

evaluated at this time. High density polyethylene (HDPE) was selected because of its widespread use. A randomly selected roll of commercially available 1.5 mm thick HDPE geomembrane was used for this entire study.

HDPE geomembrane formulations consist of weight percentages of 96 to 97.5% polyethylene (PE) resin, 2 to 3 % carbon black and up to 0.5% antioxidants. It should be recognized that HDPE geomembranes are actually manufactured using polyethylene resin with a density between 0.932 and 0.940 g/cc. This resin density is classified as medium density polyethylene according to ASTM D 883. The addition of carbon black and antioxidants, however, increases the formulated density of the final product to a range between 0.941 and 0.950 g/cc which is defined as HDPE in ASTM D 883. Therefore, the conventional term "HDPE" will be used in this paper.

- Polyethylene (PE) - The resin used for HDPE geomembranes is a linear copolymer which is polymerized using ethylene as the primary monomer and  $\alpha$ -olefin as comonomer under low pressure with appropriate types of catalysts. The amount of  $\alpha$ -olefin comonomer has a direct effect on the density of the resin; a greater amount of  $\alpha$ -olefin added to the polymerization yields a lower density polyethylene polymer.
- Carbon black - Carbon black is added to a 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 the level of opacity, the higher the loading of carbon black, the greater is the degree of ultraviolet light stability. However, the addition of carbon black above the opacity level (which is around 3%) will not further improve ultraviolet resistance (Accorsi and Romero, 1995).
- Antioxidants - Antioxidants are introduced to an HDPE geomembrane formulation for the purposes of oxidation prevention during extrusion and to ensure long-term service life of the product. (The latter being the focus of this paper). There are many types of antioxidants and each of them is somewhat unique. Usually, synergistic mixtures of antioxidants of more than one type are used. Although the total amount of antioxidants in the geomembrane is relatively small, less than 0.5%, their existence is vital to the longevity of the product. Details of the reaction mechanisms will be discussed in a later part of the paper.

## STAGES OF DEGRADATION IN HDPE GEOMEMBRANES

After proper placement of the geomembrane rolls and seaming them together into a liner system, the geomembrane must be covered in a timely manner. During the subsequent service life, aging of the geomembrane takes place. The aging process can be considered to be a combination of: physical aging and chemical aging. Both aging mechanisms take place simultaneously. Physical aging is associated with the slow process that accompanies the material as it attempts to establish equilibrium from its as-manufactured (non-equilibrium) state. For semi-crystalline polymers like HDPE, the process involves changes in the crystallinity of the material (Petermann et. al., 1976), however, 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 a reduction in engineering properties. Therefore, from an applications point of view, chemical aging is the important degradation mechanism. In this section, the different stages of chemical aging of HDPE geomembranes are described.

Conceptually, the chemical aging process of a HDPE geomembrane can be considered in three distinct stages, as shown in Fig. 1. These three stages are designated as (a) depletion time of antioxidants, (b) induction time to the onset of polymer degradation and (c) degradation of the polymer resulting in a decrease of some property(s) to an arbitrary level, e.g., to 50% of its original value.

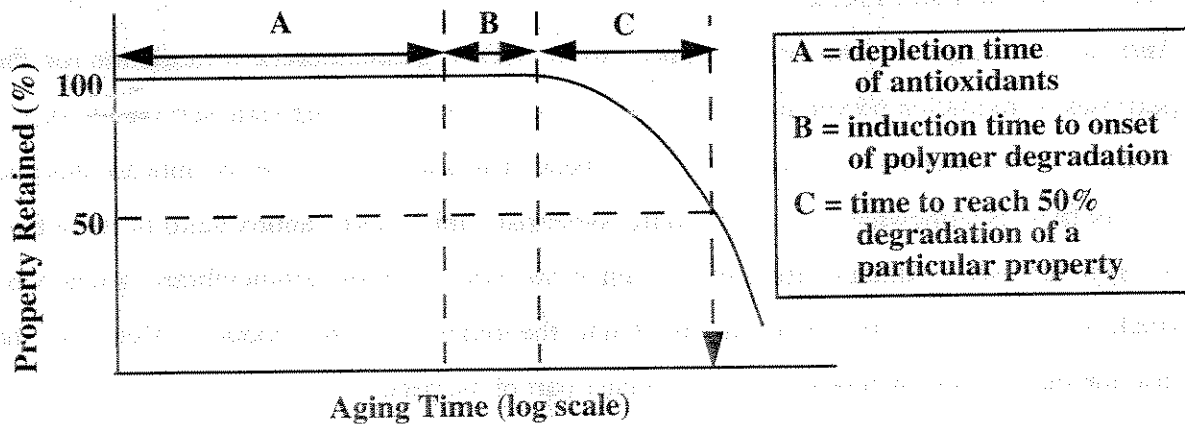


Fig. 1. Three Conceptual Stages in Chemical Aging of HDPE Geomembranes

### **Depletion of Antioxidants - Stage A**

The purposes of antioxidants are (a) to prevent polymer degradation during processing and (b) to prevent oxidation reactions taking place during the first stage of service life. Obviously, there can only be a given amount of antioxidants in any formulation. Once the antioxidants are completely depleted, additional oxygen will begin to attack the polymer, leading to subsequent stages shown in Fig. 1. The duration of this antioxidant depletion stage depends on the types and amount of antioxidants.

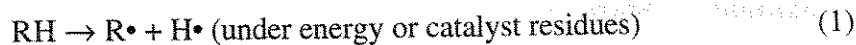
The depletion of antioxidants is the consequence of two processes: chemical reactions with the oxygen diffusing into the geomembrane and physical loss of the antioxidants from the geomembrane. The chemical process involves two main functions: the scavenging of free radicals, converting them into stable molecules, and the reaction with unstable hydroperoxide (ROOH) forming a more stable substance. Regarding the physical loss, the process involves the distribution of antioxidants in the geomembrane and their volatility and extractability.

Hence, the rate of depletion of antioxidants is related to the type and amount of antioxidants, the service temperature and the nature of the site specific environment. Since antioxidant depletion is the subject of this paper, a detailed investigation of these two processes will be presented in a later section.

### **Induction Time - Stage B**

In a pure polyethylene resin, i.e., one without carbon black and antioxidants, oxidation occurs extremely slow at the beginning, often immeasurably slow. Eventually, oxidation occurs rapidly. The reaction then decelerates and once again becomes very slow. This progression is illustrated by the curve of Fig. 2(a). The initial portion of the curve (before measurable degradation takes place) is called the induction period (or induction time) of the polymer. In the induction period, the polymer reacts with oxygen forming hydroperoxide (ROOH), as indicated in Equation (1) to (3). However, the amount of ROOH in this stage is very small and does not further decompose into other free radicals. Thus, the acceleration stage of oxidation cannot be achieved.

In a stabilized polymer such as one with antioxidants, the accelerated oxidation stage takes a even longer time to reach. The antioxidants create an additional depletion time stage prior to the onset of the induction time, as shown in Fig. 2(b).



(where RH represents the polyethylene polymer chains, and the symbol “•” represents free radicals which are highly reactive molecules)

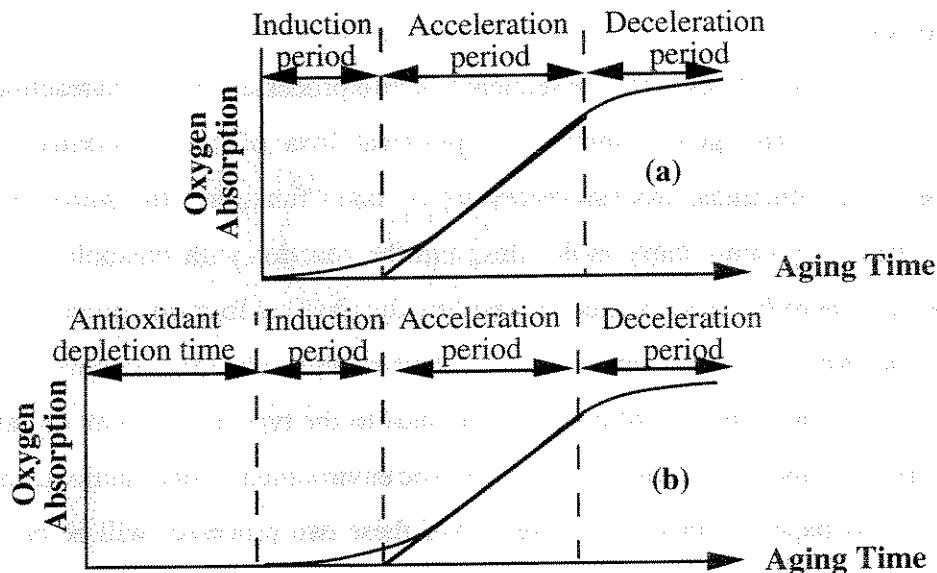


Fig. 2. Curves illustrating the various stage of oxidation for (a) Pure Unstabilized Polyethylene, (b) Stabilized Polyethylene

### Polymer Degradation - Stage C

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



The oxidation produces a substantial amount of free radical polymer chains ( $R\bullet$ ), called alkyl radicals, which can proceed further reactions leading to either cross-linking or chain scission in the polymer. As the degradation of polymer continues, the physical and mechanical properties of the polymer start to change. The most noticeable change in physical properties is the melt index, since it relates to the molecular weight of the polymer. As for mechanical properties, both 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 change 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 of polymeric materials is often selected as a 50% reduction in a specific design property. This is commonly referred to as the half-lifetime, or simply the "halflife". It should be noted that even at halflife the material still exists and can function albeit at a decreased performance level.

## **OVERVIEW OF ANTIOXIDANTS**

Since the subject of the paper is the depletion of antioxidants, discussion on the performance of antioxidants during their depletion period is necessary. Three items are discussed; the function of antioxidant, the types of antioxidants, and the antioxidant depletion mechanisms.

### **Function of Antioxidants**

The sequence of oxidation reactions in HDPE geomembranes indicated by Equations (1) to (6) can be interconnected by cycles "A" and "B" illustrated in Fig. 3. 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 these links. Since the involved molecular species 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.

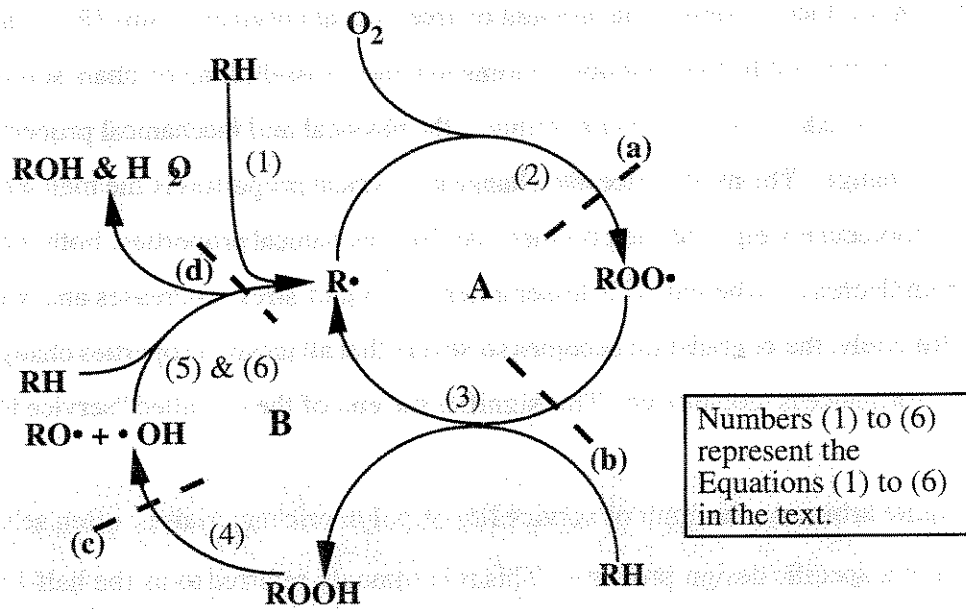


Fig. 3. Oxidation Cycles in Polyethylene (Grassie and Scott, 1985).

Primary antioxidants stabilize the polymer by trapping or deactivating free radical species after they are formed, i.e., breaking links (a), (b) and (d). The antioxidants which intercept the links (b) and (d) function in that they donate an electron. The electrons react with free radicals  $ROO\cdot$ ,  $RO\cdot$  and  $\cdot OH$  converting them to  $ROOH$ ,  $ROH$  and  $H_2O$ , respectively. The types of antioxidants that break link (a) are electron acceptors. They convert alkyl free radicals ( $R\cdot$ ) to form a stable polymer chain.

Secondary antioxidants are designed to intercept the link (c) in the "B" cycle. Their function is to decompose hydroperoxides ( $ROOH$ ), preventing them from becoming free radicals. The chemical reactions change the  $ROOH$  to a stable alcohol ( $ROH$ ).

### Types and Characteristics of Antioxidants

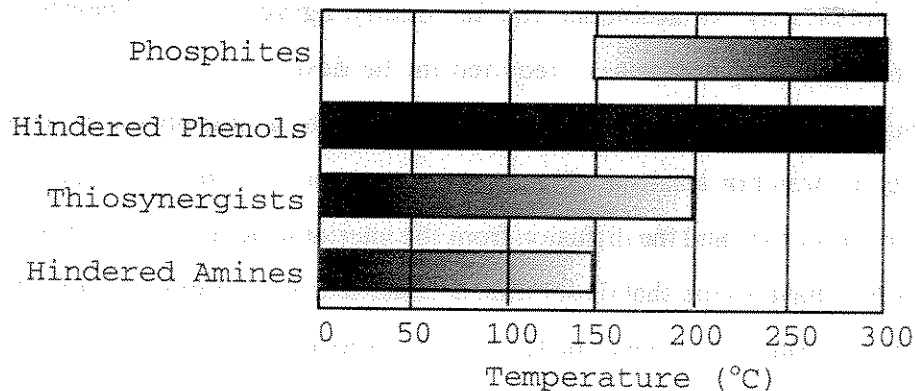
Apart from the two categories just described, antioxidants can be further classified into four large chemical types within which many different products are included. Table 1 lists the chemical type and some of the commercially available antioxidants that can be used in polyethylene geomembranes. To ensure long term durability, a manufacturer will use two or more types of antioxidants; at least one from each category.

**Table 1. Types of Antioxidants**

Category	Chemical Type	Examples of Commercially Available Antioxidants
Primary	Hindered Phenol	Irganox®1076, Irganox®1010, Santowhite Crystals
	Hindered Amines (HALS*)	Various Types of Tinuvin®, Chimassorb®944
Secondary	Phosphites	Irgafos®168
	Sulfur Compounds (Thiosynergists)	dilauryl thiodipropionate (DLTDP), distearyl thiodipropionate (DSTDP)
	Hindered Amines (HALS*)	Various Types of Tinuvin®, Chimassorb®944

\* HALS = hindered amine light stabilizer

There is yet another issue that needs to be considered during the selection of antioxidants. That is the effective temperature range for each of the selected antioxidants. The antioxidant "package" should protect the geomembrane at both the high temperature during the extrusion process and the significant lower temperature during its service lifetime. Thus the functioning temperature range for each type of antioxidant should be recognized. For the four chemical types listed above, the effective temperature ranges are given in Fig. 4. The graph shows that phosphites have an effective temperature range above 150°C. They are considered to be processing stabilizers. Either hindered phenols, thiosynergists, or hindered amines will be added to the formulation to provide the low temperature service protection. For a formulation consisting of hindered phenols, a wide range of temperatures are covered; from ambient to process temperatures. However, hindered phenols are only primary stabilizers. A secondary antioxidant is also required which can be either thiosynergists or hindered amines.



**Fig. 4. Effective Temperature Ranges of Four Antioxidant Types. (Fay and King, 1984)**

## Antioxidant Depletion Mechanisms

The amount of antioxidants in a HDPE geomembrane decreases gradually as aging progresses. As mentioned earlier, two mechanisms are involved; (a) chemical reactions and (b) physical loss. These two mechanisms often occur simultaneously.

(a) Chemical reactions: As a chemical reaction, the antioxidants are consumed by oxygen, free radicals and alkylperoxides present in the material, as described in previous section. The rate of consumption (which progresses from the surfaces of the geomembrane inward) depends on the concentration of these species. Since phenolic and phosphite types of stabilizers are utilized in the processing stage, the antioxidants that remain in geomembranes for longevity protection are a combination of residue phenolic types along with either thiosynergists or hindered amines.

(b) Physical loss: The two major concerns with respect to the physical stability of antioxidants in the polymer are their volatility and extractability (Luston, 1986). The distribution of antioxidants in semicrystalline polymers is not uniform, owing to the presence of crystalline and amorphous phases. It appears that a greater concentration of antioxidants is found in the amorphous region which is fortunate because the amorphous region is also the most sensitive to degradation. Hence the mobility of antioxidants in the amorphous phase controls both volatility and extractability. The volatility of antioxidants is a thermally activated process and temperature changes effect not only the evaporation of the stabilizers from the surface of the polymer but also their diffusion from the interior to the surface layer. For HDPE geomembranes, the typical operating temperature is well below 60°C. Hence volatility is probably not a major concern in field applications. In accelerated laboratory incubation, however, one must avoid inducing such mechanism. Hence very high laboratory testing temperatures should not be utilized. Yet, elevated temperature is necessarily to accelerate the laboratory aging study. Therefore a careful consideration of target temperature(s) is required in the design of any laboratory incubation program. Extractability of antioxidants plays a part wherever the geomembrane comes into contact with liquids, such as water or leachate. The rate of extraction is controlled by the dissolution of antioxidants from the surface and the diffusion from the interior structure to the surface. However, Smith et. al., (1992) have found that dissolution is faster than evaporation for a medium density polyethylene pipe material. They performed a study by exposing a pipe to water internally and air externally. The antioxidant depletion across the thickness of the pipe was monitored via oxidative



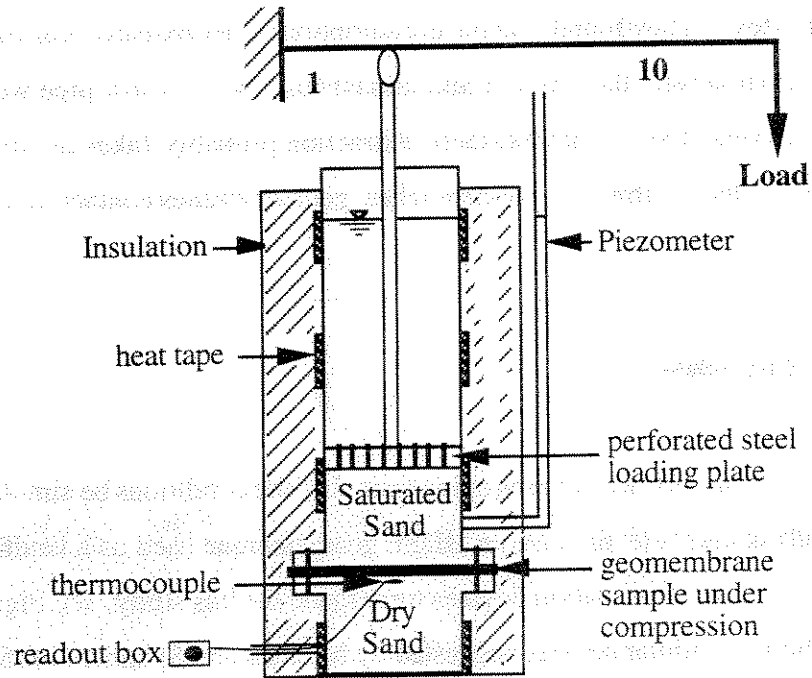
induction time (OIT) tests. They found that the consumption of antioxidants was three times faster in water than in air. However, the types of antioxidants used in their test pipe were not defined. Therefore in the physical loss of antioxidants, extraction probably takes an important role in lifetime predictions. Clearly, this is a concern when geomembranes contact liquids during their service life.

## **EXPERIMENTAL DESIGNS**

It is important in laboratory acceleration aging tests that site conditions be simulated as close as possible. This study attempts to simulate an HDPE geomembrane used as a landfill liner beneath 30 m of solid waste. Special incubation devices were made for this study, see Figs. 5(a) and (b). They are modifications of similar devices suggested by Mitchell and Spanner (1985). Twenty (20) identical units of this type are being used in this study. Using a 10 to 1 mechanical advantage, a static compressive stress of 260 kPa is applied to each sample. The stress is transmitted via a perforated load plate to 100 mm of sand and then to the geomembrane sample. A 300 mm head of water is maintained above the geomembrane. Beneath each sample is dry soil with a small vent to the atmosphere. Five devices are maintained at each of four constant test temperatures; 55, 65, 75, and 85°C. The incubated samples are retrieved at various time intervals and evaluated by a number of tests to monitor changes in their physical, chemical and mechanical properties.

## **EVALUATION TESTS ON INCUBATED SAMPLES**

The geomembrane samples in the incubation devices are retrieved after predetermined lengths of time. The progression of the aging process is monitored by the results of a set of physical, chemical and mechanical tests. Table 2 shows the tests that are being used to track the behavior of the incubated geomembrane samples. Each of the test methods is briefly described in this section. Particular attention will be placed on the two oxidative induction time (OIT) tests; standard OIT test and high pressure OIT test.



(a). Schematic Diagram of the Incubation Device



(b) Photograph Showing the Setup of Twenty Incubation Devices

Fig. 5. Diagram and Photograph of the Incubation Devices

**Table 2. Tests Used to Evaluate Incubated Samples**

Test Description	ASTM Test Methods	Property Being Tracked
Density	D 1505	crystallinity
Standard OIT	D 3895	total antioxidant amount
High Pressure OIT	D 5885	total antioxidant amount
Melt Flow Index	D1238, condition E	molecular weight (indirect)
Tensile Properties	D 638, Type V	stress and strain (yield and break)

Two different OIT tests were used to measure the amount of antioxidant remaining in the incubated geomembrane samples. OIT is the time required for the geomembrane test specimen to be oxidized under a specific pressure and temperature. Since antioxidants protect the geomembrane from oxidation, 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 antioxidant concentration in the same formulation package. However, for different antioxidant packages, direct comparison between two single OIT values can be misleading and caution must be expressed. Since this study is only investigating a single geomembrane type and its particular antioxidant package, this caution is not a concern.

#### **Standard Oxidative Induction Time (Std-OIT) Test**

The Std-OIT test was performed according to ASTM D3895. The test uses a differential scanning calorimeter (DSC) with a specimen testing cell that can sustain a 35 kPa gauge pressure. A 5 mg test specimen was taken from the incubated samples. The specimen was cut from surface to surface across the thickness of the geomembrane near the center portion of the sample. Therefore, the resulting OIT values represent the average amount of antioxidant across the thickness of the test specimens. 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 minutes. 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, hence oxidation of the geomembrane, was detected. An example thermal curve with its identified OIT value is shown in Fig. 6.

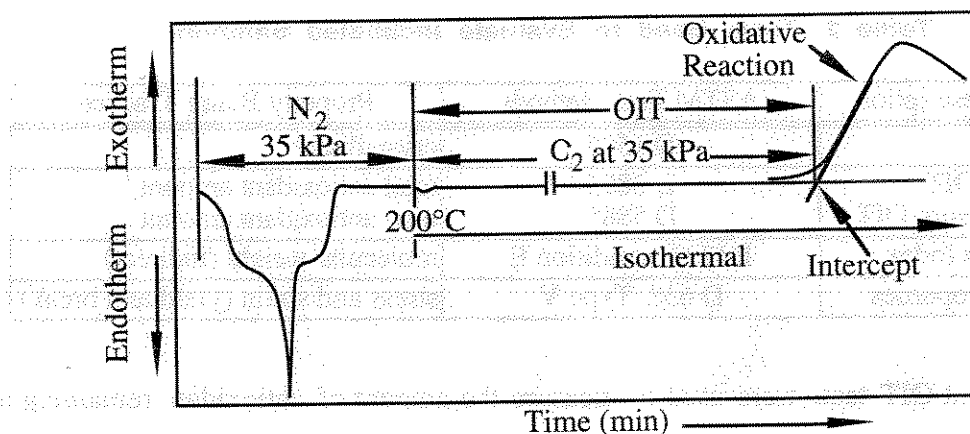


Fig. 6. Thermal Curve from a Standard OIT Test

### High Pressure Oxidative Induction Time (HP-OIT) Test

The HP-OIT test was also performed using a differential scanning calorimeter (DSC) except now using a different cell that can sustain a pressure of 5500 kPa. This type of cell is called a high pressure cell and consequently the test is called high pressure OIT. The HP-OIT test procedure was performed according to ASTM D5885, with a minor modification. A 5 mg test specimen was cut from surface to surface across the thickness of the incubated sample near the center portion of the sample. The specimen was heated from room temperature to 150°C at a heating rate of 20°C/min under a nitrogen atmosphere. The pressure of the cell in this nitrogen stage was maintained at 35 kPa gauge pressure. The gas flow rate was not monitored. (The ASTM standard requires the DSC cell to be saturated with oxygen at a pressure of 3500 kPa before heating is started). When 150°C temperature was reached, the cell was maintained in an isothermal condition for 5 minutes. The gas was then changed from nitrogen to oxygen. The oxygen pressure in the cell was increased to 3500 kPa within 1 minute. The test was terminated after an exothermic peak was detected. The response thermal curve is similar to that shown in Fig. 6 for the Std-OIT test.

The 150°C isothermal temperature is specified because HDPE reaches complete melting at approximately 140°C. The thermal oxidation of the specimen should proceed in a fully molten stage in order to eliminate any residual effects from the manufacturing processes. In addition, this is the highest temperature one should consider to minimize degradation of hindered amine antioxidants, recall Fig. 4. Regarding the cell pressure, Tikuisis, et al., (1993) have performed a

study on the effect of pressure and temperature on HP-OIT values, finding that pressure above 3500 kPa resulted in little change in the HP-OIT value.

The main reason behind developing the HP-OIT test is that the 200°C testing temperature used in the Std-OIT test is unable to bring out the stabilization effect of hindered amine antioxidants. As shown in Fig. 4, the maximum effective temperature of hindered amines is below 150°C. At 200 °C, hindered amine molecules rapidly volatilize from the geomembrane thus losing their designed effect as occurs at in-situ temperatures. As a result, geomembranes with hindered amine antioxidants will exhibit a shorter OIT value than those without (Thomas and Ancelet, 1995 and Hsuan and Guan, 1997). Yet the long term performance of these geomembranes may be very similar, or even better than those without hindered amine antioxidants. In the HP-OIT test, the test temperature is lowered to 150°C which is the minimum temperature to ensure complete melting of the HDPE geomembrane specimen. The low testing temperature, however, results in an relatively long test at the standard pressure of 35 kPa, making the test somewhat unpractical. Hence a high pressure is applied. At a higher oxygen pressure, the concentration gradient of oxygen atoms becomes greater. This increases the number of oxygen atoms diffusing into the molten specimen, thereby accelerating the oxidation and reducing the testing time.

In this study both Std-OIT and HP-OIT tests were conducted on all incubated samples and the results will be compared to one another.

### **Commentary on the Different Oxidative Induction Time Tests**

The major differences between the two OIT tests are oxygen pressure and isothermal temperature. For the Std-OIT test, a relatively low pressure and high temperature are used. For the HP-OIT test, a relatively high pressure and low temperature are utilized. Their differences create somewhat of a dilemma insofar as the selection of a preferred test method for OIT. Table 3 summarizes the advantages and disadvantages.

**Table 3. Differences Between the Standard and High Pressure OIT Tests**

Test	Advantages	Disadvantages
Std-OIT (200°C, 35 kPa)	<ul style="list-style-type: none"> <li>• short testing time (&lt; 200 min.).</li> <li>• simply to operate.</li> <li>• high sensitivity (i.e. can detect very short OIT value.)</li> </ul>	<ul style="list-style-type: none"> <li>• high temperature may bias the test results for certain types of antioxidants, such as HALS antioxidants</li> </ul>
HP-OIT (150°C, 3500 kPa)	<ul style="list-style-type: none"> <li>• able to distinguish different types of antioxidants.</li> <li>• lower temperature relates closer to service conditions.</li> </ul>	<ul style="list-style-type: none"> <li>• long testing time (&gt;300 min.).</li> <li>• special testing cell and set up are required.</li> <li>• less sensitive results, particular for short OIT values</li> </ul>

### Density Test

Physical aging starts immediately after the geomembrane is manufactured. The geomembrane gradually increases its crystallinity which directly relates to the density of the material. A higher density reflects a greater amount of crystallinity. The density test was performed according to ASTM D 1505. Three replicates were evaluated and averaged for each incubated sample.

### Melt Flow Index Test

As described in the early part of the paper, oxidative degradation of the polymer will induce either a cross-linking reaction or a chain scission reaction in the polymer, 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 melt flow index test, ASTM D 1238, is a qualitative method to assess molecular weight of the polymer, thus, it can be considered to be an indicator of oxidation. The melt index test measures the amount of molten polymer at 190°C extruded through an orifice with a defined diameter under a load of 2.16 Kg within a duration of 10 minutes. The result is expressed in units of g/10 minutes. A high melt index value indicates a low molecular weight, and vice versa. Hence the melt index value will decrease for cross-linking reactions and increase for chain scission reactions.

In this study, 3 g of material were taken from the incubated geomembranes. The material was cut in small pieces approximately 2 to 3 mm cubes in sizes. The amount of molten polymer extruded in 6 minutes was determined. The result was then converted to g/10 min. Two replicates were tested for each incubated geomembrane and the results were averaged.

## Mechanical Tests

The mechanical performance of the incubated geomembrane samples was evaluated using a tensile test, since stress and strain are the essential design parameters for the material. Due to the relatively small size of the incubated samples (150 mm diameter), the test was performed according to ASTM D 638, Type V instead of Type IV which is commonly used in evaluating the tensile properties of HDPE geomembranes. Type V uses a 60 mm long dumbbell specimen with a 3.2 mm narrow section width. The distance between grips is 25 mm. The test is performed at a constant rate of 10 mm/min. This test will result a considerably higher strain values than those obtained from Type IV tests. Four tensile properties were monitored in the investigation. They were yield stress, yield strain, break stress and break strain. Three replicate tests were performed and average values are reported. It should be recognized that break strain and break stress have a greater sensitivity towards molecular changes in the polymer than yield strain and yield stress. Also, modulus is such a contentious issue in geomembrane testing that it is the least attractive property to evaluate for the purposes of this study. Hence, it is not reported.

## TEST MATERIAL

As mentioned earlier, a single type of commercially available HDPE geomembrane was used. The physical, chemical and mechanical properties of the original material were performed according the test methods described in the previous section and are listed in Table 4. Although the detailed antioxidant package was not provided by the manufacturer, the major antioxidant types were able to be deduced by comparing the performance of the OIT tests to other geomembranes with a known antioxidant packages. This will be discussed later.

Table 4. Average Properties of Original Non incubated Geomembrane

Std-OIT (min.)	HP-OIT (min.)	Density (g/ml)	Melt Index (g/10 min.)	Yield Stress (MPa)	Yield Strain (%)	Break Stress (MPa)	Break Strain (%)
80.5	210	0.9488	0.23	19.2	33	36.1	2570

## TEST RESULTS

In order to evaluate the entire three stages of the lifetime, per Fig. 1, incubation at the lowest temperature of 55°C will probably take 10 to 15 years. Rather than wait this long for reporting of this program, there is sufficient data to predict the depletion lifetime of the antioxidant. This time period is represented as Stage A in Fig. 1. The incubated samples were retrieved after predetermined incubation periods. The retrieved samples were equilibrated at room temperature for 24 hours. They were then cleaned with tap water to remove surface soil. The cleaned samples were placed in a plastic bag and stored in a cabinet until testing.

### Behaviors of Std-OIT and HP-OIT Test Results

The OIT test results on specimens taken from the retrieved incubated samples are shown in Fig. 7 for Std-OIT and Fig. 8 for HP-OIT. While some scatter is seen, the exponentially decreasing trends in all incubation temperatures is obvious. Also seen is that the OIT depletion rate increases with incubation temperature.

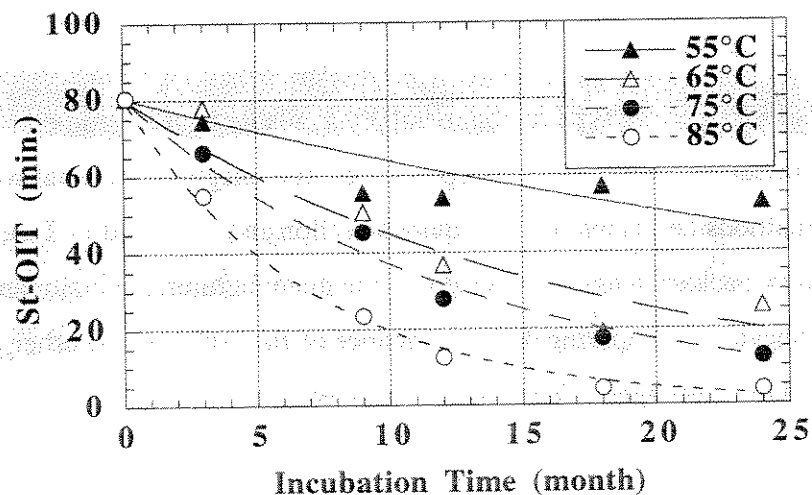


Fig. 7. Standard OIT Versus Incubation Time



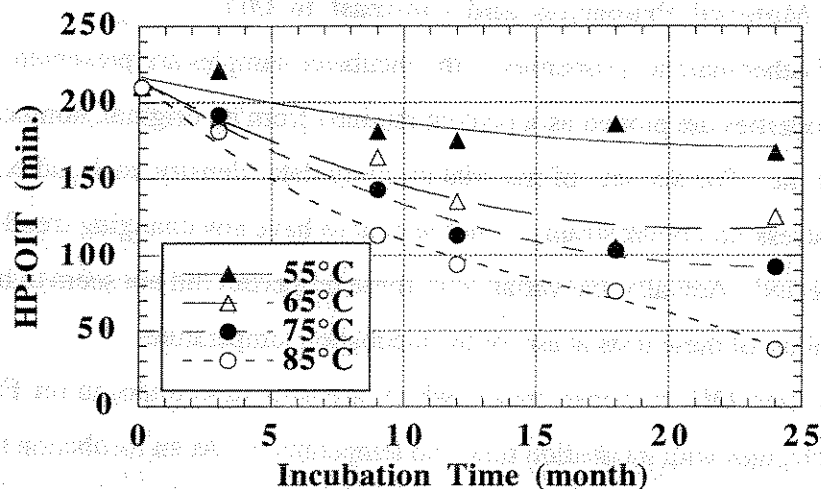


Fig. 8. HP-OIT Versus Incubation Time

### Comparison Between Std-OIT and HP-OIT

The OIT behavior in each test indicates that the depletion of OIT decreased continuously and gradually as incubation time increased in both tests. OIT of both tests exhibited very similar depletion trends, although, the depletion rates of the HP-OIT data were slower than that of the Std-OIT. A linear correlation was found between these two sets of OIT values, as shown in Fig. 9. However, the linear relationship no longer held true when the percent retained from the HP-OIT test decreased below 30% at 85°C after which its depletion rate decreased at a faster rate, as can be seen in the highest temperature curve in Figure 8. In contrast, the percent retained of Std-OIT maintained a steady decline.

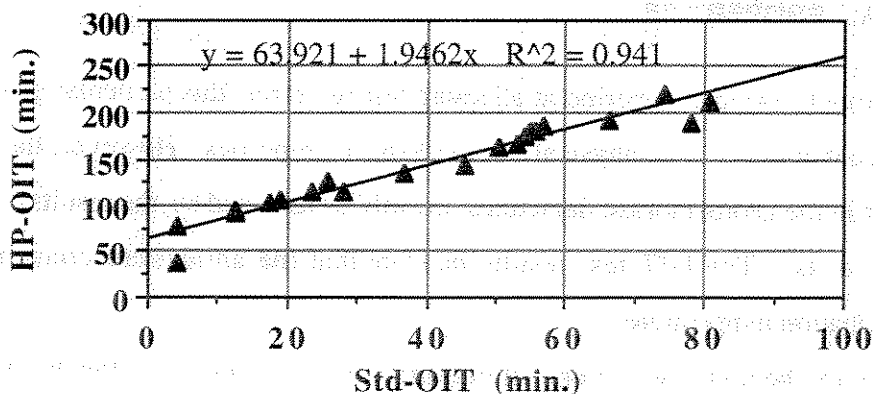


Fig. 9. Correlation Between Std-OIT and HP-OIT Values

Comparison Between OIT and Other Material Properties

## **Results of Other Material Properties and Contrast to OIT**

The response of other material properties of the incubated samples are presented in Figs. 10 to 13. Each of the properties are plotted as a percent retained from its original, nonincubated, value against incubation time. The six sets of material property data (density, melt index, yield stress, yield strain, break stress and break strain) do not appear to have any changing trends over the 24-month incubation period. Actually, the variation in these properties did not seem to be greater than the statistical variability of these tests at any of the incubation temperatures.

Conversely, the two OIT response curves which are also superimposed on Figs. 10 to 13 exhibit substantial changes with incubation time and temperatures. At an incubation temperature of 55°C, the Std-OIT reduced to 60% whereas the HP-OIT decreased to 80%. For the six material properties, they remained within  $\pm 10\%$  of the original value. At an incubation temperature of 65°C, Std-OIT and HP-OIT decreased to approximately 30% and 60%, respectively. In contrast, the material properties still remained a less than  $\pm 10\%$  changes. At an incubation temperature of 75°C, Std-OIT and HP-OIT decreased to 20% and 40%, respectively. The six material properties stayed within  $\pm 10\%$  of the original values. At the highest incubation temperature of 85°C, the Std-OIT and HP-OIT showed a rapid depletion; their percent retained after 24 months incubation decreased to 5% and 20%, respectively. Comparatively, the six material properties remained essentially unchanged, except for the break stress and the break strain which dropped approximately 20%.

## **DISCUSSION ON THE PERFORMANCE OF OIT TESTS AND THEIR CORRELATION WITH OTHER MATERIAL PROPERTIES**

During the 24 month incubation period at all tested temperatures, this particular geomembrane showed no significant changes in its physical and mechanical properties. However, the amount of antioxidant present in the geomembrane depleted uniformly as reflected by the results of both Std-OIT and HP-OIT tests. The OIT test results indicate that the antioxidant consumption rate increased with incubation temperature.

The OIT depletion behavior was very similar in both tests, although the HP-OIT values exhibited a slower reduction rate than the Std-OIT values. A linear relationship was found between these two set of data. The similar response in both OIT tests suggests that the major

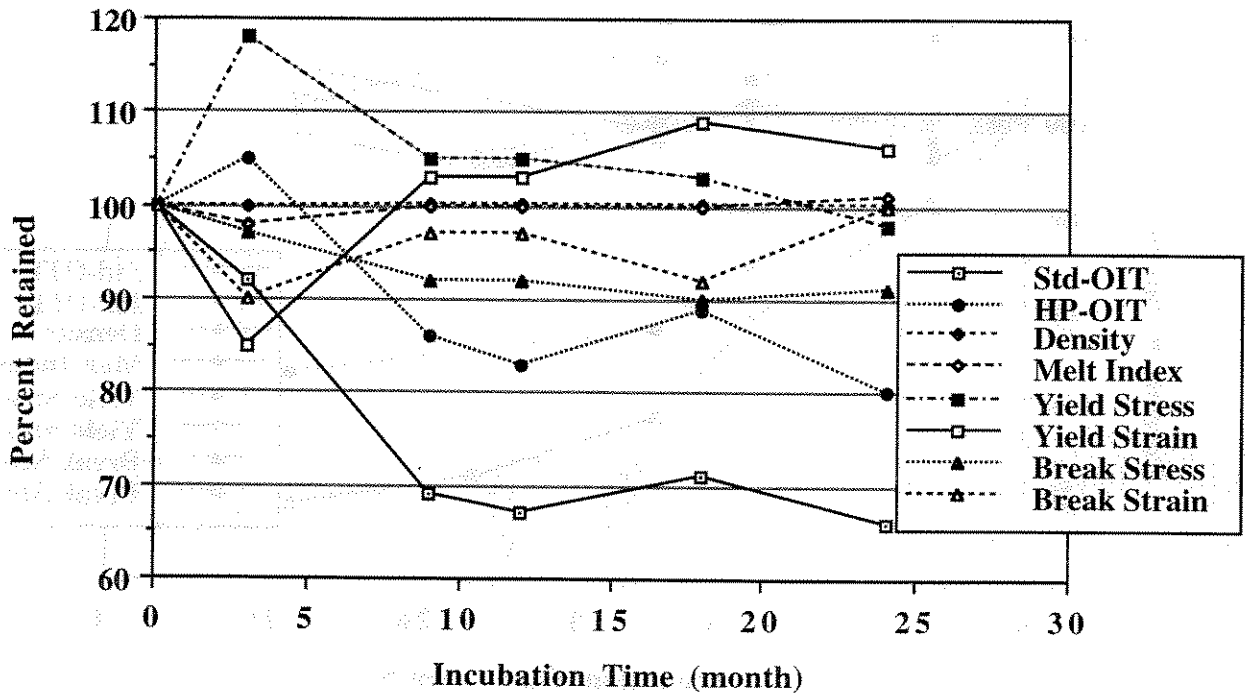


Fig. 10. Changes in Eight Properties with Incubation Time at 55°C

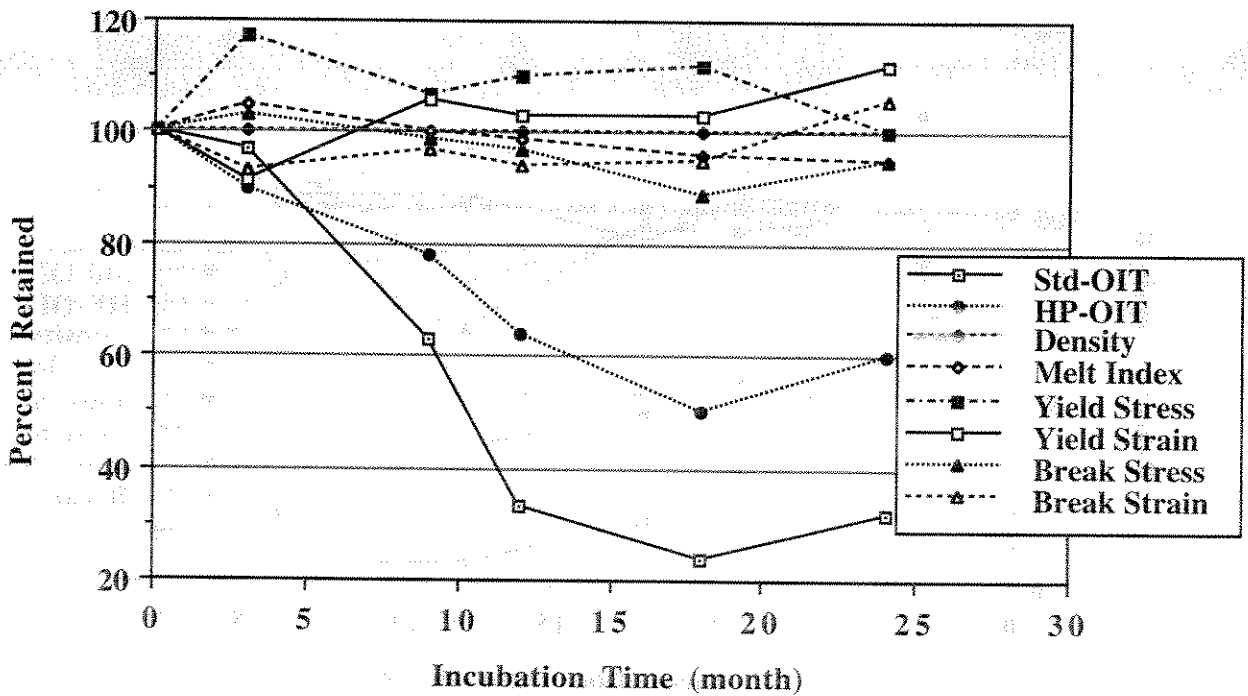


Fig. 11. Changes in Eight Properties with Incubation Time at 65°C

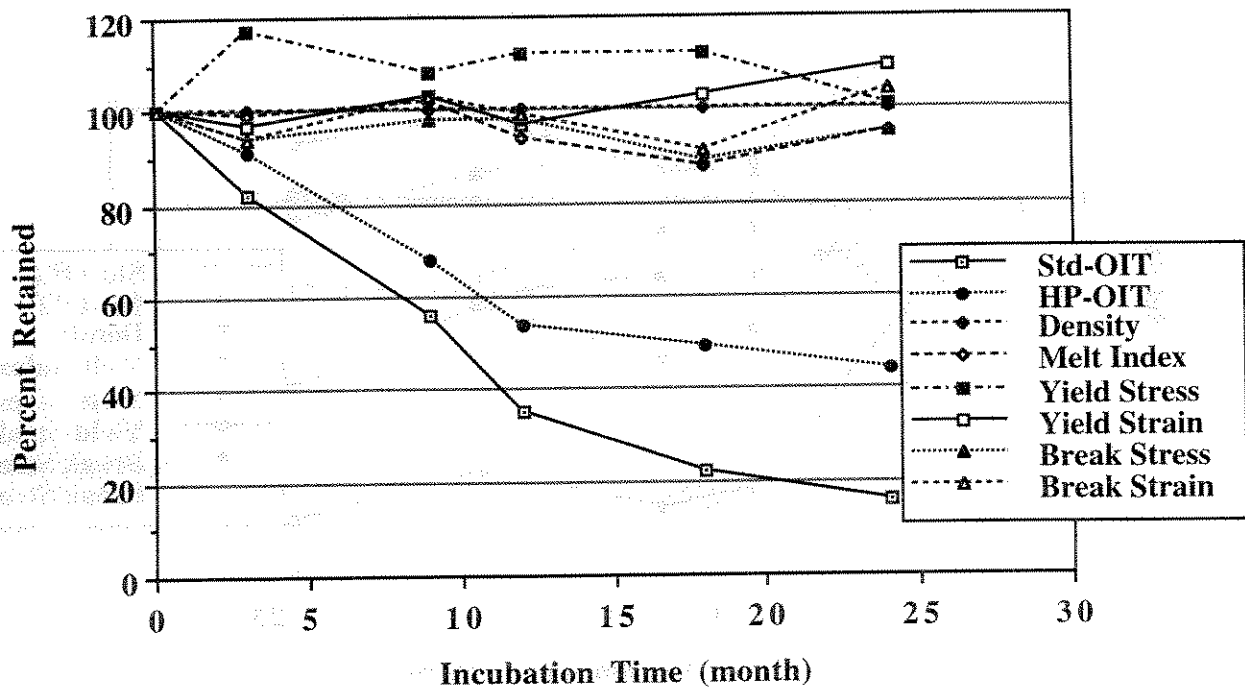


Fig. 12. Changes in Eight Properties with Incubation Time at 75°C

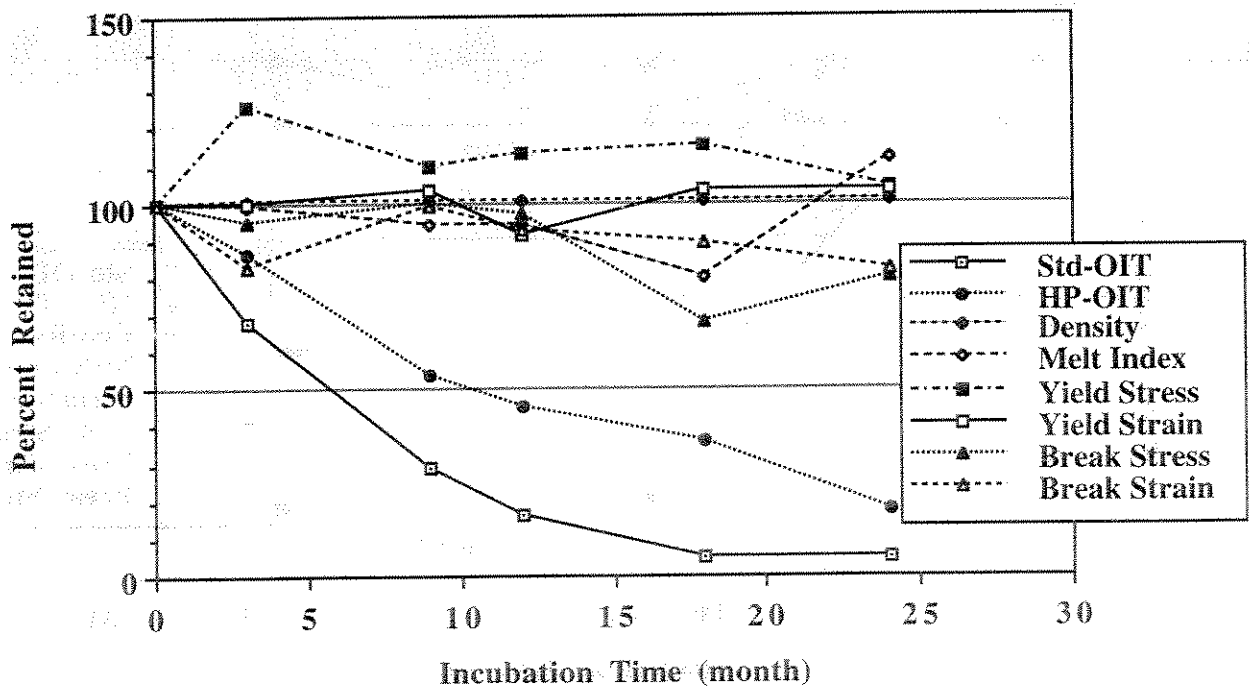


Fig. 13. Changes in Eight Properties with Incubation Time at 85°C

antioxidants in this geomembrane consisted of phosphites and hindered phenols, as observed by Hsuan and Guan (1996). This antioxidant package is one of the common types used by many geomembrane manufacturers to stabilize the HDPE geomembrane. In retrospect, the easier-to-perform Std-OIT test could have been used by itself.

The comparison between OIT results and other six material properties, including density, melt index and tensile properties, clearly demonstrate that these properties remained unchanged as long as antioxidants existed in the geomembrane. This observation also substantiates the hypothesis of lifetime being in successive stages as shown in Fig. 1. 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 zero. This again demonstrates the key role of antioxidants in that they must be depleted before engineering property degradation is noted.

#### LIFETIME PREDICTION OF ANTIOXIDANTS

The important of antioxidants to the longevity of the geomembrane has been illustrated. Now it remains to quantify the antioxidant depletion lifetime of the geomembrane as illustrated in Fig. 1.

To provide this quantification, the lifetime of the antioxidant is determined based on the depletion rate of the OIT values. Figs. 14 and 15 reproduce the OIT data in Figs. 7 and 8, respectively, by plotting  $\ln(\text{OIT})$  against incubation time. A set of linear response curves result. The slope of the lines represent the OIT depletion rate at each particular temperature. It should be noted that at the 85°C, the HP-OIT value showed a slight deviation from the exponential relationship after 18 months. Due to such change, the extrapolation based on the HP-OIT data will probably result in a greater error than that using the Std-OIT data.

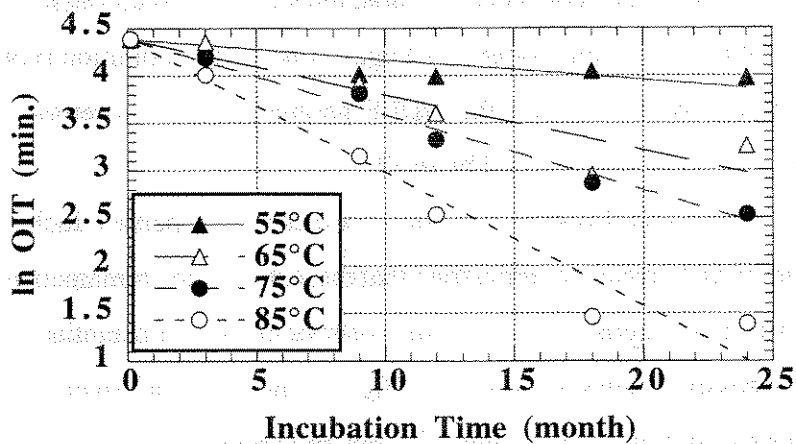


Fig. 14. Ln(OIT) Versus Incubation Time for Standard OIT Tests

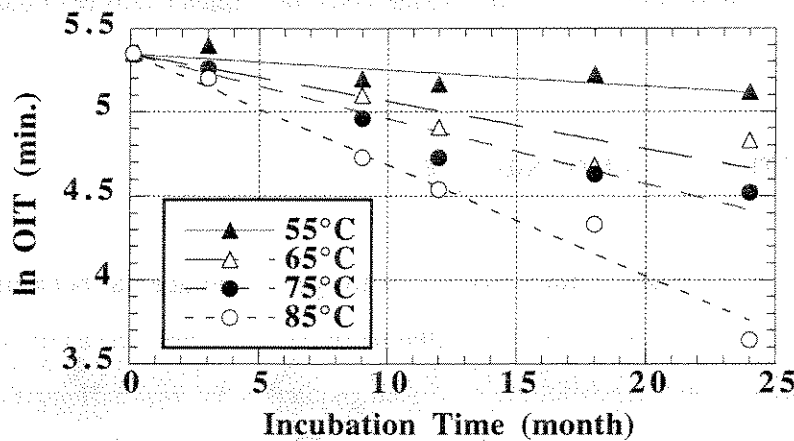


Fig. 15. Ln(OIT) Versus Incubation Time for HP-OIT Tests

### Antioxidant Lifetime Extrapolation Methodology

Based on Figs. 14 and 15, the generalized equation for each of the straight lines is expressed by Equation (7).

$$\ln(\text{OIT}) = \ln(P) - (S) \cdot (t) \quad (7)$$

where: OIT = OIT time (minutes)

S = OIT depletion rate (minute/month)

t = incubation time (months)

P = constant (the original value of OIT time of the geomembrane)

The depletion rate of OIT in each test at each incubation temperature can be obtained and is listed in Table 5.

26

**Table 5. Antioxidant Depletion Rates (min/month) at Different Incubation Temperatures**

Test Temperature	Std-OIT	HP-OIT
55°C	0.0217	0.0097
65°C	0.0589	0.0284
75°C	0.0798	0.0387
85°C	0.1404	0.0661

The next step in the analysis is to extrapolate the OIT depletion rate to a lower temperature, such as the site specific temperature. This is performed utilizing the Arrhenius equation, as described in Equations 8 and 9.

$$S = A \cdot \text{Exp}(-E/RT) \quad (8)$$

$$\ln(S) = \ln(A) + (-E/R) \cdot (1/T) \quad (9)$$

where:

S = OIT depletion rate (values listed in Table 5)

E = Activation energy of the antioxidant depletion reaction under this set of test conditions (kJ/mol)

R = gas constant (8.31 J/mol)

T = test temperature in absolute Kelvin degrees (K)

A = constant

A linear relationship is established between  $\ln(S)$  and inverse temperature, as shown in Fig. 16. The activation energy is taken from the slopes of the lines which results in values of 56 KJ/mol for the Std-OIT and 58 KJ/mol for the HP-OIT result. These two values are extremely similar to one another, since they are essentially evaluating the same reaction mechanisms. The corresponding Arrhenius Equations for Std-OIT and HP-OIT are expressed by Equations 10 and 11, respectively.

$$\ln(S) = 17.045 - 6798/T \quad (\text{for Std-OIT tests}) \quad (10)$$

$$\ln(S) = 16.850 - 6989/T \quad (\text{for HP-OIT tests}) \quad (11)$$

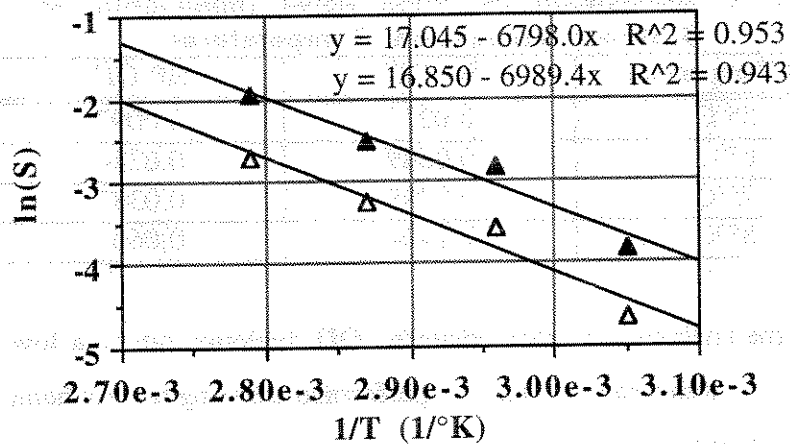


Fig. 16. Arrhenius Plot of OIT Rate of Depletion

Using Equations 10 and 11, the OIT depletion rates at a typical site specific (and lower) temperature can be obtained. Koerner, G.R., et. al. (1995) and Yazadini, et. al. (1995) found that the temperatures at the base of two municipal solid waste landfills in Pennsylvania and California vary between 19 and 22 °C. The landfills have been monitored for 4 and 5 years, respectively. Thus 20°C is used to demonstrate the extrapolation calculation. The extrapolated OIT depletion rates for both OIT tests at 20°C are as follows:

$$S = \underline{0.00212} \quad (\text{for Std-OIT tests})$$

$$S = \underline{0.000909} \quad (\text{for HP-OIT tests})$$

In order to predict the aging time that is required to deplete the antioxidants in the HDPE geomembrane, Equation 7 is utilized. The calculation procedures to obtain the depletion times at 20°C are as follows:

For the Std. OIT test: The OIT value for a pure unstabilized (i.e., no antioxidants) HDPE resin was found to be 0.5 minutes. Thus 0.5 minutes is taken to be the OIT value when essentially all of the antioxidants in the incubated HDPE geomembranes are consumed. The calculation to find the time for this depletion at a service temperature of 20°C is as follows:

$$\ln(\text{OIT}) = \ln(P) - (S) * (t) \quad (7)$$

$$\ln(0.5) = \ln(80.5) - (0.00212) * (t)$$

$$t = \underline{\underline{2397 \text{ months (or 200 years)}}}$$



For the HP-OIT test: The OIT value for a pure unstabilized HDPE resin was found to be 20 minutes which is taken to be the OIT value when the antioxidants are essentially consumed.

$$\ln(\text{OIT}) = \ln(P) - (S) * (t) \quad (7)$$

$$\ln(20) = \ln(210) - (0.000909) * (t)$$

$$t = \underline{\underline{2590 \text{ months (or 215 years)}}}$$

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.

### DISCUSSION ON ANTIOXIDANT LIFETIME PREDICTION

In spite of the potential error by utilizing the HP-OIT data to extrapolate the lifetime of the antioxidant due to its change in the depletion rate at 85°C, the predicted lifetimes from both sets of OIT data are seen to be very consistent. In addition, the two activation energy values are very similar, approximately 56 KJ/mol versus 58 KJ/mol. This suggests that both tests are monitoring the same reaction.

Although the HP-OIT had a slower depletion rate than the Std-OIT at all incubation temperatures, as indicated by the slope values in Table 5, the predicted lifetime obtained from the HP-OIT data was only slightly longer than that of the Std-OIT. This is because a high minimum OIT was detected for the non-stabilized HDPE resin and this value was used in the HP-OIT data extrapolation.

The average predicted lifetime of this particular antioxidant package is at least 200 years under the conditions replicated by the test design environment, i.e., the geomembrane sandwiched between saturated soil and dry soil and under compression loading.

### CONCLUSIONS

The service lifetime of a geomembrane in a containment application is a very important and a contentious issue. A qualitative lifetime estimate is often desired by regulators, owners, manufacturers and designers. In order to quantify the lifetime of the geomembrane, there are two

options; monitoring actual field performance or using accelerated laboratory simulation tests. This study utilizes the latter approach.

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 twenty incubation devices were designed to simulate a landfill (wet above and dry beneath) under approximately 30 m of solid waste.

The focus of this paper is on the depletion lifetime of the antioxidant in the geomembrane. This is the first stage of the overall degradation of HDPE geomembranes. The subsequent stages are induction time and time to reach half-life of a relevant engineering property. For the geomembrane used in this study, either Std-OIT or HP-OIT test could be used to monitor the antioxidant consumption of the incubated geomembrane samples. The results show exponentially decreasing OIT values with increasing incubation time. As anticipated, the depletion rate increased with incubation temperature. Arrhenius modeling was utilized to extrapolate the depletion rate of antioxidant from elevated test temperatures to lower, site-specific, temperatures. Subsequently, the time to deplete all antioxidant in the geomembrane was calculated. For this particular HDPE formulation under conditions utilized in this study, the lifetime of antioxidants at 20°C is 200 to 215 years. The value of 20°C was selected based on field temperature monitoring of municipal solid waste landfill liners in Pennsylvania and California. Higher in-situ temperatures will increase the depletion rate consequently lowering the lifetime, and vice versa.

In addition to tracking the antioxidant depletion, physical and mechanical properties of the incubated samples were also monitored. These properties included density, melt index and tensile properties (yield stress, yield strain, break stress and break strain). Within statistical variation of these tests, there were essentially no changes in these properties over the 24-month incubation process. These results provide strong evidence that as long as there are antioxidants present in the geomembrane, the physical and mechanical properties will be preserved. The depletion of antioxidant stage in the total lifetime of an HDPE geomembrane is a separate and unique stage which precedes changes in engineering properties. The successive two stages (induction time and half-life of properties) remain to be evaluated. This study is being continued in this regard. It

should be noted, however, that it may take years of "accelerated" incubation before the lifetime of remanning two stages can be quantified.

Lastly, it should be recognized that this study is for HDPE geomembranes, with one particular antioxidant package. Performance of other types of antioxidant packages cannot be deduced from the results of this study. However, the results of this study certainly provide a reference point for other antioxidant packages.

## **RECOMMENDATION**

The value of the antioxidant package insofar as lifetime of the HDPE geomembrane is concerned has been shown by the results of this study. It now remains for the regulatory, owner and engineering designer to specify minimum OIT test values (hence amount of antioxidants) for various applications. Even further, one could craft different accelerated incubation environments to verify that the depletion rate is not excessive.

## **ACKNOWLEDGEMENTS**

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## Degradation of Polymeric Materials and Products

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"Research Developments  
for Improving Solid  
Waste Management"  
Cincinnati, OH, Feb. 1991

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### ABSTRACT

This paper describes the most common forms of degradation of polymeric materials and products from the perspective of their burial in a landfill environment. Both the liner systems used to contain solid waste and the polymer waste products themselves are considered. In this context, oxidation and chemical degradation, coupled with various types of superimposed stresses, are felt to be the primary sources of initial degradation. Eventually, and after many years, it is likely that biological degradation will also occur but only after the molecular weight of the polymer has drastically decreased.

The quantification of polymer degradation is generally approached by accelerated testing at elevated temperatures. In this procedure, samples are incubated for various times, removed and tested by a variety of procedures. By plotting the resulting data points on an Arrhenius plot, degradation at a site specific temperature can be estimated. The general procedure is also known as the time-temperature superposition principle.

Critically important, however, is how the test data is generated. A number of test methods are reviewed in this paper. They are keyed to the type and degree of degradation that one is focusing upon. The paper concludes on a cautionary note in that the time for complete degradation (i.e., the ultimate lifetime) promises to be quite long. This suggests that assumptions and inaccuracies can easily influence the estimation and not be readily detectable. Clearly, a considerable amount of investigation needs to be performed on the topic of polymeric materials and product degradation before reliable lifetime estimates can be developed.

## INTRODUCTION

The inter-related questions of degradation and lifetime prediction of polymeric materials are being asked by many groups for various purposes. Clearly, the group which is involved with polymeric liners for waste containment purposes is vitally interested in assessing the performance limit of these particular products. As will be seen, however, this type of performance, or functional, limit is by no means the ultimate lifetime of the various polymer materials. Within the landfill environment, for example, polymeric waste products will have an additional time frame for large scale degradation (usually via embrittlement and subsequent cracking) to occur. Still longer in time, for groups interested in the ultimate fate of polymer products and waste materials will be a lowering of the molecular weight to where other mechanisms, like biological activity, might cause degradation. This final stage will eventually lead to the ultimate degradation of the polymer material at the molecular scale. Thus, any degradation prediction must be categorized under the caveat of what degree of degradation? This, in turn, involves the question of the specific nature of the various degradation mechanisms.

In this paper, the most common types of polymer degradation will be reviewed. These important issues are immediately followed by a challenge as to the nature of the incubation process and the subsequent testing process. As will be seen, a large variety of tests are available for use in assessing the degree of degradation. These have been arbitrarily placed in the physical, mechanical and chemical property categories. This must be followed by questions as to the type of prediction method that should, or can, be utilized. Here we will use the time-temperature superposition principle, also called Arrhenius modeling, recognizing that several important assumptions are inherent in this type of approach. Some concluding remarks about the assumptions involved and the risks associated with this approach are also presented.

## STAGES OF POLYMER DEGRADATION

As mentioned in the introduction, the question of degradation prediction must be associated with "what stage is of interest"? When referring to polymeric materials there can be at least three discrete stages (and possibly many more) depending upon the vantage point of the questioner. These stages are listed in Table 1 as "end of functionality", "brittle sections/pieces", and "soft particles/powders". The "end of functionality" stage is that point in time in which the performance of the material or product no longer provides its intended purpose. This could be a polymeric liner failing, a waste product collapsing, or other tangible evidence of nonperformance. It should be noted that this stage has probably been the focus of most of the degradation studies (and subsequent lifetime prediction work) to date.

Further on in time, however, another stage will be reached. In Table 1 this is called the "brittle sections/pieces" stage. In this stage the polymer has had chain scission and bond breaking occur to the point where the material or product is undergoing widescale embrittlement and cracking. The result is that the original material is now in many sections or pieces. These pieces have been degraded from their original state to the point where the average molecular weight has decreased substantially.

Still further in time, the molecular weight will decrease to the point where the pieces become relatively soft and waxy. Thus other degradation mechanisms may "kick-in", e.g., biological degradation. The ultimate fate at this point is probably degradation down to the fundamental units of matter.

The tagging of molecular weight values in Table 1, is based on relationships as shown in Figure 1. This situation is for polyethylene but may be representative of other common polymers as well. The original material or product range is generally above 30,000, and often above 100,000. It lowers with chain scission and bond breaking, i.e. degradation, through the point of nonperformance and into the other two stages described. We have used an order of magnitude to separate each stage, i.e., from 100,000 to 10,000 and finally to 1000. At this point the polymeric material is capable of a large array of degradation mechanisms including that of biological degradation.

Table 1 - Stages of Polymeric Material Lifetimes in Waste Disposal Scenarios\*

Focal Groups

"Typical"

Implications

Physical

Degradation

polymeric materials which is involved in assessing the life cycle of this type of various polymer products will have an impact and subsequent fate of polymer products. Where other agencies will eventually be involved. Thus, any assessment of degradation? adaptation.

reviewed. These tests are the incubation of tests are arbitrarily placed in a flow chart followed by a table. Here we will be dealing, recognizing the approach are also

on must be materials there can be a advantage point of brittle stage is that point in its intended life, or other tangible, has been the focus of date.

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Table 1 - Stages of Polymeric Material Lifetimes in Waste Disposal Scenarios\*

Degradation Stages	Physical Evidence	Implications To Material	"Typical" Molecular Weight**	Focal Groups Concerned
"end of functionality"	loss of mechanical properties to point of non-serviceability or non-performance	liners and leachate collection systems malfunction, containers break apart, etc.	~ 100,000	landfill owner/operators; geosynthetic design/testing firms; manufacturers; and regulatory agencies.
"brittle sections/pieces"	large scale cracking of polymer due to brittle behavior	polymer materials and products start splitting into small sections	~ 10,000	waste recycling groups; regulatory agencies.
"soft particles/powders"	continued polymer breakdown into extremely small and soft units	ultimate breakdown into viscous particles or powders	~ 1,000	public-at-large; regulatory agencies.

\*The table is quite arbitrary but is used in this paper to define testing methods and perspective as to predictive methods.

\*\*These values are for polyethylene, but other polymers might have similar trends.



## DEGRADATION MECHANISMS

The degradation mechanisms which bring about the above described stages of a polymeric material are numerous. A few comments regarding each of them is in order.

### (a) Ultraviolet Degradation

The spectrum of light is broken into three major regions (infrared, visible, and ultraviolet) according to the wavelength of solar radiation. It is well established in the polymer literature that certain wavelengths within the ultraviolet portion (less than 400 nm) are particularly degrading to polymeric materials. Van Zaten<sup>(2)</sup> makes mention of the following commonly used polymers and their most sensitive wavelengths, all of which are in the ultraviolet region.

- polyethylene = 300 nm
- polyester = 325 nm
- polypropylene = 370 nm

The mechanism of ultraviolet degradation of polymers is well understood. The light with the most sensitive wavelengths enters into the molecular structure of the polymer liberating free radicals which cause bond scission in the primary bonding of the polymer's backbone. This mechanism, in direct proportion to the exposure time, causes a reduction in mechanical properties to the eventual point where the polymer becomes brittle and cracks to unacceptable levels. Note that the above degradation mechanism is greatly reduced by the addition of chemical stabilizers and/or carbon black in the polymer formulation.

At issue for this paper, however, is that by burying the polymer material or product in a landfill (or beneath other types of soil cover), ultraviolet light is eliminated. Thus, degradation of this type becomes a non-issue for the purposes of this paper.

### (b) Radiation Degradation

There are many reviews on the effects of radiation on polymer properties, e.g., Phillips<sup>(3)</sup> and Charlesby<sup>(4)</sup>. In general, the effects of  $\gamma$ -rays, neutrons and  $\beta$ -rays are essentially equivalent when their different penetrating powers are considered.  $\beta$ -rays (electrons) penetrate about a millimeter into a given polymer, whereas  $\gamma$ -rays and neutrons penetrate much further.  $\alpha$ -rays (helium nuclei) penetrate only micrometers, hence are only involved with very near surface damage.

The basic mechanical short term properties of a typical polymer start to change at a total radiation dose of between  $10^6$  and  $10^7$  rads. A rad is equivalent to 100 ergs of absorbed energy per gram of material and, for reference purposes, the lethal dose of radiation to a human is about 100 to 200 rads. Therefore it would appear that for most landfill situations, radiation degradation is not very significant since radioactive waste is usually not co-disposed with domestic and industrial waste. The exception is the disposal of high level or transuranic wastes, which requires completely different containment strategies than do most domestic facilities.

### (c) Biological Degradation

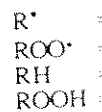
Within the various forms of biological life, i.e., bacteria, actinomycetes, fungi and algae, degradation of polymer materials and products is highly unlikely due to the high molecular weight of the resins used in formulating common polymer products. In order for such degradation to occur, the chain ends must be accessible and this is highly unlikely for molecular weights greater than 3000, let alone 30,000 to 300,000 which is the range for many commercial resins. Biological degradation of the plasticizers or additives compounded with the resin might be possible but information is not authoritative on this subject.

Recalling Table 1 and Figure 1, however, forces one to consider situations where the polymer eventually lowers in molecular weight to the point of becoming soft, waxy, grease-like and even liquid. At this point (i.e., the final stage listed in Table 1) the molecular weight is probably 1000, or lower, and biological degradation is not only possible, it should actually be anticipated.

### (d) Oxidation De

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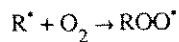
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#### (d) Oxidation Degradation

Whenever a free radical is created, e.g., on a carbon atom in a polyethylene chain, oxygen can create large scale degradation. The oxygen combines with the free radical to form a hydroperoxy radical, which is passed around within the molecular structure. It eventually reacts with another polymer chain creating a new free radical causing chain scission. The reaction generally accelerates once it is triggered as shown in the following equations.



where

- $R^{\bullet}$  = free radical
- $ROO^{\bullet}$  = hydroperoxy free radical
- $RH$  = polymer chain
- $ROOH$  = oxidized polymer chain

Anti-oxidation additives are added to the compound to react with, or scavenge, these free radicals in order to halt, or at least to interfere with, the process. These additives, or stabilizers, are specific to each type of resin. The additive area is very sophisticated and quite advanced with all resin manufacturers being involved in a meaningful and positive way. The specific amount and type of anti-oxidants are usually proprietary.

Removal of oxygen from the polymer's surface, or course, eliminates the concern. Thus, once placed and covered with waste, degradation by oxidation should be greatly retarded. Note, however, that the oxidation phenomenon is never completely eliminated. Even when the polymer is submerged in a liquid, e.g., leachate, there is some amount of oxygen present which will eventually cause degradation of the polymer.

#### (e) Chemical Degradation

The reaction of various polymeric materials to chemicals has been evaluated to a considerable extent. Most of the work is laboratory oriented via simple immersion tests, but the body of knowledge is so great that a reasonable confidence level can be associated with manufacturers listings and recommendations. Complex waste streams like leachate, however, are usually not addressed and must be evaluated on a site specific basis. For this reason, the U.S. EPA developed the Method 9090 procedure<sup>(9)</sup>. In this method, samples of the candidate geomembrane are exposed to the site-specific leachate at both 23°C and at 50°C and are removed after 30, 60, 90 and 120 days. Various physical and mechanical tests are performed and the results are compared to the unexposed geomembrane. A percent change in this behavior is then calculated. When plotted for the various exposure times, trends can be established. Depending on the type of leachate vis-a-vis the polymeric compound from which the polymer product is made, a number of reactions may occur.

- No reaction, which indicates that the polymer is resistant to the leachate; at least for the time periods and temperatures evaluated.
- Swelling of the polymer may occur which in itself may not be significant. Many polymers can accommodate liquid in their amorphous regions without a sacrifice of physical or mechanical properties. Swelling, however, is often the first stage of subsequent degradation and a small loss in modulus and strength may occur. The effect is often reversible when the liquid is removed.
- A finite change of physical and mechanical properties, of course, signifies some type of chemical reaction. The variations are enormous. Quite often the elongation at break in a tensile test will be the first property to show signs of change. It will first occur with the 50°C incubation data, since this can be considered to be an accelerated test over the 23°C incubation data.
- A large change of physical and mechanical properties signifies an unacceptable performance of the polymer. Limits of acceptability are available, see Koerner<sup>(6)</sup>, but they are very subjective.

Critically important, however, is that all of this work is focused on chemical degradation only toward the "end of functionality" stage. As seen in Table 1, many groups are interested in degradation well beyond this level, i.e., down to the molecular level. This level of degradation has not been investigated to our knowledge.

#### (f) Synergistic and Accelerating Effects

Before closing this section, it must be noted that the very complex issue of polymer degradation becomes even more complex when synergism is considered. The above degradation processes often do not act individually, but collectively. For example, oxidation and chemical effects may act together. Furthermore, the effects of heat and stress were not even mentioned. Clearly, elevated temperatures have an accelerating effect on all of the degradation mechanisms listed. In fact, elevated temperature testing will be the key phenomenon to be used later when considering Arrhenius modeling. Lastly, the issue of degradation of a polymeric material under stress, versus nonstressed, has had very little attention. Our suggestion will be to site-specifically model the stress situation as close as possible so that test results reflect a realistic situation as closely as possible.

#### ARRHENIUS MODELING

In order to model polymer degradation, one generally accelerates the process via the incubation of representative samples at elevated temperatures. When done in the site specific environment (e.g., in leachate) and under simulated stress conditions, temperature/time superposition concepts can possibly be utilized. We will refer to the procedure as Arrhenius modeling.

The type of incubation chamber for the polymer samples might appear as shown in Figure 2, after Mitchell and Spanner.<sup>(7)</sup> It is indeed an elaborate device, however it has the capability of including the synergistic effects of elevated temperature, compressive stress, and the chemical environment that the polymer (in this case a polymeric liner) will experience. Note that the target of this type of experiment is an assessment of the "end of functionality" stage, not the subsequent stages listed in Table 1.

After a given period of time, the samples are removed and tested for some particular physical, mechanical or chemical property. By repeating the experiment, at gradually lengthened time periods, a trend should be established for this particular value of incubation temperature, e.g., see the hypothetical curves of Figure 3. The entire set of time experiments are now repeated, but at a different temperature, to obtain a second response curve. This process is then repeated at least once again at a third temperature, and perhaps even at a fourth temperature. The family of curves for the four different temperatures might appear as shown in Figure 3, where any one of a number of properties (which will be discussed later) could be under investigation.

An important decision must now be made as to the limiting value of functionality that one is focusing upon. If one is looking for a 20% reduction in original property (as is approximately shown in Figure 3), the times for this change to occur at each temperature are obtained. The inverse of these values (in time) are then plotted against the inverse of the temperature, as shown in Figure 4. There will be one point for each temperature evaluated. It should be noted that Figure 4 is actual data plotted for the 50% impact strength reduction at four different temperatures for a particular polyethylene cable shielding.<sup>(9)</sup> This type of plot is called an Arrhenius plot and embodies the concept of time/temperature superposition.

Having this information (and within the limitations to be discussed later), one can extrapolate the time for the targeted strength reduction at any site-specific (and generally lower) temperature.

As an example of the technique, we will use information from the Underwriters Laboratory Standard<sup>(9)</sup> regarding polyethylene shielding of electric cables as shown in Figure 4. The illustration of reaction rate is for 50% strength reduction from the original and unaged value using an impact test. The slope of the Arrhenius plot shown in Figure 4 is the activation

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energy " $E_{act}$ ", divided by the gas constant " $R$ ".<sup>(8)</sup> Numerically, it is as follows:

$$\frac{E_{act}}{R} = \frac{\ln 10^{-5} - \ln 10^{-2}}{0.00247 - 0.00198}$$
$$= -14,100 \text{ (}^\circ\text{K)}$$

As an illustration of predicting low temperature behavior, consider the elevated temperature data point at

$$1/T = 0.00213$$

$$T = 469^\circ\text{K}$$

$$T = 196^\circ\text{C}$$

and project this reaction rate to the site specific temperature of  $100^\circ\text{C}$ . Using the Arrhenius equation shown below<sup>(8)</sup>:

$$\frac{R_r @ T_1}{R_r @ T_2} = e^{\frac{E_{act}}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]}$$

$$\frac{R_r @ 196}{R_r @ 100} = e^{-14100 \left[ \frac{1}{469} - \frac{1}{373} \right]}$$
$$= 2290$$

Since the reaction at  $196^\circ\text{C}$  took 1000 hours (1/0.001 from Figure 4) to complete, then the comparable reaction rate at  $100^\circ\text{C}$  would take the following time to complete.

$$R_r @ 100^\circ\text{C} = 2,290 (1000)$$
$$= 2,290,000 \text{ hrs.}$$
$$= 260 \text{ yrs.}$$

It must be noted that the temperatures of the experiments used in this example are quite high and are relatively limited, i.e., bunched together. Extrapolation down to the site specific temperature mentioned may be completely invalid, but this example nevertheless illustrates the technique of Arrhenius modeling. One does not know which, if any, of the properties of geosynthetics will be amenable to the Arrhenius approach, but it is extremely important to investigate the various possibilities.

Within the context of the above assumptions, we have absolutely no idea as to how the technique might work to predict the more advanced stages of degradation mentioned in Table 1. Perhaps all one can safely say is that the times will be considerably longer.

#### TEST METHODS TO EVALUATE INCUBATED SAMPLES

The type of test method used to generate the graphs of Figures 3 and 4 (which follows the incubation process) is obviously important and warrants a discussion in its own right. For "end of functionality" predictions, the test methods can be grouped into physical, mechanical and chemical categories, see Table 2.

Table 2 - Possible Test Methods to be Used with Arrhenius Modeling in Polymer Degradation Predictions

Test Category	Test Property	Test Method or Device
"Physical"	density	immersion test
	hardness	hardness test
	glass transition	thermomechanical analysis (TMA)
"Mechanical"	strength	tensile, tear, impact, puncture tests
	elongation	tensile, tear, impact, puncture tests
	modulus	tensile, tear, impact, puncture tests
	creep	constant stress test
	stress relaxation	constant strain test
"Chemical"	loss/storage ratio ( $\tan \alpha$ )	dynamic mechanical analysis (DMA)
	crystallinity	differential scanning calorimetry (DSC)
	oxidative induction time	high pressure DSC
	oxygen absorption	oxygen absorption test
	carbonyl index	infrared spectroscopy (IR)
molecular weight	gel permeation chromatography (GPC)	

Details, along with some limited response values, are available in reference #8. It must be noted, however, that these test methods are generally conducted on the intact polymer materials. Thus, their focus is on the "end of functionality" stage. It is quite unknown which test would be used beyond this stage. If one method was singled out, however, it would probably be molecular weight (or molecular weight distribution) as determined by gel permeation chromatography (GPC). This method has the potential to track the degraded polymer down to its basic unit, recall Figure 1. Unfortunately, GPC is a very tedious, time-consuming, and expensive test to perform particularly on polyolefine polymers, i.e., polypropylene and polyethylene.

#### CONCLUSIONS

To assess polymer degradation as it relates to its performance, or functionality, lifetime is a difficult task. One needs to generate relatively sophisticated data from expensive and time consuming test methods. These tests should replicate the degradation processes which are occurring in the field as closely as possible. Thus incubation liquid, available oxygen, stress levels and other unique site-specific characteristics should be included in the procedure.

In order to accelerate the degradation, elevated temperatures are generally used for the incubation tests. By proper sequencing of the tests, one can use temperature-time superposition concepts to extrapolate the situation to a site specific (and lower) temperature. This is usually performed using an Arrhenius plot of inverse temperature versus inverse reaction rate and is essentially a curve fitting method. Even with all of this detail, the procedure is not without major assumptions. Perhaps the principal one is the assumption of the constancy of the activation energy. The value of " $E_{act}$ " must be reasonably linear throughout the test temperature range (which can be verified) and throughout the extrapolated temperature range (which, unfortunately, cannot be verified).

The additional challenge that this paper presents is to take this concept well beyond the functionality stage into the brittle, and then the soft, degradation stages (recall Table 1). To do so, the method of testing must reflect this advanced degree of degradation. This will require the use of method(s) which can assess chain scission and bond breaking of the molecular structure of the polymers. Probably the choice of test method would be gel permeation chromatography (GPC).

While we have degradation down (i.e., nonhazardous slow. This is due to hazardous leachate biological activity rates and eventually quite certain; that is on a site specific as warranted before a

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#### ACKNOWLEDG

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While we have no idea as to the time scale involved for "complete" polymer degradation down to the molecular level, it will quite possibly be very long. Under typical (i.e., nonhazardous) domestic waste leachate, for example, the reaction promises to be quite slow. This is due to the low chemical loading of domestic leachate versus, for example, hazardous leachate. Conversely, the relatively warm temperatures generated by anaerobic biological activity in a domestic landfill might be conducive to relatively rapid degradation rates and eventually to an accelerated form of biological degradation. One thing, however, is quite certain; that is, that each polymeric material will have its own "lifetime" and that will be on a site specific and very localized basis. Clearly, much research in this entire area is warranted before a clearer, more definitive, perspective can be offered.

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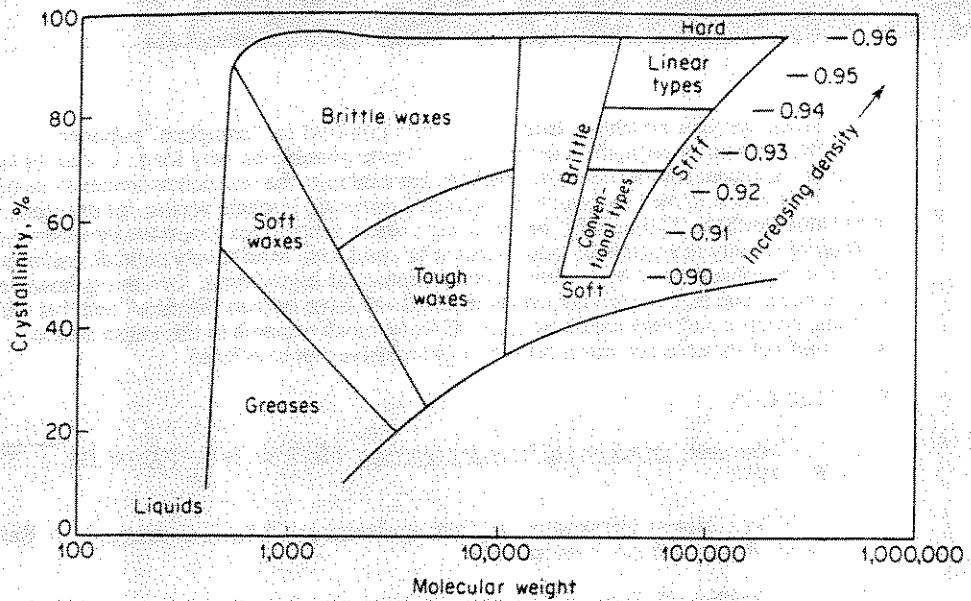


Figure 1 Relationship between crystallinity and molecular weight illustrating different stages of polyethylene materials, after Rodriguez<sup>(1)</sup>

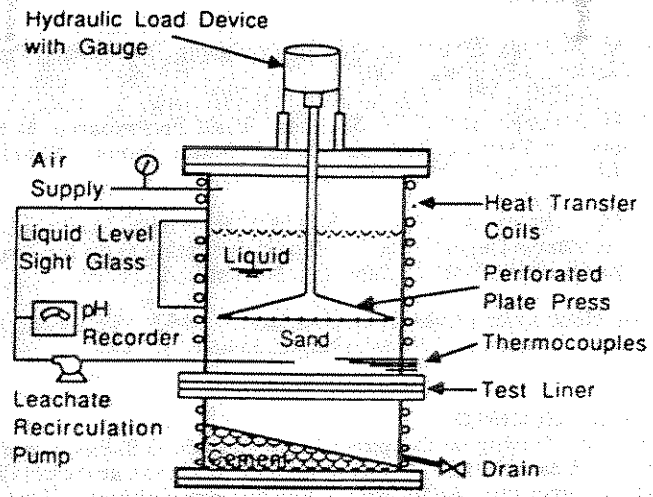


Figure 2 Schematic diagram of incubation device for accelerated aging of a polymeric liner material (after Mitchell and Spanner<sup>(7)</sup>)



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## ENVIRONMENTALLY RESPONSIBLE MINING: RESULTS AND THOUGHTS REGARDING A SURVEY OF NORTH AMERICAN METALLIC MINERAL MINES

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the Technology, the People, the Commitment***  
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## INTRODUCTION

A Precambrian volcanogenic massive sulfide mineral belt in northern Wisconsin has attracted the attention of mining and mineral exploration companies for over 25 years. To date, two commercially viable deposits have been discovered: the Flambeau deposit in Ladysmith, and the Crandon deposit in Crandon. Flambeau Mining Company, a subsidiary of Kennecott Corporation is in the final stages of mining the Flambeau copper and gold deposit. Crandon Mining Company (CMC), a partnership between Exxon Coal and Minerals Company and Rio Algom Mining Corp. is currently in the permitting process for the Crandon zinc and copper deposit.

For most of this 25 years, hard rock metallic mineral exploration and mining in Wisconsin have been the subject of intense debate. Public policy discussions about mining in Wisconsin have recently centered around proposed legislation that challenges the mining industry to prove sulfide mining can be done in an environmentally safe and responsible manner. The opponents to mining in Wisconsin allege that there are no environmentally safe sulfide mines in the U.S. or Canada, and point to environmental problems, especially acid rock drainage (ARD), at old hard rock mines in the western U.S. with the implication that mining today will create the same types of environmental problems. The sulfidic nature of these Wisconsin massive sulfide orebodies is one of the focal points of the current controversy over mining in Wisconsin. Mining opponents contend that mining and concentrating sulfidic rock and ultimate closure and reclamation of these operations cannot be done to control and contain acidification of sulfide-bearing materials and the resultant ARD.

This debate is not unique to Wisconsin. Across North America, mining industry detractors rely on outmoded images of mining of the past to foment public concern about mining and to justify their opposition to proposed mining projects and their support of anti-mining legislation. These public policy discussions about mining and the environment are taking place on the local, state, and federal levels.

## MINING INDUSTRY ENVIRONMENTAL SURVEY

In support of its planning and permitting process, and its position that the hard rock mining industry is attuned to environmentally aware operations and has the appropriate science and technology to predict, prevent, and control ARD and other environmental problems, CMC commissioned a comprehensive study to survey the industry. The objectives of this study were to determine the extent and degree of environmental awareness and sensitivity in mining and processing operations and to locate examples of environmentally responsible operations in a sulfide ore environment.

CMC retained the services of the authors to conduct this survey based on their experience, background, and qualifications. Mr. Todd has degrees in wildlife ecology and more than 23 years experience in environmental and regulatory affairs in the metallic mining industry. Ms. Struhsacker is a geologist with over 20 years of experience in the mining industry, 11 of which have dealt with environmental and regulatory issues. Both authors are well known within the industry and have travelled extensively to both active and closed mine sites throughout North America.

### Methodology

The survey was initiated in the Fall of 1995. Because of the large number of active, inactive, and closed operations, a phased approach was implemented. Hundreds of potential sites were screened initially to determine specifically which were operating within or had historically operated within a sulfide ore zone. Following this initial screening, contacts were established by telephone and fax with corporate and mine site environmental directors and managers, and with various state and federal regulatory agencies to discuss the scope of the study and determine which sites met the general criteria of operating within a sulfide zone. Over the course of several months, more than 150 telephone discussions with the companies, regulatory agencies, and organizations shown in Table 1 led to a narrowing of the field. As is

typical of these types of surveys, many individuals identified additional leads during their interviews. Some of these leads provided additional sites for review or people to contact. Although the survey was designed to be fairly comprehensive, it is not considered "all-inclusive". Indeed, it is likely that some operations meeting the criteria of operating in an environmentally responsible manner were overlooked. Additionally, the authors are fully aware that there are numerous examples of environmentally responsible operations that were not included in this survey for reasons of simple logistics and time constraints.

During the course of the telephone interviews, the initially proposed Wisconsin legislation (1995 Assembly Bill 758) pertaining to sulfide mining was discussed in order to determine whether there were any operations that categorically meet the criteria set forth in that proposal. Quickly, it became evident several *active* operations appeared to satisfy the operating criteria of 144.851 (2) (a), *to wit*, "...that a mining operation has operated in a sulfide ore body in the United States and Canada for at least 10 years without polluting groundwater or surface water from acid drainage at the tailings site or at the mine site of from release of heavy metals."

It also became readily apparent that examples of *formally reclaimed and closed* sulfide mining operations meeting the closure and reclamation criteria of 144.851 (2) (b) "...that a mining operation that operated in a sulfide ore body in the United States or Canada has been closed for at least 10 years without polluting groundwater or surface water from acid drainage at the tailings site or at the mine site or from the release of heavy metals." were difficult to find because of the arbitrary and inappropriate time frame criteria proposed in the bill. In restricting the analysis to mines that have been closed for at least 10 years, the bill eliminates from consideration many exemplary mines that used state-of-the-art technology and environmental controls but that have been closed and reclaimed for less than ten years.

It was also recognized at an initial point in the survey that there are abandoned mines in selected old mining districts throughout the country that meet both the operational and the closure criteria proposed in the legislation. One such district in southwestern Wisconsin is described in this paper. However, it was decided that the survey should evaluate environmental practices at modern mines and identify active, reclaimed, closed, and partially closed mines that employ sound, proactive, and contemporary environmental management practices, rather than conducting an intensive survey of old, abandoned mines. In this manner, the survey focused on identifying environmentally responsible mines that have been developed under the current environmental regulatory framework and that have used modern pollution prevention and environmental protection technology.

The ensuing investigation process identified more than two dozen active and closed operations throughout North America that merited site visits. Subsequently, based on additional telephone investigations, logistics, and weather-related constraints, 14 mines were visited during the Fall of 1996. Because of logistics and weather considerations, visits were limited to the contiguous 48 states, although several sites in Canada were identified which are worthy of a visit.

Mine site visits included inspections of operations presently active, in temporary closure, and permanently closed. Generally, visits consisted of three parts: 1) introductory discussions with site personnel explaining the purpose and objectives of the visit; 2) tour and inspection of the site and facilities of interest; 3) follow-up discussions and, sometimes, file and document reviews in the site office; and 4) discussions with regulators and community leaders at selected sites. These tours were documented by photos and videos taken at will.

Although not unexpected, the responses from both telephone interviewees and personnel at the sites visited consistently impressed the authors. The metallic mining industry in both the United States and Canada has been extraordinarily open, positive, and responsive concerning this survey.

The situation regarding mining industry-specific restrictive legislation in the State of Wisconsin has captured the attention of the entire industry.

## Results and Discussion

The survey resulted in several definitive findings of fact:

- 1) Today's mines are highly regulated and make extensive use of pollution prevention and environmental protection technology. In contrast, old mines were largely unregulated, and operated with few if any measures to protect the environment. Therefore, it is inappropriate to use environmental problems at antiquated mine sites to predict what will occur in the future at modern mines;
- 2) Environmentally responsible operations are evident at every active mining operation explored by this survey;
- 3) There are examples of currently active sulfide mines that have been in operation for more than 10 years and have not caused surface or groundwater pollution;
- 4) There are at least several successfully closed and reclaimed mines that meet the operating criterion but do not yet meet the closure criterion. Thorough environmental monitoring at these sites indicates they are complying with all environmental protection standards and there is every expectation that they will continue to be in compliance at year ten and beyond following closure;
- 5) There are a number of old lead-zinc sulfide mines in southwestern Wisconsin that operated for more than 10 years, were either closed or abandoned more than 10 years ago, and have caused no known surface water or groundwater pollution problems. These sites meet both the operating and the closure criteria in the proposed legislation; and
- 6) Operations that mined sulfide ore for more than 10 years, were formally reclaimed, have

been closed for more than 10 years, and have not caused surface or groundwater pollution are difficult to locate due to the arbitrary time criteria established in the proposed legislation. A more meaningful measure of compliance with all applicable environmental protection standards would evaluate operating and closed sites that are subject to rigorous and regular monitoring, reporting, and inspection requirements.

The remainder of this paper discusses the survey findings in more detail.

### The Abandoned Mine Problem

Mining opponents often contend that the ARD problems at some old and abandoned mines are representative of what will occur at modern operations and newly proposed mines. Their premise is that mining today will create problems similar to mining of the past. This contention is without merit because modern mining operations are highly regulated at the federal, state, and local levels. Today, even operations proposing to mine oxide materials are required to conduct extensive waste characterization tests to determine the potential for generation of ARD. If the potential for ARD exists, waste management plans must be developed to prevent, minimize and control acid generation before construction can proceed. *Modern mines are designed for closure* to avoid, minimize, and mitigate potential long-term environmental concerns.

In contrast, unregulated mines of the past typically disposed of mine wastes without any environmental controls or constraints. Prior to the advent of current environmental laws and regulations, mine waste disposal sites were located for operational convenience rather than environmental concern. Mine wastes were deposited adjacent to the mines or directly down-gradient in the nearest valley much as domestic wastes of the time were sent to the nearest moving water body. Gravity was considered the great equalizer -- the miners' and other industrial waste generators' best friend. Once the commercial ore was depleted, operators commonly abandoned sites with little, if any,

thought to reclamation. In many settings, these old mine wastes remain vulnerable to wind and water erosion and, with the right geochemistry, the generation of ARD. The effective manner in which anti-mining activists use environmental issues at historic mines to create public concern about mining points to the importance of developing an industry program to help solve the abandoned mine problem.

### **Changes in the Regulatory Framework for Mines**

In evaluating the environmental track record of the modern mining industry, it is essential to consider the enormous difference in the environmental regulatory climate that has developed in the last 20 years compared to the regulatory requirements for mines that operated prior to the late 1970s. Starting in about 1970, environmental laws and regulations to protect environmental resources such as groundwater, surface water, air quality, wildlife, and cultural and historic features were developed on both the federal and state levels. Just like any other industry, mines must comply with these regulations.

Table 2 shows the dates of enactment of some of the federal and state environmental laws and regulations affecting mining, and the approximate dates at which significant mining activities began at some major U.S. mining districts. It is evident from Table 2 that mining at many metallic mining districts throughout the country began well before the advent of environmental laws and regulations. Nearly all of the environmental laws and regulations affecting metallic mining were enacted since about 1970, with many significant state and federal environmental regulations being developed within the last decade. In contrast, mining at a number of important U.S. mining districts commenced more than a century before the enactment of the environmental laws listed in Table 2. It should be noted that the examples of environmentally responsible mines discussed below were developed concurrent with or after the establishment of the environmental laws and regulations shown in Table 2.

Metallic mining under the modern, stringent, environmentally sensitive regulatory climate prevalent at the state and federal levels is a completely different enterprise than 100 years ago...or even 20 years ago. State and federal regulators take their jobs very seriously and perform them in a very responsible manner. In the authors' combined years of experience, they have never encountered a regulator who desired to have an environmentally problematic mine on his or her watch. Likewise, although unintended incidents and accidents do occur, as in any facet of life, there are no mine or mill managers or mining companies who wish to be tagged as environmentally irresponsible. Mine operators at sites at which environmental problems develop have undertaken aggressive and responsive environmental remediation measures. The results of this survey support these conclusions. By definition, modern mining is, and will remain, environmentally responsible.

### **Environmentally Responsible Mining Operations: The Norm**

It is important to emphasize that the sulfide mining operations singled out for discussion in this paper in no way detract from the environmentally responsible operations of the dozens of other metallic mining operations reviewed and, in some cases, visited during this survey. In many instances, the mines not specifically described in this paper display even higher levels of environmental awareness and proaction than those discussed. The vast majority of these mines have been in operation between five and ten years. During their operating periods, many have not exceeded any environmental standards and have maintained sparkling compliance records. Some, while excellent examples of environmentally sensitive operations, have had unexpected, and mostly minor, system upsets causing short-term exceedences of standards for which they were issued regulatory notices. This situation is not atypical for all industries, municipalities, and indeed, even U.S. natural resource regulatory agencies. Without exception, the operators at these sites responded aggressively and effectively to correct the noted problems. In most of these cases,

the identified issues created regulatory compliance problems (i.e., an arbitrary standard may have been exceeded) but did not result in significant impairment of environmental resources (e.g. wildlife, air, soil, water, etc.) or jeopardy to public health and safety.

Every active operation, modern and historic, has some positive environmental story to tell; some large and showy, others more understated. This statement is not to be misconstrued as a rosy-hued Pollyanna-type declaration. Environmental problems and issues do, indeed, exist at some mines, particularly older operations, where initial planning and facility designs (generally pre-1975) were significantly less sensitive (or "insensitive" in some cases) to environmental concerns than in later years. However, even those operations with significant problems are presently working toward either permanent resolution or control and maintenance of those problems in a manner consistent with today's standards. Modern mining statutes and regulations at the state and federal levels, modern business practices, and criteria established by the international financial community require no less.

The most prominent general examples of positive environmental stories observed or documented during this survey and during the careers of the authors include the following areas in which many mining operations have gone the extra step beyond regulatory requirements. Again, the authors do not imply that the following examples are by any means all inclusive.

- *Improvement of water quality.* In some cases, new mines have been permitted within old mining districts that are the loci of poor quality water discharging from historic workings, waste rock piles, or tailing impoundments. Similarly, there are some older mines still in operation. Where this scenario occurs, it is typical for the active operation to either remediate the contaminated drainages outright, or, at some sites, to divert contaminated drainages into the active process water return and treatment system. The end result in several instances is a radical improvement in

downstream water quality over historic levels, including rehabilitation of public sport fisheries and increased viability of threatened or endangered species habitats.

- *Wildlife Protection and Habitat Enhancement.* Probably the most ubiquitous example of environmental responsibility by mining operations is in the area of terrestrial and aquatic wildlife resources. Granted, some form of wildlife protection or mitigation plan is required for today's mines. Many operations go well beyond the scope of these requirements to implement resource protection and habitat improvement programs. Even many of those older and, in some cases historic, operations maintain or sponsor ongoing wildlife projects. As is typical of any human population group employed in the natural resource fields, most employees in the metallic mining industry are oriented toward outdoor activities, not the least of which are hunting, fishing, camping, and wildlife observation and photography. Thus, many operations can exhibit examples of wildlife protection and habitat enhancement programs including projects to save threatened amphibians, to reintroduce peregrine falcons (an endangered species), to improve in-stream fisheries habitat, and large mammal telemetry projects. Indeed, the results of this survey revealed that most mine site reclamation plans are geared toward wildlife habitat restoration, creation, or enhancement as the primary beneficial post-mining land use.
- *Wetlands.* Development, enhancement, or restoration of wetlands is a commonly required mitigation for modern mining in settings where operations will disturb or otherwise impact existing wetland areas. Wetlands mitigation is common in today's mine permitting world. However, there are a number of examples of both historic and newer active operations where the extra step has been taken to create or enhance wetlands. Mine operators are learning the multiple benefits that natural and created wetlands have for active and inactive operations. These

benefits include passive aerobic and anaerobic water treatment, sediment control and water clarification, control of stormwater run-off and run-on, aesthetic appeal, and valuable wildlife habitat.

- *Reclamation.* Post-mining reclamation of disturbances on federal, state, and private lands is a requirement in all states and in most foreign countries. Those states with active metallic mining operations, without exception, have promulgated stringent, specific, and detailed rules and regulations concerning mined land reclamation over the past 20 years. Therefore, the issue of environmentally responsible mining is not whether a mine site will be reclaimed, but rather, the manner in which reclamation is accomplished. In its most basic form, mined land reclamation is a "green is good" proposition; stabilize it and grow grass. While some operations continue to subscribe to this "one size fits all" format, a number of others have expanded upon their reclamation requirements and have made virtual showcases of their sites even while still operating by taking extra measures to blend the site into the surrounding landscape and to create aesthetically pleasing and productive post-mining land uses. As with other environmental components at mine sites, high quality, responsible reclamation simply makes good business sense. A number of operators believe that if they go beyond the letter of the law in their reclamation practices, these efforts will enhance their working relationship with the regulatory community and the public at large. Many times this is an accurate presumption as "reputation" literally can mean the difference in millions of dollars and years of time in today's metallic mineral permitting environment.
- *Cultural Resources.* The National Historic Preservation Act and various state laws require assessment and protection of significant archaeological and historic resources located on federal and state lands. In assessing, protecting, and mitigating necessary disturbances to these resources, a number of

active operations have taken the extra step to preserve interesting and significant sites located on private and patented lands under their control. In a number of instances, mining interests have worked with state and federal regulatory agencies to join in protective covenants and to erect interpretive signs and centers for public use. This sensitivity to historic interests is particularly evident where newer operations have been developed within historic mining districts. Historic mining artifacts and their history are as much an interest to operators of modern mines as they are to the general public.

- *Community Relations.* Every active operation has some form of community relations programs that go well beyond any regulatory or legal requirements. Mining managers and employees live in the communities most affected by their operations; they are active members of those communities. As such, it is in the best interests of their companies, their families, and their employees' families to establish, promote, and maintain the mutual respect that is the foundation of good relations. Without exception, all active operations investigated during this survey worked closely with and contributed to the local communities and counties in which they reside. Programs included financial assistance with community infrastructure such as roads, schools, police and fire departments, as well as contributions to hospitals, health clinics, and local and national conservation organizations. In at least one instance, heavy equipment and operators from an active, older mine were virtually on call by the nearby communities when assistance was needed for even minor emergencies. The survey also found that most active operations conduct business in the spirit of open planning, and consult with community leaders and citizens when expansions or changes to operating scenarios occurred. The majority of active operations give public and educational tours of their operations - some on virtually no notice. In addition to conducting formal tours, several operations offer self-guided "tours" from nearby vantage points.

### Operations Active for More than 10 Years

The survey located six active metallic mining and milling operations that: 1) mine and mill sulfide ores; 2) have been in continuous operation for periods ranging from 10 to 83 years; and 3) have received no regulatory notices or orders for releasing ARD or metals to surface or groundwaters. Several of these mines are described at the end of this paper.

These active operations are located in either sensitive, high quality resource areas (scenic, fish and wildlife, etc.) or within heavily used recreational areas or both. These mine sites, located in California, Colorado, Montana, Missouri, and New York, have the following elements in common:

- Each has an active and dedicated professional environmental staff at the site. These personnel maintain integrated working communications with and support from both the mine managers and the corporate environmental directors and managers;
- All have excellent relations with surrounding communities; each maintaining an open planning policy with the public;
- All display examples of superior reclamation practices, fish and wildlife habitat preservation and enhancement programs, wetlands protection and enhancement, or other environmentally oriented programs. Typically, these programs go beyond the letter of regulatory requirements;
- Each displays a solid qualitative and quantitative understanding of the environment in which it operates, the ecological relationships within that environment, and the potential impacts of operations on the components of that environment; and
- As with all active mining operations, each is strictly regulated by local government, state agencies and, depending upon location and land ownership, the federal government.

Of these six active sites, three have been operating continuously for more than 20 years, and two of those truly can be considered "historic." In the latter two cases, the present operations have upgraded their facilities and operations as modern times have dictated to maintain compliance with increasingly more stringent environmental rules and regulations. Where past practices, acceptable at those times, caused environmental impacts, these operations have expended considerable effort and resources to remediate those impacts.

### Operations Inactive for More than 10 Years

The arbitrary time criteria in the proposed legislation are not a meaningful yardstick with which to measure the environmental performance of today's mining industry. In assessing the environmental track record of the modern mining industry, considerable weight should be placed upon the large number of currently operating environmentally responsible mines, some of which are more than 10 years old, and the number of successfully reclaimed sites even though they do not meet the 10 year closure criterion.

There should be no doubt that active mine sites prove that environmentally responsible mining is occurring throughout the country. The regular basis with which mining environmental professionals, regulators, and in some cases, citizens monitor and inspect active mine sites provides real time, concrete evidence of their environmental performance. The fact that these sites have not yet been reclaimed for 10 years is irrelevant.

Similarly, mines that have been successfully reclaimed for fewer than 10 years cannot be dismissed as compelling evidence of the mining industry's ability to operate in an environmentally responsible manner. Many of these reclaimed sites are still in a post-closure monitoring and maintenance status that requires mine operators to monitor the sites and provide regular monitoring and compliance reports to state and/or federal regulatory agencies. Additionally, regulatory authorities are required to inspect these sites on a

regular basis. Sites reclaimed within the last 10 years are thus the subject of considerable environmental monitoring and regulatory scrutiny to detect any potential environmental problems. Therefore, the 10 year closure criterion proposed in the bill is an arbitrary and meaningless measurement that does not provide regulators or citizens with useful information. The ongoing monitoring and scrutiny at recently closed sites provides substantive documentation of the environmental performance at these sites.

### EXAMPLES OF ENVIRONMENTALLY RESPONSIBLE MINES

This survey documents that environmentally responsible mining is taking place at numerous mines throughout the country. Every site evaluated by this survey is an example of an environmentally responsible operation. A few such sites are described below. The mines discussed in the following paragraphs by no means form an all inclusive list. These sites were selected for discussion to represent a range of commodities produced, mining and mineral processing techniques used, and geographic settings. Several of the mines described below, like many of the sites researched in this survey are located in scenic areas - some in high altitude, steep, mountainous terrain with severe climate conditions. The many environmentally responsible mines operating successfully in these scenic and environmentally sensitive settings prove that sulfide mining can be done in an environmentally responsible manner - especially in light of today's stringent mining regulations. These regulations require state-of-the-art engineering design, pollution prevention technology, monitoring, and financial guarantees to ensure that mines are built, operated, and reclaimed to the highest environmental standards.

A few examples of environmentally responsible sulfide mines include the following:

The Henderson Mine and Mill - this molybdenum sulfide mine and mill have maintained a spotless environmental compliance record since 1976 when mining and milling operations commenced. Located less than a 2-hour drive west of Denver,

Colorado at an elevation of 10,346 ft in the spectacular mountain scenery of the Colorado Front Range; the areas immediately around the mine and mill serve as Denver's backyard and receive intensive year-round recreational use. Denver residents regularly use areas adjacent to the mine and mill sites for fishing, camping, picnicking, hunting, hiking, skiing, and snowmobiling. Treated wastewater from the operation supports a thriving population of Boreal toads, a species that the U.S. Fish and Wildlife Service is considering listing as threatened and endangered. Streams downstream from both the mine and mill facilities are excellent brown and brook trout fisheries. Both the mine and the mill are located in Denver's watershed, and two reservoirs associated with the nearby reclaimed Urad Mine are used as municipal reservoirs for the city of Golden, Colorado.

The Viburnum Mine No. 27 - developed in geology similar to that found in southwestern Wisconsin's lead-zinc mining district, the water from this lead-zinc sulfide mine, which operated from 1960 to 1978, is so clean it has served as the primary domestic water source for the town of Viburnum, Missouri since 1981.

The McLaughlin Mine - straddling three counties about 70 miles north of San Francisco in the rugged mountainous terrain of California's Coast Range, this gold mine is acknowledged by regulators, environmentalists, and the mining industry to be a model of effective environmental practice. Proactive mine planning and permitting processes, pollution prevention features, and reclamation and habitat management programs are just some of the mine's successful environmental efforts that have been adapted for use at other mine sites. Comprehensive environmental monitoring of the McLaughlin Mine confirms the ecological effectiveness of these practices. This monitoring demonstrates that since its development in 1985, the mine has operated without environmental harm, and has not only protected but actually enhanced the quality of both on-site and downstream habitats and improved downstream water quality. Using ecology-based habitat management planning, resource values of the