ASSESSMENT OF THE ALKALINE HYDOLYSIS OF PET

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Abstract: Since geosynthetics of polyethylenterephthalate (PET) have been used to reinforce soil structures, the question of the hydrolytic degradation over the service life of the construction has been raised. For polyester the hydrolysis is a key reaction to crack the bonds of the molecule chains. This results in a reduction of the residual tensile strength of the reinforcement.

At natural temperatures of soil and in neutral environments the hydrolysis of PET is a slow chemical reaction, which will not have remarkable effects on the polymer after a reasonable test duration. Existing structures are not old enough to provide sufficient data for an assessment of the hydrolysis effect on PET.

The degradation process must be distinguished into two parts with different mechanisms. There is on one hand the alkaline hydrolysis which will be accelerated by a high pH-value of the environment and the neutral hydrolysis on the other. The water hydrolysis is a so-called internal hydrolysis. It affects the whole cross-section of the material.

The alkaline hydrolysis is a chemical reaction which attacks the surface of the elements. This external hydrolysis is a more rapidly process which gets an extra acceleration by higher temperatures. Two PET-geogrids with different geometries and a typical yarn have been immersed in saturated $Ca(OH)_2$ to achieve a pH-value of 12.5 and were stored at temperatures of 50, 60, 70 and 90 °C. The test duration at 50 °C has been more than 4 years.

The test series have shown that the chemical properties of the raw material and the geometry of the elements together are decisive for the hydrolysis resistance of PET-geosynthetics. An Arrhenius-plot has been used to predict the residual strength of the geosynthetics for the service life of reinforced soil structures.

Keywords: alkalinity, chemical ageing, durability, polyester

INTRODUCTION

PET is a thermoplastic material that is processed in a last step by the poly-condensation where up to 150 monomers consisting of ethylene glycol and terephthalic acid are connected to high molecular and semi-crystalline PET-molecules under special conditions and the use of catalysers. The hydrolysis is a reverse reaction of this process where water cracks the ester groups. Keeping in mind that the average temperature in soil is between 10 and 15 °C this process is very slow and has nearly no effect on service life of the construction. To predict the service life of a reinforcement of other geosynthetics an accelerated hydrolysis at high temperatures in a humid climate is needed. This leads to an increasing carboxyl end group content of the polymer. The carboxyl end group content is used to assess an ongoing degradation of PET caused by the inner hydrolysis. It goes along with a reduction of the material strength. This chemical analysis takes the whole cross section of the geosynthetics into account while the alkaline hydrolysis starts at the surface of the material and penetrates the polymer up to a certain depth where the chemical reaction nearly stops for the reason that not all compounds are available to affect the polymer as needed for a continuous reaction. In that particular case the assessment of the alkaline hydrolysis is reduced to the reduced residual strength of the geosynthetic material. Due to this chemical background, it has become common practice to use geosynthetics made of PET in neutral environments only. Because it has been accepted that the effect of the inner hydrolysis is negligibly small in soil the focus has been on the alkaline hydrolysis.

Since the fact is known that the effect of the alkaline hydrolysis depends on the relation between the area of the cross section and the surface some materials have been developed to fulfil these requirements. To prove this an industrial founded research project has been launched at the University of Applied Sciences in Muenster.

ENVIRONMENTAL CONDITIONS

PH of the surrounding soil

To cover the most demanding conditions regarding an alkaline environment for the geosynthetics, a survey of the applicable circumstances has been done. According to Martin & Dachroth (1994) most natural soils are expected to vary in their pH between 4.5 and 6.5. It is an exception if natural soils exceeds the range between pH 3.0 and 8.0. If the investigated soil contains a natural share of lime the pH may raise up to pH 8.3 and very exceptionally higher. A more alkaline reaction is normally caused by the presence of carbonates such as extracted from soda. Martin & Dachroth (1994) state that a pH above 8.5 under natural conditions is limited to chalky soil affected by salt at coast lines in central Europe. A higher pH may occur due to an accumulation of alkaline minerals in a drier climate than this in central Europe. Schreier (1993) has analyzed soils in Germany, which represents a central European situation, and found that in an extreme situation the presence of Na_2CO_3 can lead to a pH between 9 and 11. However, it is his opinion that it is more likely that a hyperacidity from environmental burden affects the soil. The pH can vary with the seasons of the year. This may be one pH unit (Schreier 1993).

In general, natural soil will not harm geosynthetics during the expected service life of a reinforced structure. One of the main advantages for the use of geosynthetics is to build the structure with the natural soil that is available on site. There have been investigations that came to the results that a combination of reinforcement and hydraulic stabilized soil will lead to the most economic solution. In that particular case the pH-value of the mixed soil may be at a level that influences the available strength of the reinforcement materials.

An assessment of the pH-values of various improved soils has been provided by Hering (2008), whose measurements have proven that a pH of sand caused by hydraulic binders can have its maximum peak at 12.6. This value occurs for approximate 5 to 10 days before the hydration process leads to a reduction (Figure 1). Hering's (2008) test series have shown that the pH in sandy soil is higher than in cohesive soil while using the same type and the same share of binder. The results indicate that the initial pH of cohesive soils remains at the same level for a longer time.

Assuming that a pH of 12.5 will be applicable for the whole service life of a construction, this is on the safe side because it does not take the time dependent reduction of the pH into account.

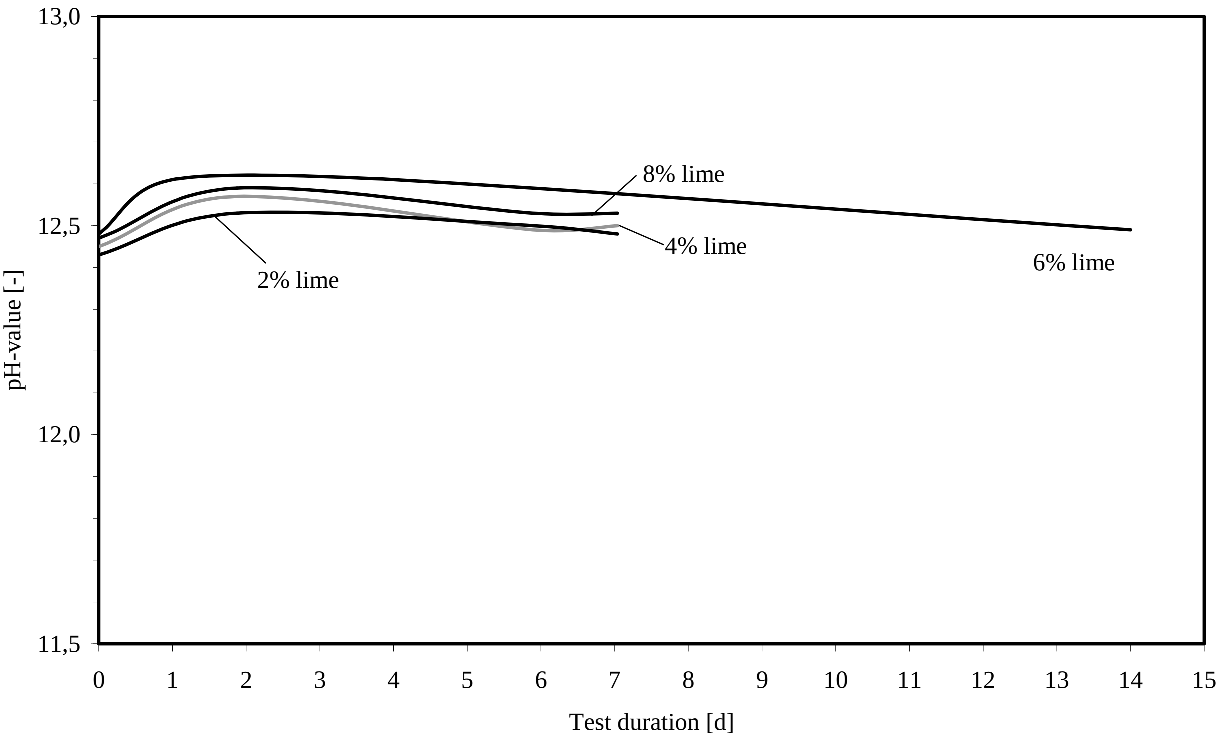

Figure 1. Time dependent pH-value of lime stabilized sand (lime content in percent)

Regarding the pH value, lime effects soil more than cement. The maximum for cement was 12.4 with 8 % cement. This large percentage will not be used to build a construction for economical reasons. A realistic percentage is between 2 and 6 %. Therefore the pH on site will not exceed 12.2 (Figure 2).

A lime stabilized soil behaves slightly different. The maximum pH using 8 % lime was 12.6. Because lime provides a sufficient content of $Ca(OH)_2$ to saturate the eluate of the mixed soil, the lines in Figure 1 are next to each other. The percentages of lime between 2 and 6 % are the ones for practical use. Both hydraulic binders show a continuous reduction of their pH-value. Even if the validity of the peak values is limited to a couple of days, a pH of approximate 12.5 has been assumed to be valid over the whole service life of the construction. This approximation was done because the pH value depends on the water content of the soil and the surrounding temperature of the soil. A fully saturated solvent has a different pH value depending on the temperature. The pH of a saturated $Ca(OH)_2$ solvent decreases slightly with lower temperature.

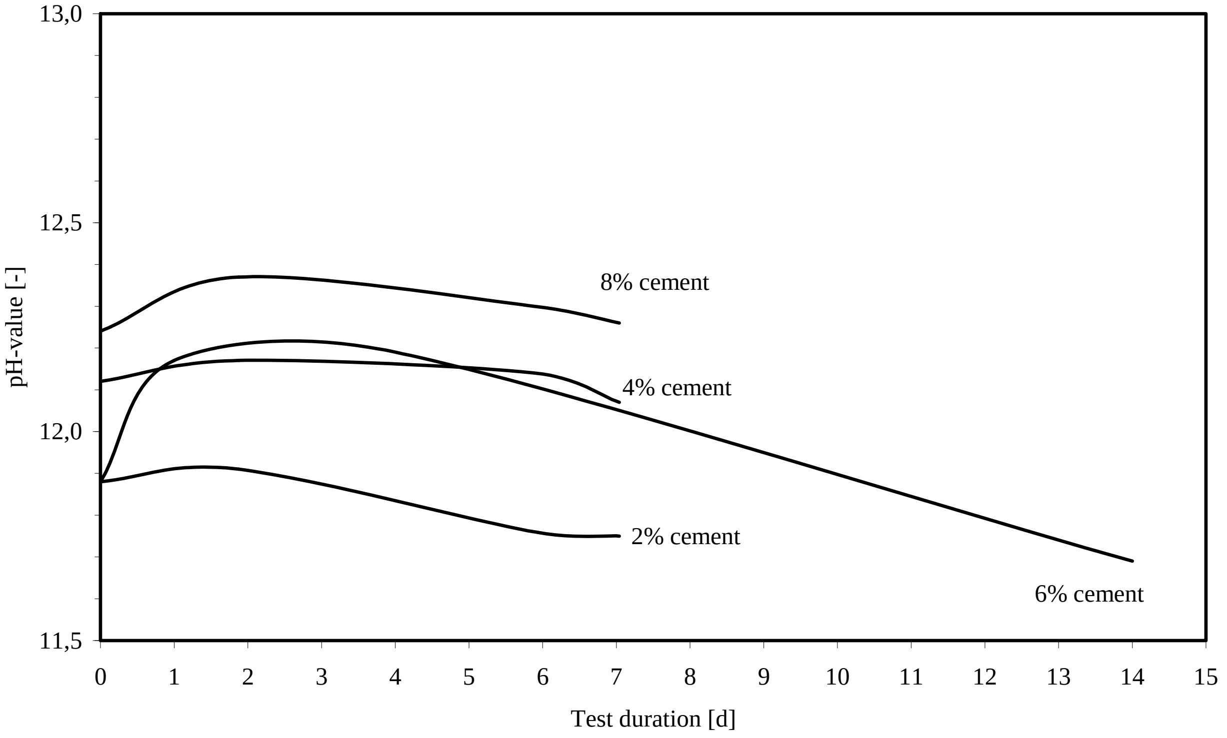

Figure 2. Time dependent pH-value of cement stabilized sand (cement content in percent)

In soil temperature

An average in soil temperature for reinforced structures between 10 and 13 °C, also measured on a construction site, has been considered as uncritical for geosynthetics made from PET (Meyer et al. 2003). The yearly temperature variation may cause fluctuations of the temperature close to the top surface of the soil. This has to be taken into account if geosynthetics are covered with a very thin layer of soil or have a green finish.

This is applicable to road constructions and steep slops formed from reinforced structures where the front protection is a wrap around of the reinforcement sheet. Measurements from a climate station, owned by the University of the Federal Armed Forces on their campus in Munich, have been made available on the internet. The data covers the years 2004 to 2006 and have been taken 1, 5 and 35 cm below the surface. Munich is a city with prominent seasons – warm summer and cold and snowy winter. The average temperatures are given in Table 1.

Table 1. In soil temperature in Munich/Germany

Depth below surface (cm)	**Year** (-)	**Yearly average temperature** (°C)
1	2005	13.10
	2006	13.53
5	2004	13.40
	2005	13.14
	2006	14.00
35	2005	12.84
	2006	13.32

An average temperature of 15 °C is a good approximation for further investigations even if there are 120 to 130 days per year were the temperature was above the 15 °C but did not exceed 25 °C during the Munich measurements. In contrast, nearly the same number of days has a temperature below 5 °C. This indicates that acceleration and deceleration of the chemical reaction are in balance at the average temperature. Finally it can be concluded that there is no remarkable difference of the average temperature depending on the depth in soil. To cover uncertainties, a temperature of 20 °C was chosen for evaluation of the tests.

LABORATORY EMPLACEMENT

Test description

The tests have been carried out in the laboratory for material research of the civil engineering department at the University of Applied Sciences in Muenster/Germany. The test samples were stored in saturated lime water (completely dissolved $Ca(OH)_2$) for the alkaline hydrolysis. By stirring the bath a constant and well distributed pH of at least 12.3 was ensured. The pH of lime water depends on the temperature and may vary between pH 12.3 at 20 °C, 12.4 at 25 °C and 12.6 at higher temperatures. The temperature of the baths used were 20, 50, 60, 70 and 90 °C. Because of the high temperatures and the humid environment an effect of the inner hydrolysis was expected. To assess the influence of this phenomena a complete set of specimens has been exposed to deionised water at the same temperature levels and for the same time. Both the temperature and the pH have been controlled during the test. The divergence of the temperature was limited to +/- 2 °C. Because of the ongoing precipitation the pH of the solvent was reduced. This was caused by chemical reactions of the terephthalic acid and ethylene glycol ion coming from the stored PET with the calcium ions of the base. If that happened the pH was adjusted by adding CaO to the bath.

The tests at 50 °C lasted for 4 years between 2001 and 2003.

Test material

With the support of the involved geosynthetics manufacturers various solid PET straps and a PET yarn have been made available for these tests. Because the dimensions of the samples were essential for the evaluation, Table 2 contains the required data.

Table 2. Cross sections of tested PET samples

Parameter		MAT 1	MAT 3	MAT 4
Material	(-)	Yarn	Strap	Strap
Area of cross section	(mm²)	0.00031	5.67	5.22

SERVICE LIFE ASSESSMENT

The investigated geosynthetics have been made from PET. This is a thermoplastic and because of its viscous-elastic behaviour that depends on temperature it fits into the Arrhenius law. For thermoplastics the effect of stress increases with time. This process can be accelerated with an increased temperature. The Arrhenius plot is a way to extrapolate this relation back to lower temperatures at normal service conditions and for a longer period of time than observed during the tests.

An essential requirement to apply the Arrhenius plot to a series of measurements is that the test itself does not cause mechanical damage of the material. The thermo-mechanical impact on the material is an investigation for the future.

The Arrhenius plot is a linear regression between the logarithm of the test duration that equals the change of the property and the reciprocal of the absolute temperature.

$$k(T) = A \bullet e \frac{-E_a}{RT} \quad \text{or}$$

$$\ln k(T) = -\frac{\mathrm{E_a}}{\mathrm{RT}} + \ln A$$

Where k is the rate constant of chemical reactions, T equals the absolute temperature in K, A is an pre-exponential factor, E_a indicates the activation energy and R is the gas constant matching 8.314 J/(mol·K).

Using this equations the activation energy E_a as the slope of the result graph can be calculated for the further service life prediction transforming the above formula into:

$$\ln k(T) = \ln A - \frac{\mathrm{E_a}}{\mathrm{R}} \bullet \frac{1}{T}$$

and further to:

$$E_a = -\mathrm{R} \bullet \mathrm{T} \bullet \ln \frac{\mathrm{k}}{\mathrm{A}}$$

The activation energy is kind of a barrier that has to be overcome to get a chemical reaction running. The activation energy does not provide information about the velocity of the reaction but has a remarkable effect on the start of the reaction and their result.

Graphs like that shown in Figure 3 have been used to calculate the residual strength that is available after a 100 years service life in a $Ca(OH)_2$ saturated environment. This evaluation includes the effects of water and the alkaline hydrolysis. On one hand this is a handicap while assessing the effect of the alkaline hydrolysis. On the other hand an alkaline environment that may harm immerged geosynthetics is linked to humid conditions that will cause water hydrolysis.

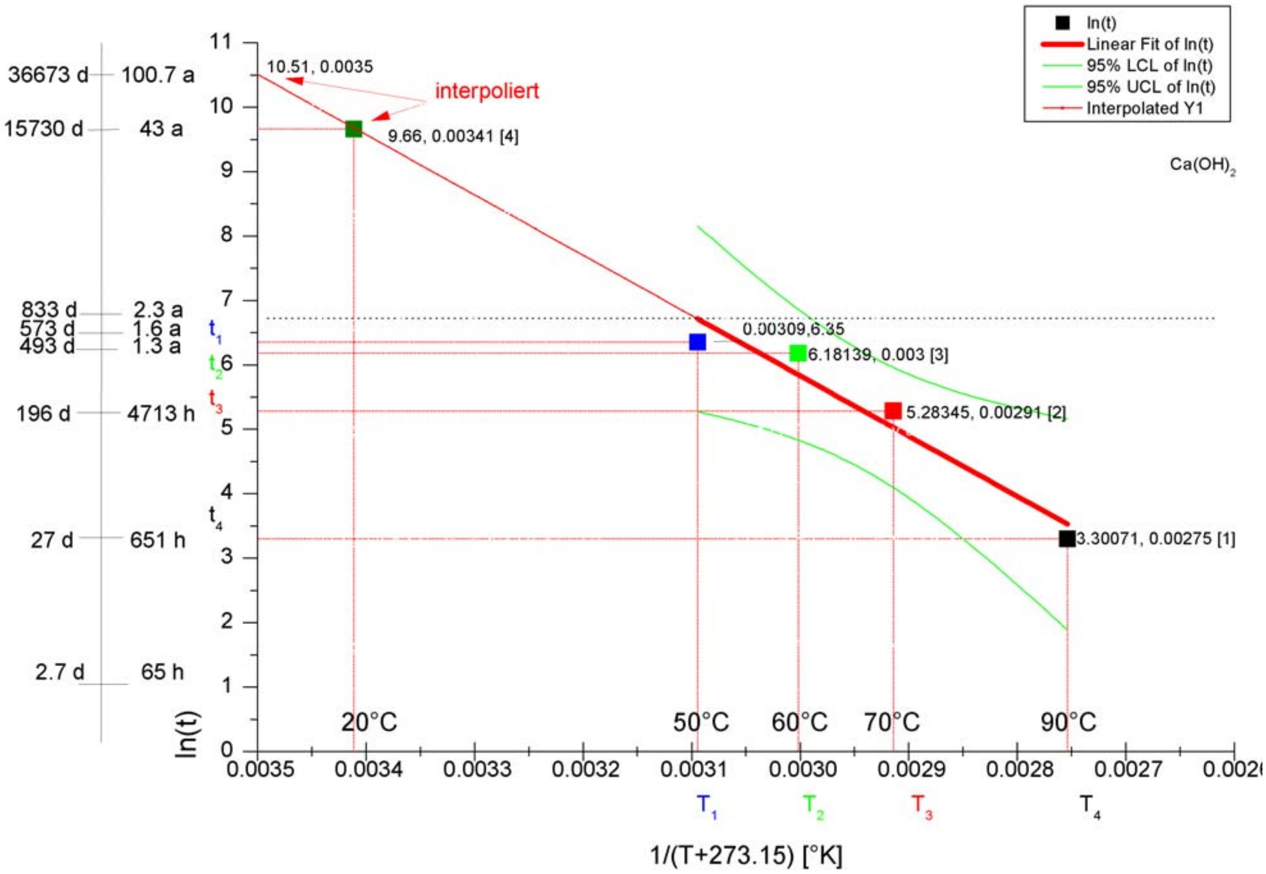

Figure 3. Arrhenius plot for MAT 3 expressing the time to 90 % residual tensile strength

This iteration process has been used to predict the behaviour of the specimens. The outcome indicates a range from total failures up to sufficient residual strength values of materials made from PET.

Some of the results of the evaluated materials according to the Arrhenius plots are summarized in Table 3.

Table 3. Results of the Arrhenius plot

Parameter		MAT 1	MAT 3	MAT 4
Material	(-)	yarn	strap	strap
Activation energy E_a	(kJ/mol)	54 - 65*	82.8 - 85.7	87 - 94
Residual tensile strength after 1.3 years @ 20°C	(%)	0	96.8	95.7

* The activation energy has been calculated for 50 % residual strength which has been achieved after 0.8 years.

Since the beginning of the tests it was obvious that a virgin yarn without any further protection, like coating or dipping, would fail very soon. The main reason is the ratio between the surface area and the volume of these materials (MAT 1). But also an appropriate ratio between the surface area and the volume, as it is the case for straps (MAT 3 and 4), does not guarantee a good resistance against attacks of an alkaline environment. Where the PET materials behaved poorly the alkaline hydrolysis has penetrated the material like corrosion pitting happens to steel. In addition to the shape, a high quality of the raw material is needed to achieve a sufficient hydrolysis resistance in a solution with a high pH value. This is to a certain extent associated to the carboxyl end group content and to the molecular weight of the PET. This means a general rule based in the dimensions of the geosynthetics elements is not applicable and each product family should be assessed individually.

Furthermore it has to be considered that the test conditions are very demanding for the tested materials. A pH value of 12.5 because of an alkaline soil improvement additive will decrease with time, especially after hardening of the soil mix is completed. The results given in Figure 2 are indicating this.

While evaluating the tests according to the Arrhenius law several influencing factors have to be taken into account. While the temperature describes the basic circumstances for the Arrhenius plot are thermo-mechanical effects or the material history is not regarded. This is applicable at all temperatures but has its major effect on the higher temperatures, where the heating of the test samples may lead to a change of the morphology. Compared to others the results at 90 °C have a large variation. A test at 90 °C is for sure above the glass transition temperature of PET and forces the material into a phase where the molecular structure may be changed by the applied energy. At this stage shrinkage of pre-stressed materials occurs and indicates the mechanical damage of materials. This changes the stress-strain behaviour of the tested materials. The strain at break has been increased though the peak strength and then drops down. This resulted in a lack of information that can not be determined with pure mechanical tensile strength tests and a comparison of the reference and the residual tensile strength of a sample. Therefore the tests for the Arrhenius plot should be accompanied with a chemical analysis of the samples.

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