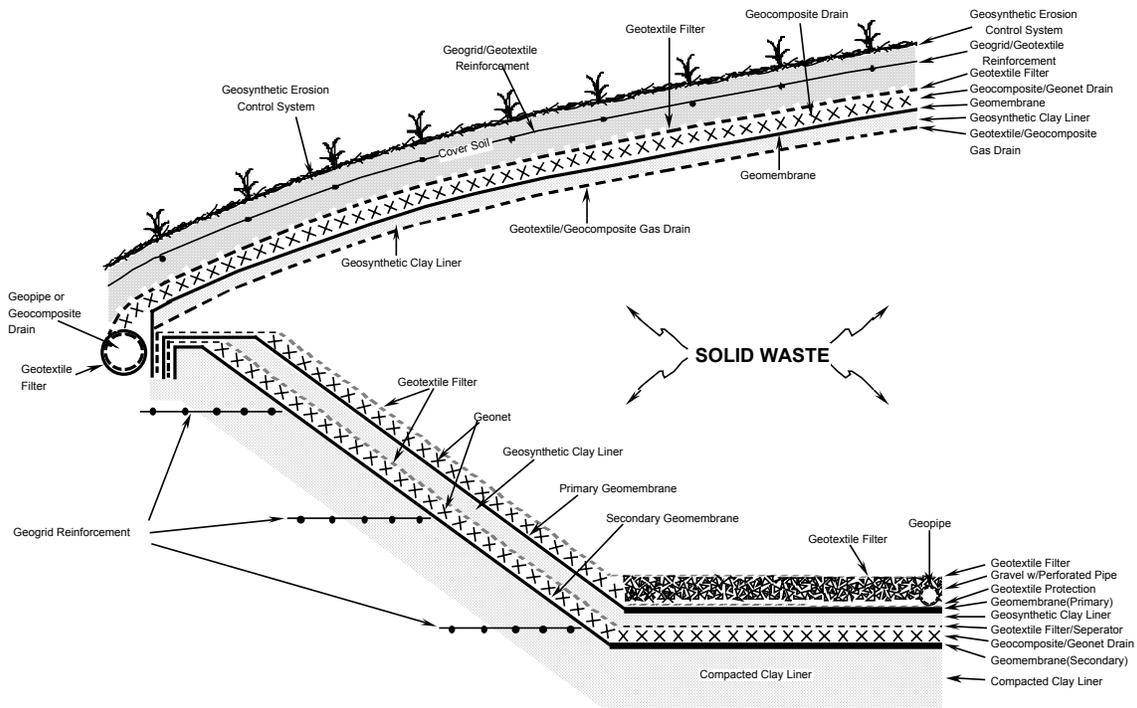
Figure 3 - Solid waste containment system with high geosynthetic utilization

WASTE MANAGEMENT METHODS

Currently in the U.S. there are three methods to manage the solid waste. They are landfilling, combustion, and recycling. The EPA refers to the complementary use of these three methods, along with source reduction, as Integrated Waste Management (IWM). In 1992, EPA set a goal of 25% recycling, and projected 20% combustion and 55% landfilling. Table 1 shows the trend of the distribution of the waste in each method from 1970 to 1990. (Information is provided by the Waste Management Inc.)

Table 1 – The percentage of waste being managed in each of three methods

Method	1970	1980	1990
Landfilling	72.3%	81.3%	66.6%
Combustion	20.6%	9.1%	16.3%
Recycling	7.1%	9.6%	17.1%
Total	100%	100%	100%

Source Reduction

Source reduction involves reduction in the quantity or toxicity of materials during the manufacturing process, or through product reuse. Improvement in manufacturing process and better quality control have decreased the amount unqualified products and by-products. In addition, continuing reduction in the weight of containers and packaging was also achieved under the improved process. Table 2 shows the reduction in weight for five different types containers.

Table 2 – Weight reduction in containers (all in unit of grams)

Container	1980	1992
2-leter PET bottle	65	51
Aluminum can	19	15
Glass soda bottle	255	177
Steel (tin) soup can	48	37
Half-pint milk carton	14	11

Recycling

In the last ten years, there is a significant increase in the recycle program. Majority of the large institutes and companies have implemented recycle program, and curbside programs have been adopted by many townships and counties. The steady increase in the percentage of recycling waste is indicated in Table 1 above. The type of materials that are being recycled is listed in Table 3 (Data provided by Waste Management Inc.)

Table 3 – Recycling materials in percentage of waste

Material	1985	1990	Projected 1992
Corrugated boxes	4.4	5.9	6.7
Newspapers	2.1	2.8	3.3
Office paper	0.7	0.9	1.0
Glass containers	0.7	1.3	1.5
Steel cans	0.1	0.3	0.5
Aluminum cans	0.4	0.5	0.5
Plastics packaging	0.1	0.2	0.2
Yard waste	0	2.2	2.7
Other	1.5	3.0	3.8
Total	10	17.1	20.2

Combustion

One way to reduce the volume of solid waste for deposal is waste-to-energy plants, which burn the waste at high temperatures and reduce its volume by up to 90%. There are 140 of combustion plants built in the U.S. However, the combustion must meet the state emission requirements, as well as the EPA Clean Air Act standards. In addition, the residual ash is considered to be hazardous material due to high concentration of heavy metals, and it should be disposed accordingly.

Landfilling

The majority of the waste is still disposed by the landfilling method. Although the percentage of the waste going into the landfill has been gradually decreased in the last 30 years, the amount of landfilled waste actually increased due to population growth. There are approximately 6,500 landfills operate in the U.S. Some 57% belong to local governments, 14% to private companies, and the rest to other government or solid waste authorities. These landfills vary greatly in size and capacity. About 30% of the landfills receive less than 30 tons of waste per day, and only 5% receive more than 500 tons.

All landfills are designed according the EPA regulations, which are different for hazardous and non-hazardous waste.

REGULATIONS

Landfill Site Selection

The site selection for non-hazardous landfill is a lengthy process. It involves detailed geographical and geotechnical investigations at the site area as well as impact to surrounding region. The following items are some of the criteria that should be considered during the initial selection stage:

- The selected site should be conformed to land use planning of the area.
- The selected site should have easy access to vehicles during the operation of the landfill.
- The site area should have adequate quantity of earth cover material that is easily handled and compacted.
- Landfill operation will not detrimentally impact surrounding environment.
- The selected site should be large enough to hold community waste for a reasonable length of time.

Landfill Design

Solid waste in the US is regulated under the Resource Conservation and Recovery Act (RCRA). Dependent on chemical constituents of the leachate, waste can be classified as either hazardous or non-hazardous waste. The term hazardous waste has a specific, legal definition (Daniel and Koerner, 1995). Waste is hazardous if:

1. It is listed as a hazardous waste (hundreds of wastes are specifically in Appendix VIII of Title 40, Code of Federal Regulations, Part 251).
2. It is mixed with or derived from hazardous waste.

3. The waste that is not specifically identified as municipal solid waste (i.e., non-hazardous waste).
4. The waste possesses any one of four characteristics:
    a. Ignitability (flash point $60^{o}C$)
    b. Corrosivity ($2 \geq pH \geq 12$)
    c. Reactivity (reacts violently with water or is capable of detonation)
    d. Toxicity as determined by the Toxicity Characteristic Leaching Procedure (TCLP) test.

For non-hazardous waste, the applicable legislation is contained in Subtitle D of RCRA. Specific EPA regulations are published in Parts 257 and 258, Title 40, Code of Federal Regulations (CFR). The minimum technology guidance (MTG for a Subtitle D landfill consists of compacted clay liner (CCL), geomembrane (GM), leachate collection and removal system (LCRS), filter layer. The cross-sectional profile of such liner is depicted in Figure 4(a). For waste materials considered hazardous, the applicable legislation is contained in Subtitle C of RCRA. Specified SPA regulations are contained in 40 CFR 264.221. The MTG for such landfill liner requires two geomembranes, and between these two geomembranes another LCRS should be installed, as can be seen in Figure 4(b). The purpose of the secondary LCRS is to monitor leakage that is occurring through the upper or primary liner. Thus, appropriate respond acting can be carried out.
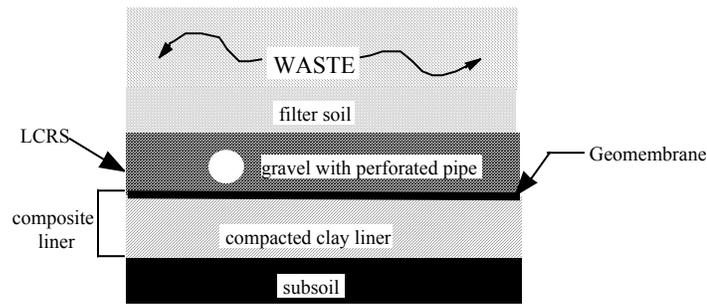
(a) Single Composite liner, per Subtitle "D" regulations
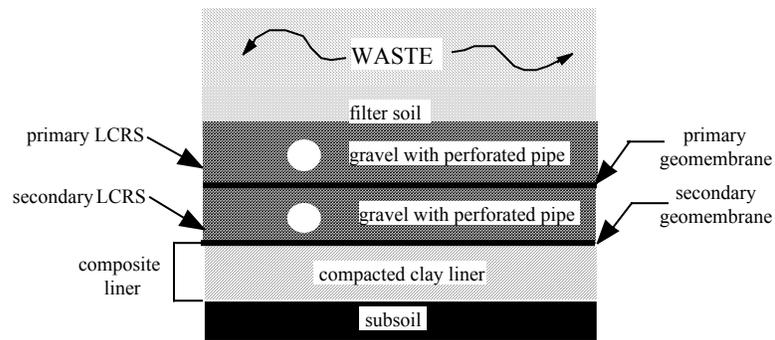
(b) Double liner system per Subtitle "C" regulations

Figure 4 - Minimum technology guidance (MTG) liner systems for
(a) non-hazardous and (b) hazardous waste containment

Note that each state must follows, or exceed, the MTG that is described above. However, many states exceed the federally mandated minima. For example, some states require the Subtitle C hazardous waste landfill design for Subtitle D non-hazardous waste (Koerner et al. 1998). Thus, the potential leakage from the primary liner can be monitored via the secondary LCRS.

In addition to the liner system beneath and on the side slopes of the landfill, a cover must be placed over the completed waste mass once the waste reaches the permitted height. Similar to the liner system, requirements for landfill covers are also covered under federal regulations. Figures 5 (a) and (b) show the minimum cover system required by EPA for non-hazardous and hazardous landfills, respectively. The landfill cover design varies greatly from state to state, particularly between the northern and southern states. The frost penetration in the northern is an important concern in the design.
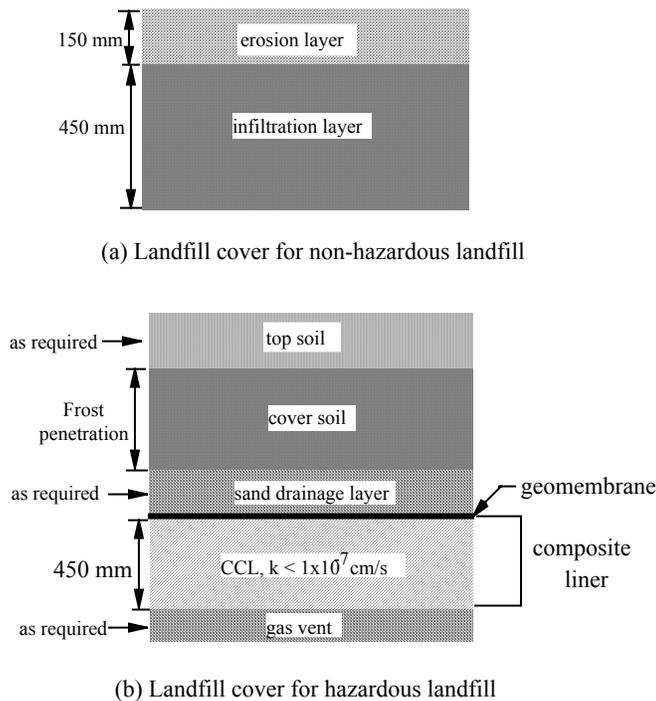

(a) Landfill cover for non-hazardous landfill

(b) Landfill cover for hazardous landfill

Figure 5 - Minimum cover system for (a) non-hazardous
and (b) hazardous landfills

Geosynthetics Used in Landfill Application

Both federal and state legislations permit alternative materials that show "technical equivalency" being used in place of the normal design. This allows the possibility of using engineering materials to replace natural soil materials; subsequently many different types of geosynthetic products were developed and utilized. The following substitutions are often considered in the landfill design (Daniel and Koerner, 1995):

- Geonet (GN) drains may be considered to replace or augment soil drainage layers in the LCRS, particularly on the side slope where coarse soil could have difficulty to be placed.
- Geotextile (GT) filters may be used replace soil filter layers between the waste and the LCRS. In addition, GT may be incorporated in the design to prevent puncture of the geomembrane from the coarse aggregate above.
- Geosynthetic clay liner (GCL) barriers may be used to replace or augment compacted clay liners (CCLs). This is particularly applicable in the cover system.
- Geogrid (GG) reinforcement layers may be needed for stabilizing soil slopes, cover soils, and/or waste mass.

With these potential alternatives and applications, the overall cross section of the landfill liner and cover can be illustrated in Figure 3, which is displaced in the earlier section of the paper. Detailed information regarding geosynthetics' design and applications can be found in a book by Koerner (1997).

Note that in the above geosynthetic list, geomembrane (GM) is not included, since it has already integrated as a required component in the landfill design as indicated in the EPA MTG. Geomembranes are essentially impermeable polymeric sheets, and they are usually placed directly upon a clay liner to create a composite liner system. The purpose of the composite is to limit the leakage area over the CCL, as shown in Figure 6. Giroud and Bonaparte (1989) showed that the composite liner decreases leakage rate 1000 times in comparison to geomembrane/sand combination.
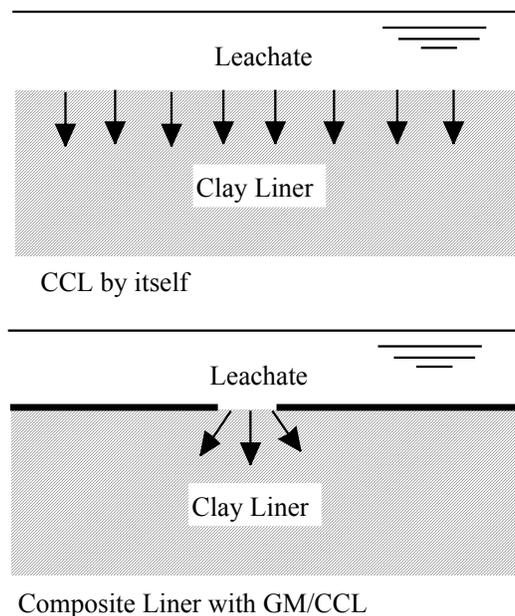
Leachate

Clay Liner

CCL by itself

Leachate

Clay Liner

Composite Liner with GM/CCL

Figure 6 - Composite liner concept

HIGH DENSITY POLYETHYLENE (HDPE) GEOMEMBRANE

As stated in previous sections, geomembranes play a critical role in the performance of the landfill. A failure in the geomembrane will lead to increase in the leakage rate, and impose a greater challenge to the clay liner beneath. This section provides an overview on all geomembranes that are currently used in the waste containment industry. However, the focus is on the HDPE geomembrane, which is the most widely use in the landfill liner system due to the high chemical resistance.

Table 5 lists the type of geomembranes that are either widely or limited used in the containment industry. Each type of geomembrane is named according to the polymer that the geomembrane is made from. There are as many as six basic types of geomembranes. Some of them are manufactured in both homogenous sheet and scrim reinforced sheet.

Table 6 – Type of geomembranes used in waste containment

Widely Used Geomembranes	Limited Used Geomembranes
High density polyethylene geomembrane	Flexible polypropylene (f-PP) Geomembrane
Linear low density polyethylene (LLDPE) geomembrane	Chlorosulfonated polyethylene (CSPE) geomembrane
Polyvinyl chloride (PVC) geomembrane	Ethylene interpolymer alloy (EIA) geomembrane

As a landfill liner geomembranes must be able to contain leachate generated from the waste throughout the service life of the facility. It is foremost importance to evaluate the chemical compatibility between the geomembrane and the liquid to be contained so that potential degradation of the geomembrane can be prevented. The method used to assess the chemical resistance of geomembranes is ASTM D 5747. Geomembranes that show degradation is eliminated from the consideration, and those exhibit good chemical resistance would be selected. Due to the high crystallinity of the HDPE geomembrane, it generally has greater chemical resistance than the other types of geomembranes. This is one of the reasons that HDPE geomembranes are often selected as landfill liner material.

HDPE Geomembrane Compositions

HDPE geomembrane formulations consist of weight percentages of 96 to 97.5% polyethylene resin, 2 to 3% carbon black, and up to 0.5% of antioxidants. The final density of the HDPE geomembrane is in the range between 0.941 to 0.950 g/cc. The three components of the HDPE geomembrane are described as follows:

- Polyethylene (PE). The resin used for HDPE geomembranes is a linear copolymer that is polymerized using ethylene as the primary monomer and α-olefin as comonomer under low pressure with appropriate types of catalysts. The amount of α-olefin comonomer has a direct effect on the density of the resin; a greater amount of α-olefin yields a lower density polyethylene.

- Carbon black. Carbon black is added to an HDPE geomembrane formulation mainly for ultraviolet light stabilization. The loading range of carbon black in geomembranes is typically 2 to 3% per ASTM D 1603. Up to 3%, which is the opacity level, the higher the loading of carbon black the greater is the degree of ultraviolet light stability.
- Antioxidants. Antioxidants are introduced for the purposes of oxidation prevention during extrusion and to ensure long-term service life of the product. There are many types of antioxidants, and each of them behaves differently. Usually, synergistic mixtures of antioxidants of more one type are used. Although the total amount of antioxidants in the geomembrane is relatively small, their existence is vital to the longevity of the product.

DEGRADATION IN HDPE GEOMEMBRANES

After the HDPE geomembrane is installed in the landfill liner system, it is expected to service for many years. During the service period, aging takes place in the geomembrane. The ageing process can be considered to be a combination of physical and chemical aging; both of them take place simultaneously. Physical aging is associated with a process that proceeds as the polymer attempts to establish equilibrium form its as-manufactured state. There are no primary (covalent) bonds broken. Chemical aging indicates some type of degradation process involving the breaking of covalent bonds, e.g., thermal-oxidation, radioactive-degradation, etc. (Struik, 1978). This process eventually leads to degradation in engineering properties. Therefore, from an applications point of view, chemical aging is the degradation that needs to be understood.

Conceptually, the chemical aging process of an HDPE geomembrane can be considered in three distinct stages, as shown in Figure 7.
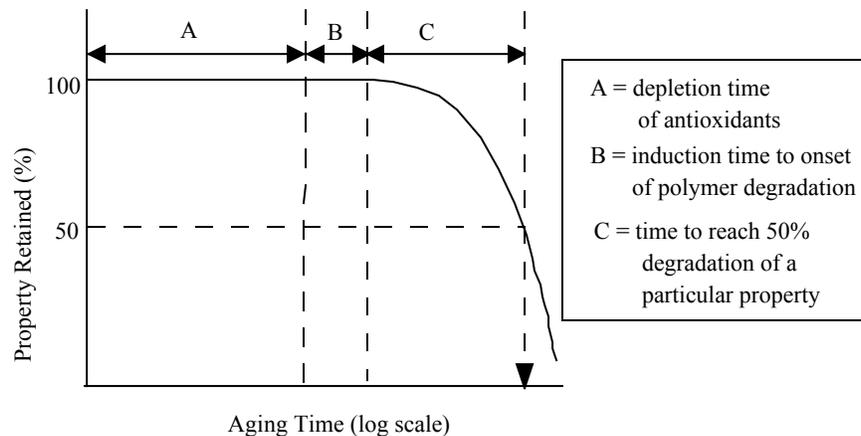

Figure 7 - Three conceptual stages in Chemical aging of HDPE geomembranes

Stage A – Depletion of Antioxidants

The purposes of antioxidant are (1) to prevent polymer degradation during processing; and (2) to prevent oxidation reactions from taking place during the service

life of the product. Obviously, there can only be a given amount of antioxidants in any formulation. Once the antioxidants are completely depleted, oxygen will begin to attack the polymer leading to subsequent stages in Figure 7. The duration of Stage A depends on the types and amount of antioxidants additional to the ambient conditions of the application.

Stage B – Induction Time
    In a pure polyethylene resin, oxidation occurs extremely slowly at the beginning. Eventually, oxidation occurs rapidly. The reaction then decelerates and once again becomes very slow. This progression is illustrated by the curve of Figure 8(a). The initial portion of the curve is called the induction period. In the induction period, polymer reacts with oxygen forming hydroperoxide (ROOH), as indicated in reactions (1) to (3). However, the amount of ROOH in this stage is very small and the peroxide does not further decompose into other free radicals. Thus, the acceleration stage oxidation cannot be achieved.
    In a stabilized polymer such as one with antioxidants, the accelerated oxidation stage takes an even longer time to reach. The antioxidants create an additional depletion time stage prior to the onset of the induction time, as shown in Figure 8(b).
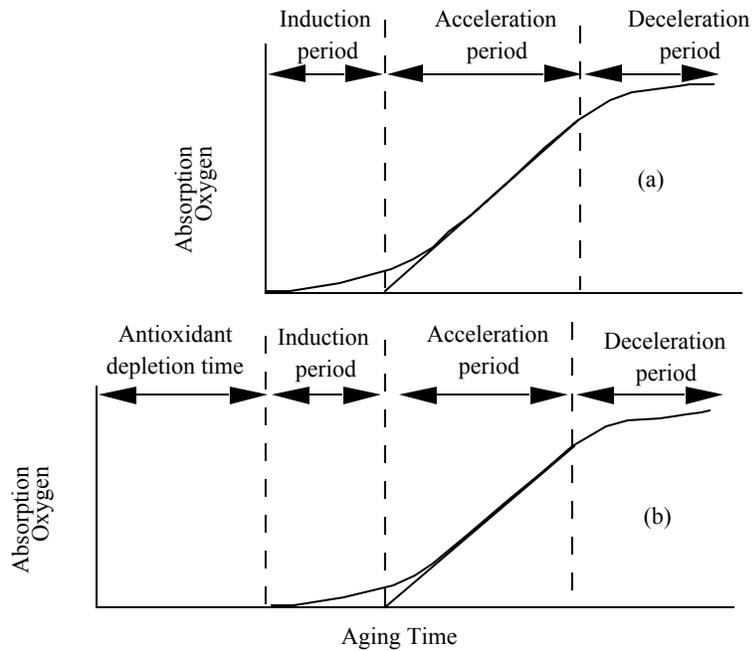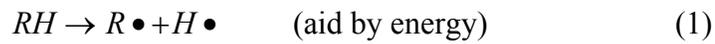

Figure 8 - Curves illustrating various stage of oxidation for
(a) pure polyethylene and (b) stabilized polyethylene

$$RH \rightarrow R \bullet + H \bullet \qquad \text{(aid by energy)} \qquad\qquad (1)$$
$$R \bullet + O_2 \rightarrow ROO \bullet \qquad\qquad\qquad\qquad\qquad (2)$$

$$ROO \bullet + RH \rightarrow ROOH + R \bullet \qquad\qquad (3)$$

where:

RH represents the polyethylene chains, and the symbol "•" represents free radicals, which are highly reactive molecules.

Stage C – Polymer Degradation

As oxidation continues, additional ROOH molecules are formed. Once the concentration ROOH reaches a critical level, decomposition of ROOH begins, leading to a substantial increase in the amount of free radicals, as indicated in reactions (4) to (6). The free radicals attack the polymer chain readily, resulting an accelerated chain reaction, signifying the end of the induction period (Rapoport and Zaikov 1986).

$$ROOH \rightarrow RO \bullet + OH \bullet \qquad \text{(aided by energy)} \qquad (4)$$
$$RO \bullet + RH \rightarrow ROH + R \bullet \qquad\qquad\qquad (5)$$
$$OH \bullet + RH \rightarrow H_2O + R \bullet \qquad\qquad\qquad (6)$$

The oxidation produces a substantial amount of free radicals (R•), which can generate further reactions, leading to either cross-linking or chain scission in the polymer. Subsequently the physical and mechanical properties of the polymer start to change. For the mechanical properties, both tensile break stress and break strain decrease, whereas to a lesser extent the yield stress increases and yield strain decreases. Ultimately, the degradation becomes so severe that all tensile properties decrease and the engineering performance is jeopardized. This signifies the end of the so called "service life" of the geomembrane.

Although quite arbitrary, the limit of service life to polymeric materials is often selected as a 50% reduction in a specific design property. This commonly referred to as the half-lifetime, or simply the "half-life". It should be noted that even at half-life, the material still exists and can function, albeit at a decreased performance level with factor of safety lower than the initial design value.

OVERVIEW OF ANTIOXIDANTS

Since antioxidants are the major contributor in the long-term performance of HDPE geomembrane, understanding the performance and function of antioxidant during the depletion period is necessary.

Function of Antioxidants

The sequence of oxidation reactions in HDPE geomembrane indicated by reactions from (1) to (6) can be interconnected by cycles A and B, illustrated in Figure 9. There are four important links in these two cycles, designated (a) to (d). If any of the links are broken, the rate of oxidation of the polymer will be retarded. If all four links are broken, then oxidation will be stopped. The purpose of antioxidants in the polymer formulation is to break all these links. Since molecular species involved in each of the four-cycle links are different, different types of antioxidants are designed to interrupt specific links. Basically there are two categories of antioxidants: primary and secondary.

Primary antioxidants stabilize the polymer by trapping or deactivating free radical species after they are formed. The secondary antioxidants are designed to decompose hydroperoxides (ROOH) preventing them form becoming free radicals.
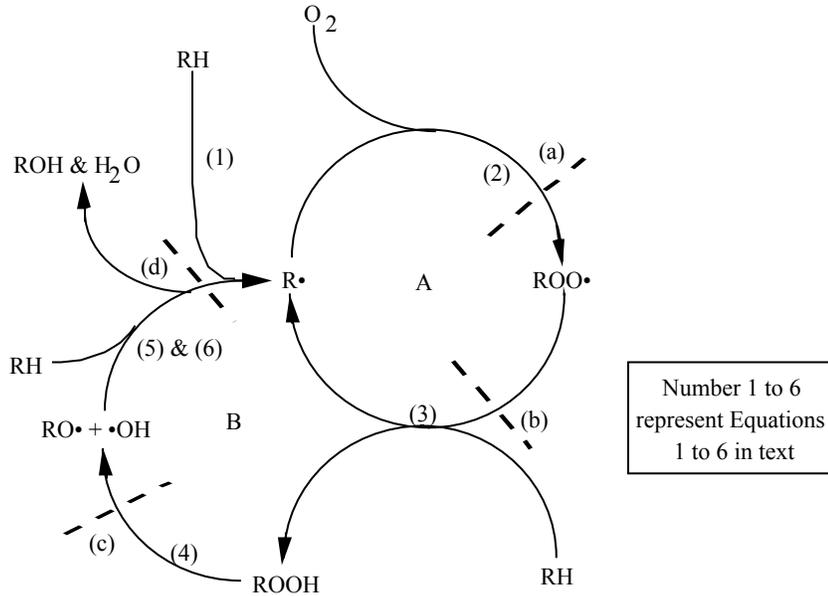

Figure 9 - Oxidation Cycles in Polyethylene (Grassis and Scott, 1985)

Types and Characteristics and Antioxidants

Based on the two categories just described, antioxidants can be manufactured from different types of chemicals. Table 7 shows the chemical type and some of the commercially available antioxidants that can be used in polyethylene geomembranes.

Table 7 – Types of antioxidants

Category	Chemical type	Example of commercially Antioxidants
Primary	Hindered phenol	Irganox® 1076, Irganox® 1010, Santowhite crystals
	Hindered amines	Various types of Tinuvin®, Chimassorb® 944
Secondary	Phosphites	Irgafos® 168
	Sulfur compounds (Thiosynergists)	Dilauryl thiodipropionate (DLTDP) Distearyl thiodipropionate (DSTDP)
	Hindered amine	Various types of Tinuvin®, Chimassorb® 944

Another issue that needs to be considered during the selection of antioxidants is the effective temperature range for each of the selected antioxidants. The antioxidant "package" should protect the geomembrane at temperatures during the extrusion process as well as the significantly lower temperature range during its service lifetime. Thus, the functioning temperature range for each type of antioxidants should be recognized. For the four chemical types listed above, the effective temperature ranges are shown in Figure 10. The graph shows that phosphates have an effective temperature range above 150°C. They are considered to be processing stabilizers. Hindered phenols, thiosynergists, or hindered amines should be added to the formulation to provide the low temperature service protection. For a formulation consisting of hindered phenols, a wide range of temperatures is covered, from typical service temperature to process temperatures. However, hindered phenols are only primary stabilizers. A secondary antioxidant is also required, which can be either a thiosynergist or a hindered amine.
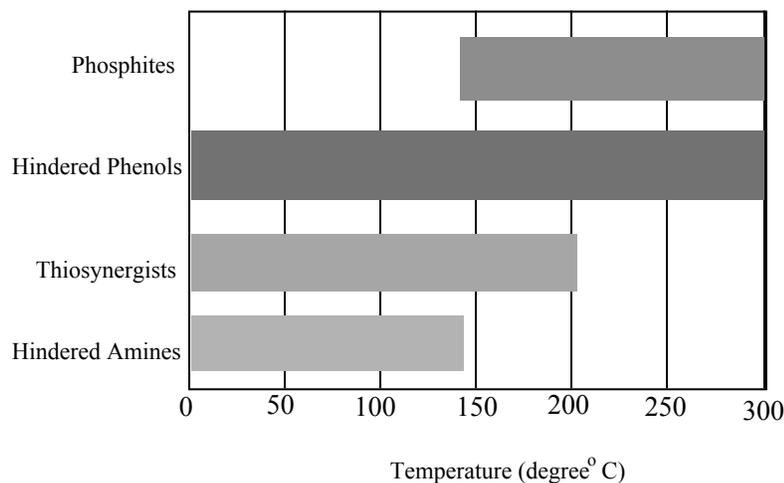
Figure 10 - Effective temperature ranges of four antioxidant types (Fay and King 1994)

LIFETIME PREDICTION OF HDPE GEOMEMBRANES

The most unequivocal way to assess service lifetime is use case histories as demonstrated proof. However, the first generation of geomembrane-lined landfill is only around 25 years old. Therefore, an alternative option is needed to assess the longevity of the material. In this paper, a laboratory-based time-temperature acceleration protocol is utilized. Utilizing Arrhenius modeling, test data are then extrapolate to temperatures lower than the tested temperatures.

Arrhenius Model and Equation

It is well established that chemical reactions of all types proceed more rapidly at higher temperatures that at lower temperatures. Sometimes the increase in the rate of reaction can be very dramatic for even a modest rise in temperature. With the introduction of the ideas involved in the kinetic theory of gases, in the mid-nineteen century, a "theory" became possible to explain this phenomenon. The reaction rate can be presented conceptually as follows (Morrison and Boyd, 1992):

$$\text{Rate of reaction} = X * Y * Z \tag{7}$$

Where:

- X = The collision frequency depends upon the density of particles (i.e., concentration or pressure).
- Y = The energy factor is determined by (a) the energy distribution of the gas molecules (i.e., velocity distribution, because in an ideal gas the energy is completely kinetic), and (b) the activation energy "E_{act}" for the reaction.
- Z = The probability factor is determined by how many of the colliding particles are properly oriented for the reaction. Of these three terms, the energy factor is by far the most important in determining reaction rates as a function of temperature.

Figure 11 is a schematic diagram of the potential energy involved during the course of a reaction. The reactions must surmount an energy arriver, E_{act}, before going over into a change, or reacted, state. The heat of reaction, "ΔH", is also shown. It is the net consumption of energy required for a chemical reaction. If positive, the reaction requires additional heat progress and is endothermic. If negative, it dissipates heat as the reaction proceeds and is exothermic. Usually, little is known about the exact nature of the transition state in the HDPE geomembrane degradation, but E_{act} can be determined experimentally without exact details as to the transition state.
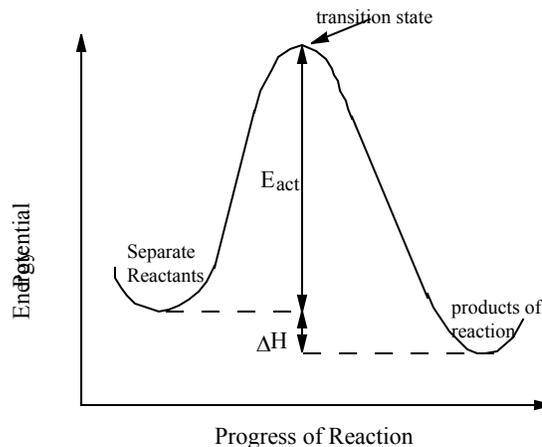

Figure 11 - Potential energy involved in the progress of an assumed reaction

The distribution of velocities (i.e., energies) in an ideal gas was derived by Maxwell in 1852, and it is the usual bell-shaped (or Gaussian) curve common in statistics. This curve is shown in Figure 12. The fraction of particles in Figure 12 having energies greater than some value "E_{act}" is given by the relationship in Equation (8):

$$e^{-\frac{E_{act}}{RT}} \tag{8}$$

where:
  E_{act} = activation energy for the particular reaction(s)
  R   = the gas constant (8.31 J/mole-K)
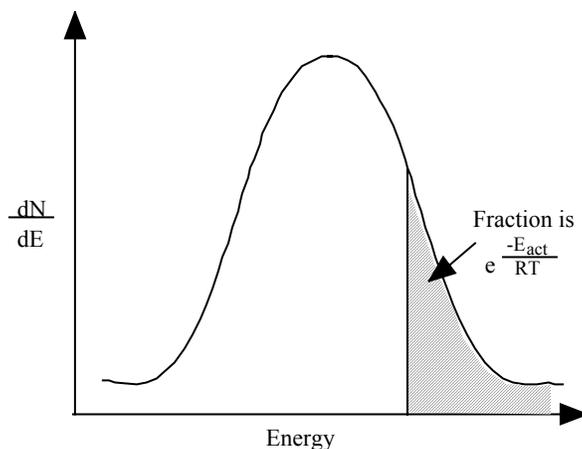 T   = absolute temperature

Figure 12 - Distribution of energy in an ideal gas

The term "E_{act}" is fundamental to any particular reaction. Its value has been the focus of a significant amount of research and experimental investigation and will be seen to be critical in the work to follow.

Rewrite equation (7) using the relationship of equation (8) for the "Y" term gives equation (9):

$$R_r = (X)(e^{-\frac{E_{act}}{RT}})(Z) \tag{9}$$

For simple gas phase reactions, the constants "X" and "Z" can be estimated reasonable well. The activation energy term "E_{act}" remains for experimental determination. Assuming "X" and "Z" are independent of temperature and can be bracketed as a constant term "A", as shown in Equation (10).

$$R_r = (A)(e^{-\frac{E_{act}}{RT}}) \tag{10}$$

Equation (10) is the most widely referenced form of the so-called Arrhenius equation.

Take the natural logarithm of both sides of Equation (10); a linear equation can be generated, as indicated in Equation (11).

$$\ln R_r = \ln A - \frac{E_{act}}{RT} \qquad (11)$$

Plotting $\ln R_r$ against inverse temperature as shown in Figure 13, the slope of the line will be "E_{act}/R" and the intercept on the vertical axis will be the constant "$\ln A$". Figure 13 is called the "Arrhenius Plot", from which reaction rates at lower temperatures can be predicted by extrapolation from higher temperature experimental data.
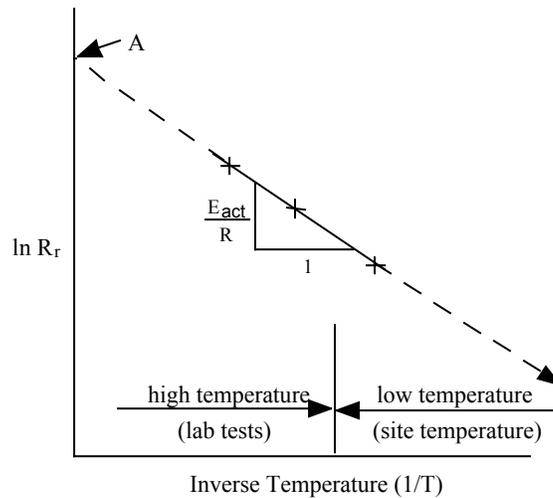

Figure 13 - Generalized Arrhenius plot used for low temperature predictions from high temperature data from labortory tests

For reactions involved more than the gas reactions used in the theory just discussed, there can be significant complex. This is probably the situation in the degradation of polymers. The main problem is that instead of single activation energy, there is often distribution of activation energies. This reflects the multiplicity of "reactions" that can lead to the final degraded product.

Laboratory Experimental Design

The most important parameter in laboratory accelerated aging tests is that site conditions must be simulated as close as possible. This study attempts to simulate an HDPE geomembrane used as a landfill beneath 30 m of solid waste. Special incubation devices were made for this study, as shown in Figure 14. They were modifications of similar devices suggested by Mitchell and Spanner (1985). Twenty identical units of this type were used in this study. Using a 10 to 1 mechanical advantage, a static compressive stress of 260 kPa was applied to each sample. The stress was transmitted via a perforated load plate to 100 mm of sand and then to the geomembrane sample. A 300 mm head of water was maintained above the geomembrane. Beneath each sample was dry soil with small vent to the atmosphere. Five devices were maintained at each of four constant

temperatures: 55, 65, 75 and 85°C. The incubated samples were retrieved at various time intervals and evaluated by a number of tests to monitor possibly properties changes.
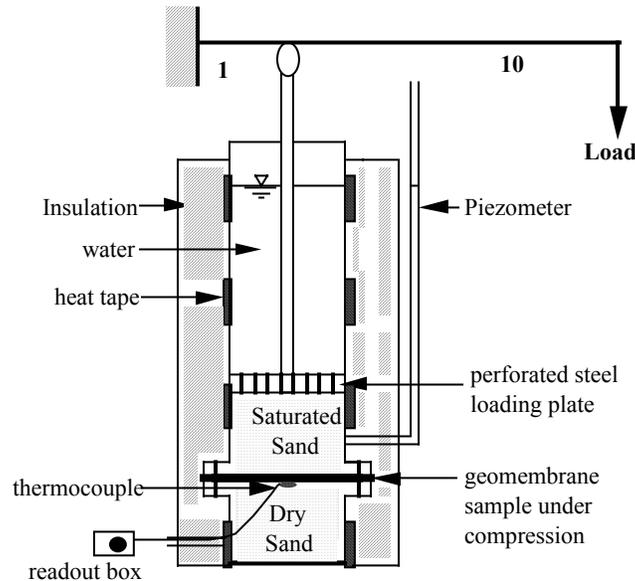

Figure 14 - Schematic diagram of incubation device

Evaluation Tests on Incubated Samples

The geomembrane samples in the incubation devices were retrieved after predetermined lengths of time. The progression of the aging process was monitored by the results of a set of tests to track the behavior of the incubated geomembrane samples. These tests are described, as follows:

Oxidative induction time (OIT)

OIT is the time required for the geomembrane specimen to be oxidized under a specific pressure and temperature. The OIT value indicates the amount of antioxidant (not the type) remaining in the test specimen. Howard (1973) showed that OIT is proportional to the antioxidants concentration in the same formulation package. However, for different antioxidant packages, direct comparison between two single OIT values can be misleading.

The test was performed according to ASTM D 3895 utilizing a differential scanning calorimeter (DSC). The specimen was heated from room temperature to 200°C at a heating rate of 20°C/min under a nitrogen atmosphere. The gas flow rate was maintained at 50 ml/min. When 200°C was reached, the cell was maintained in an isothermal condition for 5 min. The gas was then changed from nitrogen to oxygen. The pressure and flow rate of oxygen were 35 kPa gauge pressure and 50 ml/min, respectively. The test was terminated after an exothermal peak was detected. Figure 15 shows a schematic diagram of the thermal curve with its identified OIT value.
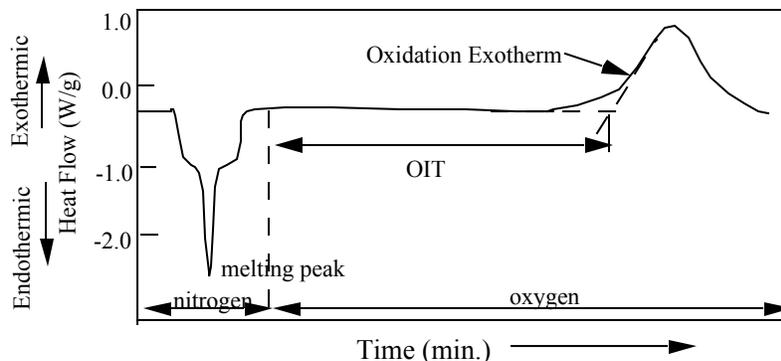
Figure 15 - Schematic diagram of a thermal curve from ASTM D 3895 OIT test

Melt index (MI) test

Oxidation degradation of the polymer will induce either a cross-linking or chain scission reaction, resulting in changes in molecular weight. Cross-linking reactions produce an increase in molecular weight, whereas chain scission reactions produce a decrease in molecular weight. The MI test, ASTM D 1238, is an indirect method to assess molecular weight of the polymer. A high melt index value indicates a low molecular weight, and vice versa. Hence, MI can be considered as an indicator of oxidation degradation.

Mechanical tests

The mechanical performance of the incubated samples was evaluated using a tensile test according to ASTM D 638 type V. Four tensile properties were monitored in the investigation: yield stress, yield strain, break stress and break strain. It should be recognized that break strain and stress have a greater sensitivity to molecular changes in the polymer than yield strain and stress.

Test Material

A single type of commercially available HDPE geomembrane was used. The properties of the original material were evaluated according to test methods described in above. The average properties of original non-incubated are as follows:

- OIT   = 80.5 min.
- MI   = 0.23g/10 min
- Yield stress = 19.2 MPa,
  Yield strain = 33%,
  Break stress = 36 MPa and
  Break strain = 2570%

However, the detailed antioxidant formulation was not provided by the manufacturer.

Test Results

Figure 16 shows the response of the material properties at 85°C. All other incubation temperatures have similar behavior but the OIT depletion is inverse proportional to the incubation temperature. The melt index and tensile properties do not appear to have any significant changes. Conversely, the OIT exhibit substantial changes with incubation time.
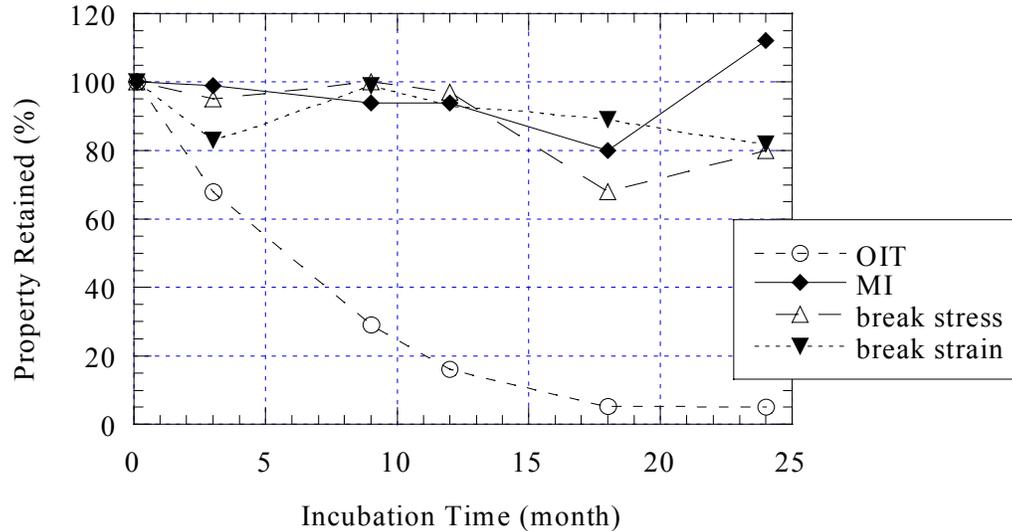

Figure 16 – Changes in properties with incubation time at 85°C

The comparison between OIT and other material properties clearly demonstrates that molecular weight and tensile properties remain unchanged as long as antioxidants exist in the geomembrane. This observation also substantiates the hypothesis of lifetime demonstrating successive stages as shown in Figure 7 earlier. In forced air oven tests at 115°C (i.e., more aggressive conditions than in this study), Hsuan and Guan (1997) have found that the break stress and break strain dropped more than 50% only after OIT values reached minimum level. This again demonstrates the key role of antioxidants in that they must be depleted before engineering property degradation is noted.

LIFETIME PREDICTION ANTIOXIDANTS

The important of antioxidant to the longevity of the geomembrane has been illustrated. Now it remains to quantify the antioxidant depletion lifetime of the geomembrane, i.e., duration of Stage A in Figure 7. To provide this quantification, the lifetime of antioxidant is determined based on the depletion rate of the OIT values. Figure 17 shows a graph by plotting log of OIT versus incubation time. A set of linear response curves results. The slope of the line represents the OIT depletion rate at each particular temperature.
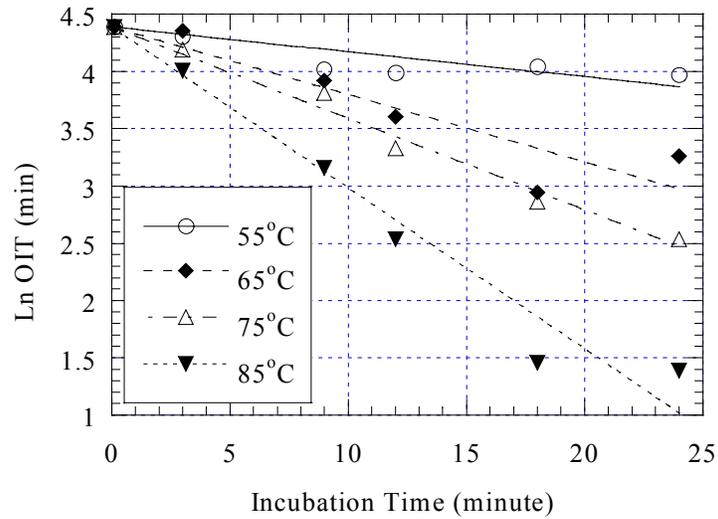
Figure 17 – Ln(OIT) versus incubation time

The generalized equation for each of the straight lines is expressed in Equation (12). The depletion rate at each incubation temperature can be obtained from Figure 17.

$$\ln(OIT) = \ln(P) - (S)(t) \tag{12}$$

Where:
OIT = OIT time (min)
S = OIT depletion rate (min/month)
T = incubation time (month)
P = constant (the original OIT value of the geomembrane)

The next step in the analysis is to extrapolate the OIT depletion rate to a lower temperature, such as the site-specific temperature. As explained by Koerner et al. (1992), Arrhenius equation can be used in such prediction. The Arrhenius equation can be expressed in Equation (13) for this study:

$$\ln(S) = \ln(A) + (-E/R)(1/T) \tag{13}$$

A linear relationship is established between ln(S) and inverse temperature, as shown in Figure 18. The activation energy is taken from the slopes of the line, which results in value of 56 kJ/mol. The corresponding Arrhenius equation is expressed in Equation (14). Koerner and Koerner (1995) and Yazadini et al. (1995) found that the temperature at the base of two municipal solid waste landfills in Pennsylvania and California vary between 19 to 22°C. These landfills have been monitored for four and five years, respectively. The average temperature of 20°C is used to demonstrate the extrapolation calculation, as shown in Equation (15).

$$\ln(S) = 17.045 - 6798/T \tag{14}$$
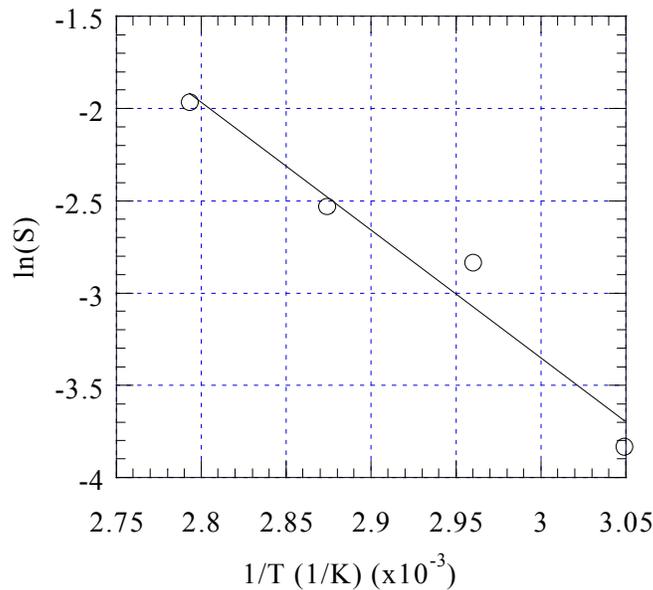$$S = 0.00212 \text{ at } 20^{o}C \tag{15}$$

Figure 18 – Arrhenius plot of OIT rate of depletion

To predict the aging time that is required to deplete all the antioxidant in the HDPE geomembrane, a minimum boundary condition must be established. The OIT value for a pure non-stabilized HDPE resin was evaluated and found to have OIT value of 0.5 minute. Substituting the minimum OIT value, original OIT value and OIT depletion rate at 20°C into Equation (12). The lifetime of the antioxidant can be determined, as shown in Equations (16) and (17):

$$\ln(0.5) = \ln(80.5) - (0.00212)\,(t) \qquad\qquad (16)$$
$$t \quad\quad = 2{,}397 \text{ months (or 200 years)} \qquad\qquad (17)$$

As a result, the predicted antioxidant lifetime at a service temperature of 20°C is approximately 200 years for this particular HDPE geomembrane formulation under the simulated test conditions presented herein.

SUMMARY

The service lifetime of a geomembrane in a containment application is a very important and contentious issue. A quantitative lifetime estimate is often desired by regulators, owners, manufacturers, and designers. To quantify the lifetime of the geomembrane, there are two options: monitoring actual field performance, or using accelerated laboratory simulation tests. This paper presents the latter case.

The critical aspect of the acceleration test is utilizing elevated temperatures to increase the rate of degradation reactions. However, the temperature cannot be so high that fundamental changes in the test material can occur. In this study, the highest temperature used in the accelerated incubation tests was 85°C together with parallel tests

performed at 75, 65 and 55°C. The 20 incubation devices were designed to simulate a landfill under approximately 30 m of solid waste.

The test data confirmed that no changes in the molecular weight and mechanical properties as long as there are antioxidants present in the geomembrane. The depletion of antioxidant stage in the total lifetime of an HDPE geomembrane is a separate and unique stage that precedes changes in engineering properties. The lifetime of the antioxidant in the geomembrane was extrapolated from elevated test temperatures to lower, site-specific temperature, utilizing Arrhenius equation. For this particular HDPE geomembrane under this specific test conditions, the lifetime of antioxidant at 20°C is approximately 200 years. Higher in-situ temperatures will increase the depletion rate consequently lowering the lifetime, and vice versa.

Regarding the induction time and half-life time of the geomembrane, separate study is currently on-going using non-stabilized geomembrane under the same incubation configuration.

FUTURE OF WASTE CONTAINMENT MANAGEMENT

Reinhart and Townsend (1997) categorized the municipal solid waste landfills into four groups: *secure landfill* tends to entomb wastes. *Monofill* accepts wastes such as combustion ash, construction and demolition debris and yard waste. *Reusable landfill* permits excavation of the landfill contents to recover metals, glass, plastics, etc. *Bioreactor landfill* is operated in manner to minimize environmental impact while optimizing waste degradation process. However, majority of the landfills are secure landfills, in which leachate is collected and transported to treatment plant. Eventually, leachate will be completely drained and the waste will be situated in a relatively dry environment. Contrary, leachate is recirculated into the landfill in the bioreactor landfill. Reinhart and Townsend (1997) reported that 130 landfills practiced some type of leachate recirculation, while only10 of 130 landfills were attempting to bring the landfill into full bioreactor moisture statue (i.e., fully saturate the waste). The bioreactor process accelerates the degradation of the waste, which can significantly decrease the waste volume providing more airspace availability. Another benefit of accelerated biodegradation is that the leachate is ultimately treated to the point where it no longer be environmentally controlled.

Leachate recirculation leading to bioreactor landfills is an exciting and worthwhile pursuit, which can revolutionize current waste containment practice

REFERENCES:

"Characterization of Municipal Solid Waste in the United States: 1992 update" (1992) EPA 1530-R-92-019, US Environmental Protection Agency, Cincinnati, Ohio.

Fay, J.J., and King, R.E., (1994) "Antioxidants for Geosynthetic Resins and Applications", *Geosynthetic Resins, Formulations and Manufacturing*, Y.G. Hsuan, and R.M. Koerner eds., GRI Conference Series, IFAI, St. Paul, MN, pp. 77-96.

Daniel, D.E., and Koerner, R.M., (1995), *Waste Containment Facilities*, ASCE Press, Page354.

Giroud and Bonaparte (1989), "Leakage through Liners Constructed with Geomembranes – Part II. Composite Liners," Journal of Geotextile and Geomembrane, Vol. 8, No. 2, PP. 71-112.

Grassie, N., and Scott, G., (1985), *Polymer Degradation and Stabilization*, Cambridge University Press, New York, N.Y.

Howard, J.B. (1973) "Data for Control of Stability in Polyolefin Wire and Cable Compounds" Polymer Engineering Science, 13(6), pp.429-434.

Hsuan, Y.G., and Guan, Z., (1997), "Evaluation of the Oxidation Behavior of Polyethylene Geomembranes using Oxidation Induction Time Tests", *Oxidative Behavior of Materials by Thermal Analytical Techniques*, ASTM STP 1326, A.T. Riga and G.H. Patterson, eds., ASTM, Philadelphia, PA, pp. 76-90.

Koerner, G.R., and Koerner, R.M., (1995), "Temperature Behavior of Field Deployed HDPE Geomembranes", Geosynthetics '95 Conference, IFAI, St. Paul, MN, pp. 921-938.

Koerner, J.R., Soong, T.Y., Koerner, R.M., (1998) "A Survey of Solid Waste Landfill Liner and Cover Regulations Part I – USA Status" GRI-Report #21, Geosynthetic Institute, Folsom, PA.

Koerner R.M. (1997) *Designing with Geosynthetics*, Fourth Edition, Prentice-Hall, Englewood, Cliffs, NJ.

Koerner, R.M., Lord, A.E. Jr., and Hsuan, Y.H., (1992), "Arrhenius Modeling to Predict Geosynthetic Degradation", J. Geotextiles and Geomembrane, 11(2), pp. 151-184.

Michell, D.H., and Spanner, G.E., (1985), *Field Performance Assessment of Synthetic Liners for Uranium Tailings Ponds*, Status Report, Battelle Pacific Northwest Laboratories, US, NRC, NUREG/CR-4023, PNL-5005.

Morrison, R.T., and Boyd, R.N., (1992) *Organic Chemistry*, 3rd ed., Published by Allyn and Bacon Inc, Boston.

Rapoport, N.Y., and Zaikov, G.E., (1986), "Kinetics and Mechanism of the Oxidation of Stressed Polymer" Developments in Polymer Stabilization – 4, G. Scott, ed., Applied Science Publishers Ltd., London, U.K., pp. 207-258.

Rathje, W., (1991), "Once and Future Landfills", National Geographic, May, pp. 117-134.

Reinhart, D.R., and Townsend, T.G., (1998), *Landfill Bioreactor Design and Operation*, Lewis Publishers, CRC Press LLC, Boca Raton.

Yazadini, R., Campbell, J.L., and Koerner, G.R., (1995), "Long-term In-situ Strain Measurements of a High Density Polyethylene Geomembrane in a Municipal Solid Waste Landfill", Geosynthetics '95 Conference, IFAI, St. Paul, MN, pp. 893-906.