Accelerated aging tests for geomembranes used in landfills

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ACCELERATED AGING TESTS FOR GEOMEMBRANES USED IN LANDFILLS

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SUMMARY :This paper presents an accelerated aging test for geomembranes which combine the different aging conditions in a landfill (chemical, mechanical and temperature). Results of physico-chemical analyses and mechanical tests conducted on aged high density polyethylene geomembrane are presented. Stress cracking and plasticizing were observed for immersion times less than 4 months.

1. INTRODUCTION

Nowadays, the use of geomembranes in landfill lining systems or in final covers can be considered as state-of-the-art in many countries. Despite the wide use of FMLs, the ubiquitous question of the service life of geomembranes in landfills is still largely unanswered.

An extensive bibliography exists on the compatibility of polymers with various chemicals. Tests conducted on this issue, mainly consist in immersing polymer samples in pure or dilute chemicals for relatively short periods and then in testing their modified characteristics. Fewer are the references concerning ageing processes affecting geomembranes, which are complex mixtures of polymers and additives. Eventually, there is a relative lack of literature on the particular issue of the long-term behaviour of geomembranes immersed in landfill leachates.

Literature surveys by Haxo (1989) and by Tisinger et al. (1991) conclude that all solid waste landfill leachates are extremely complex aqueous solutions in which potentially geomembrane-active constituents are generally present at very low concentrations. The authors underline that long-term service life of a particular geomembrane designed to be immersed in landfill leachate cannot be derived from general data on the compatibility of the material with selected chemicals, but rather has to be deduced from immersion tests in simulation aqueous solutions, or whenever possible in actual leachates.

Duquennoi et al. (1995) showed on a large array of geomembranes that immersion tests in actual leachates in laboratory conditions have to be conducted over very large periods (several years) in order to trigger aging mechanisms and analyse them. This very slow evolution of geomembrane characteristics observed in the lab has somewhat confirmed field observations by Rollin et al. (1991), Düllmann and Eisele (1993) and Fayoux et al. (1993) on HDPE and PVC geomembranes.

Practically, a durability test should not take more than several weeks. Otherwise, it would be rejected both by the geomembrane manufacturers, by the landfill operators and by the administration. It is therefore necessary to develop tests in which aging mechanisms are similar to those occurring in landfill conditions, but in an accelerated way.

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The goal of the study presented herein is to accelerate the aging of geomembranes by the means of artificial conditions. The research program involved four French laboratories : CEMAGREF (Institut de Recherche pour l'Ingénierie de l'Agriculture et de l'Environnement), INERIS (Institut National de l'Environnement et des Risques Industriels), IRIGM (Institut de Recherche Interdisciplinaire en Géologie et Mécanique, Grenoble University) and CETE (Centre d'Etude Technique de l'Equipement), under financial support from ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie).

2. AGING IN LANDFILL LEACHATES

2.1. Geomembrane aging conditions in a landfill

Solicitations to which a geomembrane may be exposed in a landfill vary with time (installation phase, waste operation phase, after-closing phase) and with location of the membrane in the landfill (bottom, slopes, cover). Most of the physical, chemical and biological solicitations a geomembrane may encounter in a landfill are presented in table 1:

solicitation	bottom	slopes	cover
Puncturing by drainage layer gravels (during installation and under static waste load)	X		
Puncturing by tools during installation	X	X	X
Tensile strain if settlement of the supporting soil	X		
Traffic during installation and waste disposal	X		
Light and climate exposure before covering	X	X	X
Immersion in leachate	X	X	
Heat produced by waste degradation	X	X	
Micro-organisms	X	X	X
Rodents	X	X	X
Permanent stress at seams and singular point	X	X	X
Puncturing by static concrete structure loads	X		
Puncturing by waste		X	
Tensile stress		X	
Contact with landfill gas or oxygen			X
Tensile strain if settlement of the waste			X
Roots			X

Table 1: solicitations in a landfill

2.2. Observed aging mechanisms

2.2.1 Solvent absorption

Many types of solvents are present in landfill leachates, the most available of them being of course water. Organic solvents are also present in leachates and may have large affinities with geomembrane materials.

Solvent absorption leads to two types of modification of the polymer properties: swelling and plasticizing.

Swelling is not considered as a geomembrane degradation proper. A large array of macromolecular solids are able to withstand swelling of their amorphous regions without exhibiting changes in their physical or mechanical properties (Koerner 1990). However, swelling enhances molecular mobility and is sometimes the first step towards severe chemical degradations.

Absorbed solvents may also plasticize the geomembrane. At the molecular level, plasticizing mainly consists in solvent molecules enhancing molecular mobility. The macroscopic impact of plasticizing concerns mechanical properties : both yield point and modulus of elasticity are lowered when plasticizing occurs. Such effects have been observed on HDPE and PVC-P geomembranes immersed in solvents like water, toluene, acetone and chloroform (Ferrand, 1995). A decrease in the elasticity modulus was also observed on PVC-P geomembranes immersed in actual leachates (Duquennoi et al. 1995) when tested in the humid state. Another effect of solvent plasticizing is the lowering of the glass transition temperature (Verdu).

It has to be underlined that solvent swelling and plasticizing are reversible physical phenomena.

2.2.2 Loss of additives

Geomembranes are always constituted of a base macromolecular (polymeric or bituminous) phase mixed with additives which function is to enhance performances of the base constituent, during the manufacturing process, or during the service life. Additives may be plasticizers, stabilisers, anti-UV, antioxidants, etc.

Under given conditions, and particularly when the geomembranes are immersed in solvents or in aqueous solutions like landfill leachates, additives may be partially or totally extracted, or chemically modified inside the geomembrane.

Consequences of loss of additives depend on the functional properties of the geomembrane enhanced by the additives. For example, extraction of plasticizers from a PVC-P geomembrane causes its elasticity modulus to increase and its elongation at break to be lowered, which means that the geomembrane is not only rigidified but also fragilized. This phenomenon has been observed in the case of PVC-P geomembranes immersed in actual leachates in the laboratory (Duquennoi et al. 1995) as well as on PVC-P geomembrane samples from water and landfill leachate storage ponds (Bernhard et al. 1995, Fayoux et al. 1993).

A loss of antioxidants, as observed in the case of a HDPE geomembrane immersed in actual leachates (Duquennoi et al. 1995), may favour oxidation phenomena under given conditions.

The principal factors affecting the loss of additives are the extraction conditions at the geomembrane surface, the diffusivity of the additives in the base constituent.The swelling of the membrane which enhances molecular mobility, and temperature which elevation favours additive migration.

The loss of additives is always non-reversible.

2.2.3 Chemical modifications of the base constituent

Among all polymer chemical aging mechanisms, oxidation is probably the most quoted in literature. It occurs more frequently in the emerged parts of a geomembrane lining structure or in final covers (reaction between the air and the polymer). The probability of oxidation reactions taking place in geomembranes at the bottom of landfill cells is much reduced, for oxidation reactions underwater occur in a much slower manner (Verdu).

Polymer chain scission is a chemical aging mechanism which may occur in the presence of absorbed water (hydrolysis) or chemicals (alcoolisis, etc.), in given chemical and temperature conditions. Example: the alcaline hydrolysis of polyester geotextiles. Nevertheless, chain scission has never been observed on geomembrane polymers in landfill conditions or similar conditions.

In reticulation reactions, additional bonds between neighbouring polymer chains are created.

The effects of reticulation are an increase in elongation and stress at break (Verdu[b]). Chain scission and reticulation are generally in competition.

All chemical modifications of the base constituent may be triggered by temperature (thermochemical aging), light (photochemical aging), radioactivity (radiochemical aging) or by the sole presence of chemicals like hydrocarbons. Chemical modifications of the base constituent are always non-reversible.

2.2.4 Stress cracking (Lord and Koerner, 1991)

Semi-cristalline polymers in the visco-elastic state, can develop two types of break:

- Ductile break obtained with a stress large enough to produce a fast yield point. Interlamellar chain tension produces intra-cristallite break.
- Brittle break obtained with a smaller stress. Break occurs in the amorphous zone (inter-cristallite break).

This phenomenon is very interesting because the two conditions to induce stress cracking are present in situ (mechanical stress and chemical agents(tensio-actif) and correspond to usual situation in landfill.

3. ACCELERATED AGING

Aging is defined as a very slow and non-reversible evolution of a functional property of the material (Verdu, 1984). Besides natural aging evolution, it seems interesting to accelerate aging without modifying natural aging process.

3.1 Goal of the study

The goal of the study is to artificially accelerate the aging of geomembrane to allow a fast and practical determination of the durability of geomembranes in contact with landfill leachates. Our final goal (not presented in this paper) will be to find accelerate factors between landfill and artificial aging by characterising mechanisms of aging.

It should be underlined that comparisons between geomembrane types in terms of durability and performance is totally out of the scope of the present work. It only aims at preparing a research-based methodology for durability determination.

This aging study concerns only High Density Poly-Ethylene (HDPE) membranes. Others material types of geomembrane will be studied later. Seamed geomembranes have also been tested for seamed area often more sensible to stresses.

Tested properties are thought to be representatively related to the barrier function of the geomembrane. The main stresses affecting the geomembrane properties are mechanical, chemical and biological. The original concept of our study is to combine mechanical and chemical stresses observed in natural aging conditions. In our experiments, aging conditions are temperature, immersion medium and mechanical stress. All the experiments tests and analyses presented in the next sections were conducted at the INERIS.

3.2 Analyses

It has to be underlined that aging depends on numerous parameters: some parameters can be isolated and others are interacting. Mechanical tests will be used to observe modifications of the mechanical properties and in parallel, physico-chemical analyses used to explain this modification

(Surmann, 1995). The final goal is to correlate analytical aspects and evolution of functional properties changes.

Combining experimental results on HDPE polymer with bibliographical analysis, unaged reference samples and aged samples are tested using the following methods:

ı Mass variation measurements: the mass change is measured after immersion, and after 48 hours drying at 60°C. This drying process is used to extract all the solvents absorbed by the geomembrane.

ı Density: It is measured by comparing the weight of the sample and the weight of water occupying the same volume as the sample.

- **Physico-chemical analyses**

ı *MFI*: Melting Flow Index. A given amount of polymer is heated in a furnace until it melts. A constant load pushes it through an orifice and in the bottom of the test device. The MFI value is the weight of extruded material in grams for a 10 minutes duration. Higher is the value of MFI, lower is the molecular weight of the polymer (Koerner, 1990).

ı *DSC*: Differential Scanning Calorimetry. With DSC, temperature of fusion and cristallinity can be determined.

ı *TG*: thermogravimetry. The weight of geomembrane samples is measured with temperature increases. With TG, we can determine the mass of residue at a given temperature and the loss of additives.

ı *OIT*: oxidative induction time. In isothermal conditions , OIT measurements gives the time when oxidation appears and specific loss of antioxidants can be deduced.

ı *IR*: infrared spectroscopy. Each material has a characteristic infrared spectrum. Through the determination of functional groups, this method leads to the determination of solvent absorption and loss of additives.

ı *GPC*: Gel Permeation Chromatography gives the molecular weight distribution. Chain scission can be detected through comparising curves before and after aging.

- **Mechanical tests:**

ı *Tensile test:* NF 84-501 (French norm). Most important tensile properties determined with tensile test are secant modulus, elongation and stress at yield point and break.

ı *Shear test:* NF 84-502 (French norm). Tensile test on seamed samples.

ı *Peel test:* NF 84-502 (French norm). Test of the quality of the seam, as showed in figure 1.

ı *Relaxation:* Measures the stress required for a constant deformation. We also measure resilience, i.e. the residual deformation after the mechanical stress is back to zero.

ı *Stress cracking :* Two conditions are necessary to develop stress cracking.

Mechanical stress: Stress cracking tests are conducted at stress levels between 35 and 60% of the stress at yield point.
Immersion medium: we compare results obtained with SIM and with water + 10% Igepal (tensio-actif).
Cracks are initiated by a notch (depth 0,2* sheet thickness) perpendicular to the uniaxial stress direction. Figure 2 presents this test.

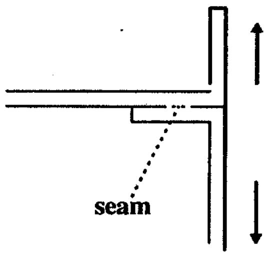

Figure 1: Peel test

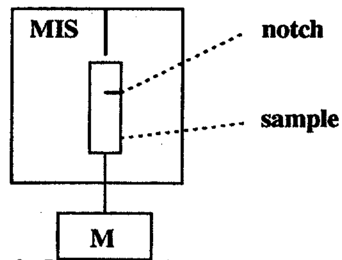

Figure 2: Stress cracking test

3.3 Study

Chemical, thermal and mechanical aging conditions have been selected on the base of literature and pre-study data. It is very difficult to elaborate a typical leachate composition because leachate composition varies enormously with sites and with time. A synthetic immersion medium (SIM) has to be designed in order to trigger aging mechanisms similar to those observed in unaccelerated conditions (ADEME, 1994). The SIM (table 2) is an aqueous solution of selected active chemicals and should not be considered as a synthetic leachate : it does not reproduce a typical leachate composition, but is rather a collection of aging-triggering agents. SIM is defined to age the geomembranes without modifying aging mechanisms.

Each solvent of the SIM represents a family of solvents, known to be interacting with geomembrane; concentrations in SIM are 10 to 3000 times higher than concentrations in the most aggressive landfill leachates.

pH		2
tensio actif	igepal Co 720	10 g/l
aliphatic chlorinated hydrocarbons	perchlorethylene	0.1 g/l
aliphatic hydrocarbons	heptane	0.1 g/l
aromatic hydrocarbons	xylene	0.1 g/l
phenol	phenol	3 g/l
cetone	cyclohexanone	30 g/l

Table1: Initial* SIM composition

Mechanical and physico-chemical analyses were conducted on unaged and aged samples in order to quantify aging in terms of evolution of key macroscopical material characteristics, and to identify the corresponding physical and chemical aging mechanisms.

Aging tests were conducted on seamed geomembranes as well as on unseamed material.

*It has been observed that the initial SIM composition changed with time (measured by mass spectroscopy). Solvent evaporation can never be completely avoided; it has to be considered as one of the experimental condition

Samples are immersed in the SIM at 60°C and under 5% tensile strain. They are regularly taken out from the tanks (every 2 months with a maximum immersion time of 8 months). Samples are then weighted (before and after drying at 60°C during 48 hours) and tested using the above described methods.

3.4 Results

. *Mass variation measurement*: The absorption appears very quickly and is reversible.

. *Density:* No change is observed.

- ***Physico-chemical analyses:***

. *DSC and TG:* We notice no significant variation. For DSC analyses, variations between aged and unaged samples are less than 3°C, which is the occuracy of the measure.

. *IR:* No significant spectral variation is observed. for the geomembranes which were immerged 8 months in SIM at 60°C, compared to the reference sample (non immerged).

. *OIT:* We can notice a significant decrease of the induction time corresponding to a loss of antioxidants (figure 3)

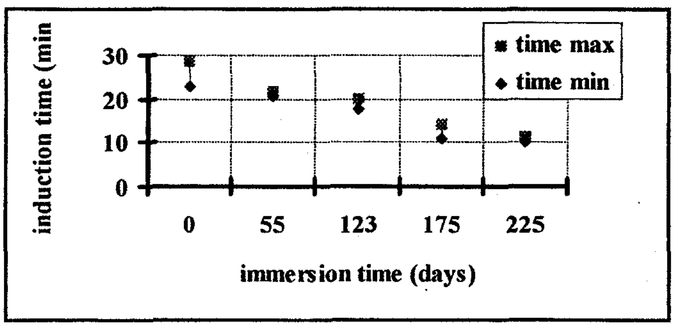

Figure 3: Oxidation induction time (T=200°C)

- ***Mechanical results:***

. *shear test*: We also notice a plasticizing presented in figures 4 and 5.

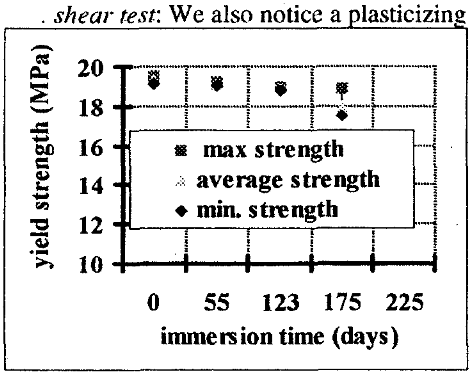

Figure 4 : Variation of strength at yield vs. time for seamed HDPE samples

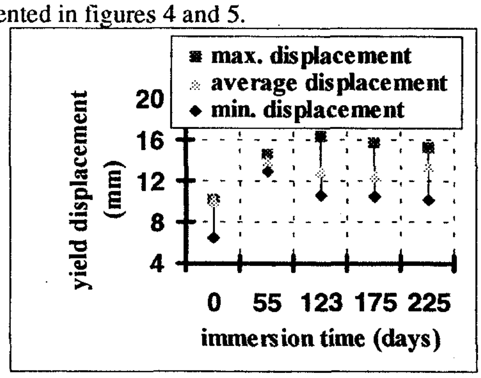

Figure 5 : Variation of deformation at yield vs. time for seamed HDPE samples

. *tensile test:* Values of secant modulus of elasticity decrease. The stress and deformation at yield also decrease: material is plasticized and becomes softer. The plasticizing appears not before 4 months.

. *peel test:* no significant variation is noticed. This test is generally used as a performance test (Lempereur, 1983).

. *relaxation:* (figure 6) a residual internal stress is observed during aging under constant strain. This residual stress is higher in unaged samples than in aged samples at the same imposed strain. This phenomenon may be attributed to the plasticizing of aged samples.

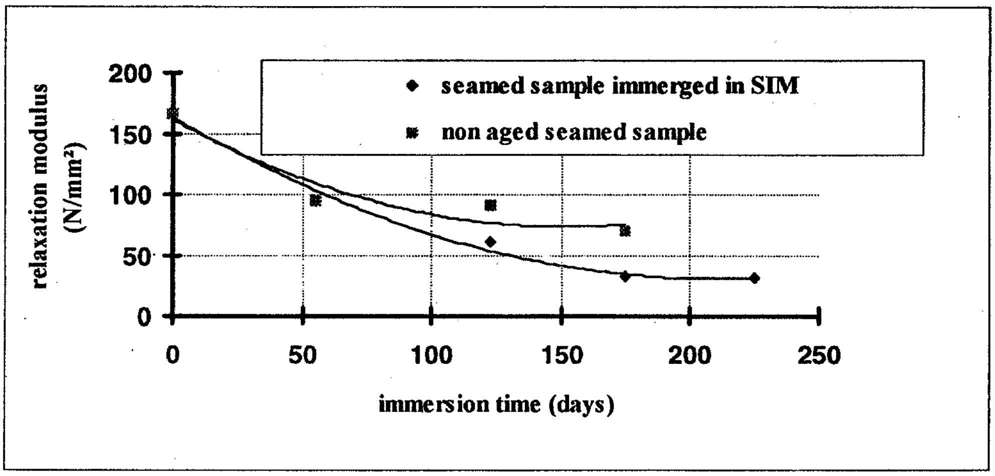

Figure 4: relaxation modulus (MPa) vs. time

. *stress cracking:* Figure 6 shows the time until break of samples submitted to different stress level. The first results show the transition from brittle break to ductile break (40% stress at yield) and confirms the sensibility of semi cristallin polymer to stress cracking, as said in 2.2.4. Photos 1 and 2 (next page) present the two types of break: ductile break (photo 1) and brittle break (photo 2).

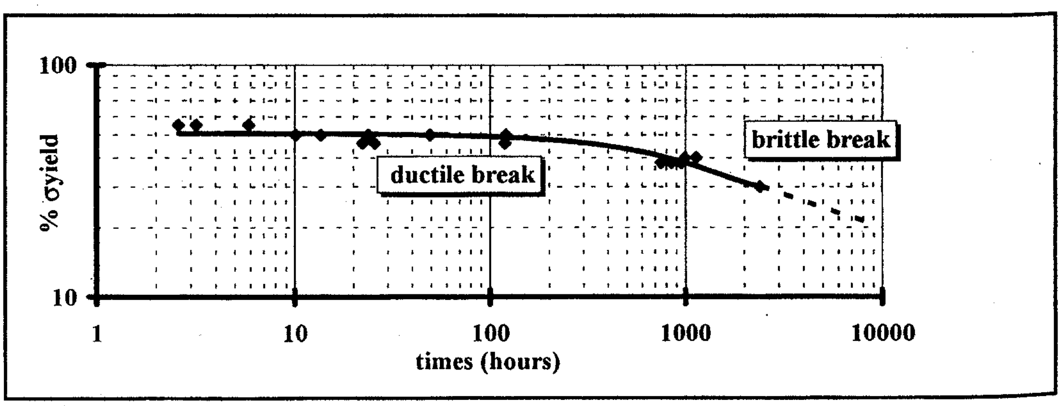

Figure 5: Stress cracking

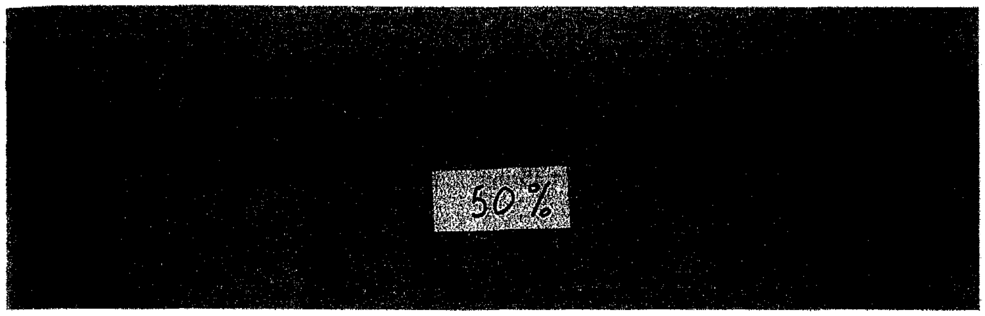

Figure 6. Ductile break for a sample submitted at a stress equivalent to 50% of the stress at yield

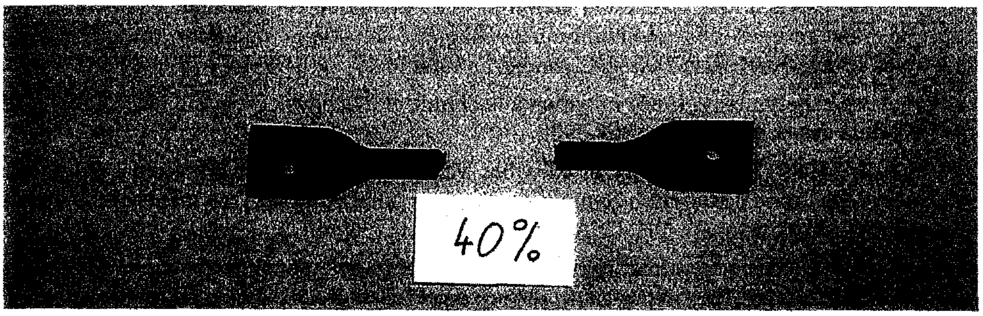

Figure 7. Brittle break for a sample submitted at a stress equivalent to 40% of the stress at yield

4. CONCLUSION

We notice no physico-chemical changes in HDPE except a loss of antioxidants.

The mechanical results show a plasticizing noticed on seamed as well as on non seamed samples. This change appears in tensile test and in relaxation measurement after about 4 months.

HDPE geomembrane have a good resistance to the applied stresses. Analytical methods reveal no differences between non aged and aged samples. Only mechanical tests show differences. Additional analyses are necessary to correlate mechanical stresses with a change in structure.

Under financial support from ADEME, this study should continue: results and interpretations for EPR-PP, PVC-P and bituminous geomembrane will be presented and discussed in future publications.

ACKOWLEDGEMENTS

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