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METHODOLOGY TO ANALYZE THE DEGRADATION OF STRUCTURAL TIMBER IN ACIDIC ATMOSPHERES

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ABSTRACT: The atmospheric composition varies according to geographic locations. In Costa Rica, part of the infrastructure is affected by corrosive atmospheres caused by volcanic activity and tropical climate humidity. The aim of this research is to propose a robust methodology to establish the influence of acid agents on the mechanical performance of structural *Tectona grandis* and *Cupressus lusitanica* specimens exposed to this environment. This research contemplates different acid pollution degrees and on-site and in laboratory analysis; Dynamic Elasticity Modulus E_{dyn}, apparent Elastic Modulus E_{app}, and chemical composition changes are the response variables. Among the highlighted results during the initial experimental stage, it was observed an estimated decline rate of 5-7% in E_{dy} and 8-11% in E_{app}, with a tendency of 3% more decrease in Cypress than in Teak. The acidic atmosphere remained between 0.5ppm and 1 ppm of SO_2 gas concentration, and pH values of acid rain were 3.92±0.33 on average. In addition, specimens were sensitive to color change ($\Delta E^*>17$) which can be considered for architecture design purposes. Since this environmental accelerates natural degradation, the proposed methodology seems suitable for monitoring wood degradation based on a six-month tracking study.

KEYWORDS: Ultrasonic technique, volcanic environmental, SO_2 degradation, *Tectona grandis*, *Cupressus lusitanica*

1 INTRODUCTION

All materials regardless of their nature and composition are degraded by the interaction's effects of climatic variables during outdoor exposure. The modification process takes place because its components seek to return to a stable chemical equilibrium with the environment. A complex combination of physiochemical, mechanical, and light energy factors contribute to what is described as weathering, which is the degradation phenomenon that occurs in the superficial layers [1].

The weathering factors responsible for changes in the wood surface are moisture (dew, rain, humidity), solar radiation (ultraviolet, visible, and infrared light), temperature, and oxygen. Of these, solar radiation is the most damaging, initiating a wide variety of chemical changes at wood surfaces such as oxidation and depolymerization of lignin and cellulose, which leads to material loss and discoloured surfaces. This process continues throughout 6-10 months, after which a stabilization or slowdown of the degradation process is expected [2].

Thus, changes in wood properties are unavoidable because climatic variables promote the conditions which contribute to wood deterioration and decay. For this reason, evaluation of wood properties as a function of outdoor exposure should be determined [3]–[5]. Several authors have made significant knowledge contributions on this subject [6]–[9]. It has also been reported that different types of aggressive chemicals may cause timber corrosion, in particular oxidizers, alkalis, and acids, which may be exposed to the wood as gases, liquids or particles. The intensity of the chemical corrosion of wood depends on the type of pollutant, its concentration, humidity and temperature level, exposure time, as well as wood permeability and the side of timber which is exposed [10][11]. Gases such as sulfur dioxide SO_2 damage wood more intensely where there is higher humidity [12], [13]. Comparatively, the chemical corrosion intensity of soft wood is usually lower compared to hardwoods, which differs in several aspects, such as fiber dimensions, chemical composition and microstructures [14], [15]. Hardwood (not only sapwood) is usually more permeable to liquids and gases, and compared to softwoods, contains slightly more hemicellulose (~25% compared to ~20%), which are the least stable components in hydrolysis. Coniferous wood, contains more lignin (30% compared to 20% in hardwoods), which resists non-oxidizing chemicals quite well [16]. Heartwood is generally more acid resistant than sapwood, probably due to lower permeability and higher extract content [17]. It was also found that chemical-atmospheric corrosion of wood was defined as the climatic degradation of wood by the effect of aggressive emissions. The typical example is degradation caused by acid rain, which contains SO_2

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nitrogen oxides NO_x, and their acids (H_2SO_3, H_2SO_4 and HNO_3). In this regard wood has shown low degradation in environments considered corrosive to metals, and therefore, it endures in places where steel and reinforced concrete structures suffer a great deterioration [18].

For this reason, timber is applied to industrial and agricultural objects, where it is exposed to gases, vapors, condensates and accidentally spilled liquids. It is also used to make multiple structural and constructive components; however, these wood products lose resistance after a prolonged period of exposure in the presence of aggressive chemicals, in particular in their surface layers [18] [19].

Wood degradation due to outdoor exposure modifies the characteristics of cellulose, particularly the crystalline fraction, which determines numerous properties of wood. Some of these include physical, mechanical, and chemical properties such as Young's modulus, density, dimensional stability, and acoustical properties, as well as moisture regain, dye sorption, and chemical reactivity [7], [8], [9].

Other natural conditions, such as temperature, humidity, and precipitation, also affect wood performance through impacts on the hygroscopic properties. These induce changes in the physio- mechanical properties of wood when its moisture content is below the fiber saturation point [10].

Of all atmospheric pollutant's sodium chloride (NaCl) and SO_2 are the most common aggressive agents in the atmosphere that cause degradation processes to materials. NaCl is incorporated from the sea while the second can come from anthropogenic origin or from volcanic areas [18], [20].

The relevance of paying attention to these comes from the fact that losses due to corrosion of metals and alloys reach very high values. It is considered that between 2% and 4.5% of the gross domestic product (GDP) of a country is lost due to this. More than 50% of these losses are due to atmospheric corrosion. atmospheric corrosion. These calculations come from studies made in non-tropical countries, and such data are higher in tropical countries, with characteristics of high temperature, humidity and main pollutants [21].

In Costa Rica´s volcanic areas the existence of high humidity and NaCl, HNO_2 (nitrous acid) or SO_2 accelerates the corrosion process. It is in these areas, where the widespread use of alternative materials to steel, such as wood, is especially interesting. The objective of this investigation is to determine how acid contamination affects timber´s mechanical performance due to changes in its chemical composition.

Nowadays there are many methods to assess the location and degree of damage to structures. although these just allow to evaluate certain types of failures, so it is necessary to combine different procedures to obtain the structure performance [22]. In this research, complementary methods were used, such as non-destructive stress wave evaluation and destructive bending test to obtain mechanical properties and thermogravimetric analysis (TGA) as well as fibre dissolution for chemical composition.

No evidence has been found that these methods have been use to study the degradation of wood by acid. Literature on studies of wood degradation by acids or its performance when it is exposed to volcanic acid atmospheres is nonexistent up to the author's knowledge. Only some investigations were found on the effects of acids in wood [23]–[27].

This research proposes to study the effects of the predominant acid variables in volcanic atmospheres (acid rain and sulphur gases) by collecting, processing and correlating the data, to integrate their interactions. Insomuch as when the environment pH changes substantially the wood resistance properties may be reduced and these effects worsen with time and humidity [17].

2 METHODOLOGY

The scientific approach to develop the methodology is to analyze the degradation of structural timber in acidic atmospheres. For this purpose, technical guidelines for wood degradation are been considered as well as the inclusion of the phenomena of acidic fiber degradation in order to identify its impact on its mechanical properties.

2.1 TIMBER SELECTION

To determine the acidic material degradation, the following considerations regarding timber were established, a) Species used in commercial applications; b) Type of wood (hardwood and softwood) which must come from forestry plantations. The data to stablish the commercial use was obtained from statistics published in the Forestry National Office [28]. The type of wood(s) selected was aligned with scientific literature availability as a complement for the present study in acidic environments [29].

2.1.1 Wood material preparation

The samples were prepared from two solid sawn wood: *Tectona grandis L.* (Teak) and *Cupresuss lusitanica Mill* (Cypress). Teak is a hardwood and Cypress is a softwood. The plantations ages were 14 and 40 years respectively, due to the maturity representation at which they are traded locally. The material was oven dried to achieve a moisture content of about (12-13) %. All the pieces were visually evaluated in order to control the defects admissibility according to local standard INTE C100:2011 [30]. Percentage of sapwood and heartwood corresponding to structural grade [31].

2.2 OUTDOOR EXPOSURE SITES

Three different locations were chosen according to the acidic atmosphere exposure (Figure 1): a) High Exposure Area (HEA), in the Poás Volcano National Park; b) intermediate exposure Area (IEA): Poasito town c) control Area (CA) witness or residual exposure in the Braulio Carrillo National Park. Table 1 shows exposure sites GPS locations.

Table 1: *GPS Location of outdoor exposure sites*

Site	GPS Location
HEA	10°10'10.36″N, 84°13'56.00″O
IEA	10°05′00″N 84°15′00″O
CA	10°09′36″N 83°58′28″O

The Poás Volcano was selected to evaluate the acidity influence as a principal acidic environment due to its high activity in Costa Rica, according to the National Volcanological and Seismological Observatory. This site is located 35 km northwest of San José, in the Central Valley (2708 meters above sea level).

Figure 1: *Areas with different exposure levels from Poás volcano activity. Adapted from* [32]

The weather parameters were monitored using meteorological stations (Davis-instruments, wireless-vantage-pro2 model including UV radiation sensors) and complementary data from other stations (Will Lambrecht rain gauges, Vaisala sensors and Campbell Scientific Dataloggers). Depending on the station, data acquisition rate varied. The measured variables are precipitation (mm), temperature (◦C), irradiation (W/m^2), wind speed (km/h) and cardinal direction. Also, rain and mist water collectors were placed next to the timber experimental units to collect acid rain monthly. The monitoring time for this study will be 36 months, every 3 months specimens will be tested considering their physical, mechanical and chemical properties.

2.3 SCOPE FOR THE ON-SITEDEGRADATION ANALYSIS

2.3.1 Experimental Units

The aspects involved in wood weathering include biological and atmospheric factors. In this study, the experimental specimens are situated above-ground to reduce the biological impact on degradation, considering the technical recommendations from previous reports on this topic [9]. The positions of the timber specimens during exposure are vertical and horizontal (0˚ and 90˚).
A total of 12 experimental units were required, they are divided into 4 per site (due to the 2 positions and 2 species and 3 exposure sites) the experimental units are facing south.
The total number of specimens was 432 (216 per species in each site). The dimensions of structural pieces are 2x4x68" (48mm x 98mm x 1720mm), with a height width ratio (d / b) greater than 3 and length was calculated as well to fulfil the requirements for the bending tests (ASTM-D198-15) [33].

For defect free specimens dimensions are 1x1x16" (25x25x410mm) according to ASTM-D-143 [34]. The pieces are arranged in a simply supported way without metal connectors that would interfere with their degradation or moisture uptake as shown in Figure 2.

Figure 2: *Experimental specimens exposed above-ground to environments with different degrees of acidic atmospheres*

2.31 Environment Acidity

The acidic atmosphere is estimated using the SO_2 and H_2S concentration, considered as the primary pollutants in volcano zones [35]. The concentration was measured using portable gas detection monitors Multirae Lite (Honeywell), that allow constant detection of gases (every minute with a resolution of ± 0.1 ppm. For the pH analysis rainwater and fog is being collected on site, in Figure 3 collectors are shown [36], [37]. The water samples are analyzed by ion chromatography to obtain the acidity level and the anions chloride (Cl-), fluoride (F-), nitrate (NO3-), and sulfate (SO42-), using a HPLC, Dionex 5000, with TCD and a IonPac ® AS23, 4 mm x 25cm column. The calibration curve method follows the manufacturer's recommendations.

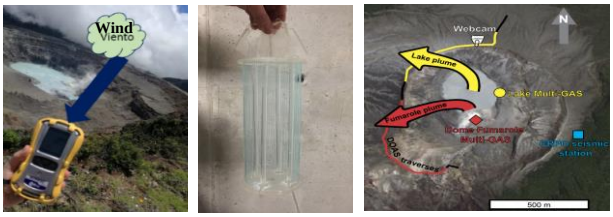

Figure 3: *Multirae gas monitoring, acid rain from fog collector image on the right adapted from* [35].

2.4 SCOPE FOR THE DEGRADATION LABORATORY ANALYSIS

The evaluation of the acidic material degradation was carried out in two lines. a) The microscopic effects were analyzed by internal climate monitoring, moisture content, density, and fiber composition changes. b) The macroscopic changes were measured through the mechanical properties of static and dynamic modulus of elasticity (E_{app} and E_{dyn} respectively) and color changes of wood surfaces (CIE Lab system color coordinates).

A) THE MICROSCOPIC EFFECTS

Internal climate (internal MC and temperature)

Internal moisture content and internal temperature is being monitored using field sensors of hygroscopic conditions (MC moisture content and internal temperature Trackers BL2 Lignomat USA) in permanent parts in the

total length of this study. The system is shown in Figure 4.

Figure 4: *Monitoring of internal MC and internal temperature with sensors inserted inside the wood.*

Moisture content and density

Prior to on-site ultrasound test (every 3 months) the moisture content (MC) of wood samples are measured on site using a portable moisture meter (General MMD900) and weight is determined using a floor scale steelyard with a capacity of 150kg (UFM B150 ABM). Wood density is calculated as the ratio of weight to volume, according to ASTM D4442 – 16 and ASTM D2395-17 [38], [39]. MC is determined following ASTM-D4442-16 [39] Method B. The equation to estimate MC is shown in Eq. (1):

$$MC = \frac{Air\ dry\ mass - Oven\ dry\ mass}{Air\ dry\ mass} x100 \quad (1)$$

Basic Specific Gravity and Density (ρ_b) is determined following ASTM D2395-17 [38] The model to estimate the ρ_b is shown in Eq. (2):

$$\rho_b = \frac{Oven\ dry\ mass}{volume\ to\ measured\ HC} \quad (2)$$

Chemical composition

Fiber composition change is done through fiber dissolution and TGA (TA Universal Analysis 2000 equipment) according to ASTM-E1131-03, ISO-11358-1:2014 [40], [41]. Samples were obtained from the thin outer layer of the structural size specimens which were exposed in the field. The samples were taken after mechanical tests, once they have failed. The surface layer thickness was cut at 2mm with a wood planer.
Subsequently, the sheets are grounded to obtain particles of a size of 1mm, sieved and oven dried. Sieved according to ASTM-E1757-19 Preparation of Biomass for Compositional Analysis [42] (Method A) the milled material is separated into two fractions, a −20/+80 mesh fraction and a −80 mesh fraction and oven according to Test Methods for direct MC measurement of wood ASTM D4442 – 16 [39]. The primary oven-drying method (Method A) was chosen since its highest accuracy. An N2 as atmosphere is required with a flow rate of 50mL/min, while the temperature range was from 40 ° C to 900 ° C, the heating rate was 10 ° C / min. On the other hand, fiber dissolution assays, acid detergent fibre, neutral detergent fiber and acid detergent lignin, were carried out simultaneously, considering pretreatment and particles size according to ASTM E1757-19 Tappi T-280-pm-99, T 222 om-02, T-257 and T 413 om-02) [42]–[45], these processes allow to establish cellulose, hemicellulose and lignin contributions.

B) THE MACROSCOPIC CHANGES

The specimens prior to laboratory tests were acclimatized for at least two weeks in a room with controlled conditions (RH 50±5% and temperature 163 ±35 F° (23°C±5%), then the moisture content is verified to be 12±1% prior to performing ultrasound and bending test.

Stress Wave Non-Destructive to estimate Dynamic Elasticity Modulus, E_{dyn}

The E_{dyn} is measured using an ultrasonic transmitting pulse method to determine the ultrasonic wave velocity (V_{us}) based on time of flight. The longitudinal ultrasonic pulse is generated with Sylvatest-Duo equipment, using a frequency of 54kHz which was elected after trials with different available equipment as shown in Figure 5.
The measurement is done by inserting one conical transducer in each piece edge. One transducer acted as a transmitter, and the other as a receiver of ultrasonic waves. Three repetitions are carried out in each point to verify the accuracy of the measurements. The average of the ultrasonic velocity is calculated and used to estimate the E_{dyn} with the wood density parameter [46]. The model to estimate the E is the same equation shown in Eq. (4):

$$E_{dyn} = \rho * v^2 \quad (4)$$

where ρ is the wood density (kg/m^3) and v is wave velocity (m s^{-1}) The ultrasonic wave velocity (v_{us}) was calculated by dividing the distance between the transducer (m) by the average of three repeated readings of time for ultrasonic wave transmittal (s). Figure 5 shows ultrasound test.

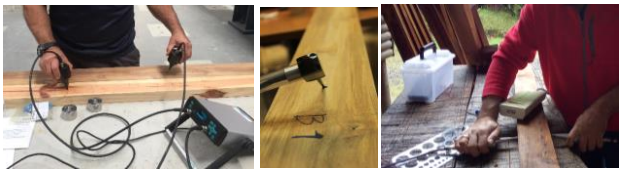

Figure 5: *Ultrasound test with different equipment, Pundit-Proceq, Utrawood and Sylvatest Duo in field.*

Bending test- structural to estimate apparent Elastic Modulus, E_{app}

For the bending test, simple supports near the ends are used, with the application of symmetrical load between supports, point loads to the thirds of the specimen are separated at L / 3. The specimens (beams) are tested in a universal machine (MTS) with a servo-controlled hydraulic jack. Meanwhile, test speed, load speed, and average time were adequate set to reach maximum load at 4 min as technical requirement. Deformimeter (LVDT) placement was verified and the moment of failure was recorded according to ASTM-D198-15 [33]. The assembly is shown in Figure 6 (left), while the model to estimate the E is shown in Eq. (3):

$$E_{app} = \frac{23\ P\ l^3}{108 b d^3 \Delta} \quad (3)$$

Where P is increased in test load below the proportionality limit and Δ is the increase in deflection associated with P. The limit of proportionality is taken as 0.6 Pmax.

Figure 6: *Bending test structural size (left) and defect free specimen (right).*

Defect free specimens are according to ASTM D143-14 [34], secondary method size 1x1x16" (25 x 25 x 410 mm) was chosen eliminate the wood defects variable. The specimens are being tested in a universal machine (MTS-810) in which the supports are provided by rollers, with a distance from the point of support to central plane not greater than the height of the specimen. The load is applied by means of a hardwood accessory through a single contact point, at a constant speed calculated by the equations of the standard. The model to estimate the Eapp is the same equation shown in Eq. (3), and the test is shown in Figure 6 (right).

Colorimetric changes measurement

Color change caused by natural weathering was evaluated through photographs taken to the specimens surface every month (30 days). Images were acquired with a Canon EOS88D Rebel Ti7, inside a portable device which works as a dark room (Travor Photo Studio Light Box 35"/90cm Adjustable Brightness), the box allows blocking the entry of natural light and enable taking pictures always with the same artificial light intensity. The images were analyzed using the digital color meter software from Mac Systems at 3 consistent focusing points for every exposure period. The software generated the L*, a*, and b* values. The color changes were determined by referring to the coordinates using CIE Lab system, in which L* denotes lightness or brightness (black to white), while a* and b* denote redness (green to red) and yellowness (blue to yellow), respectively. This system is the most common method for estimating the color of a material. The change in color (ΔE) of each sample was calculated with Eq. (5):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \qquad (5)$$

Where ΔE is the wood color change due to weathering, ΔL* is the difference between the values of initial L* and after exposure, Δa* is the difference between the values for the initial a* and after each exposure, and Δb* is the difference between the values for the initial b* and after each exposure [47].

3 RESULTS AND DISCUSSION

3.1 SITE CHARACTERIZATION

The acidic atmosphere was characterized considering the weather parameters from November 2020 to March 2021. The HEA and the CA have a very humid climate [48]. It can be observed in Figure 7 the wettest month (with the highest rainfall) in the HEA was December (25 days and 719.85 mm of precipitation). The driest month was March (11.39 days and 17 mm precipitation). The mm of precipitation had an average of 184.5 mm per month, and according to historical data average rainfall ranges around 3000mm per year. Daily average precipitation was 15.1 and 13.8 mm in HEA and CA respectably.

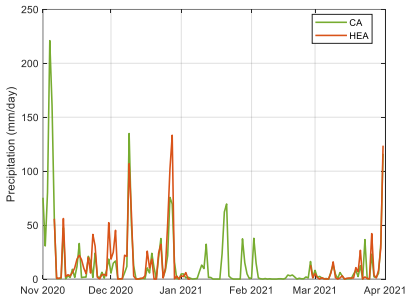

Figure 7*. Precipitation profile in mm. I.HEA, II. IEA and III CA to evaluate acidic atmosphere for six months period.*

It is observed that temperature profile is highly variable, since temperature fluctuates during daily hours. (Figure 8). Meanwhile, the average temperature seems to mark an important difference between the daily hours. The average maximum was 13.34-13.35°C average low was 9.0-7.4) in HEA and CA respectably. The warmest months were March and April, and march was the month with the most extreme temperature variations with average maximum high temperature 19.3-22.3°C, and the lowest average temperature 2.9 - 0.1°C in HEA and CA respectably

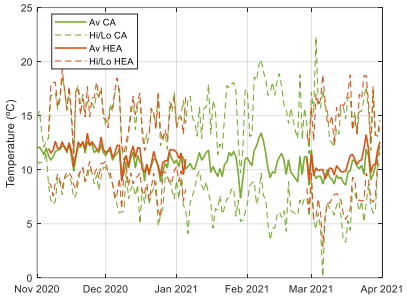

Figure 8*. Temperature profile (◦C). I.HEA, II. IEA and III. CA. to evaluate acidic atmosphere for six months period.*

As shown in Figure 9 the prevailing wind speed was 3.32 and 5.7 km/h in the HEA and the CA respectably. The wind direction at HEA was predominant towards north-west (NW) 135° respect to east, and predominant east-northeast (E-NE) 16.2° in the CA.

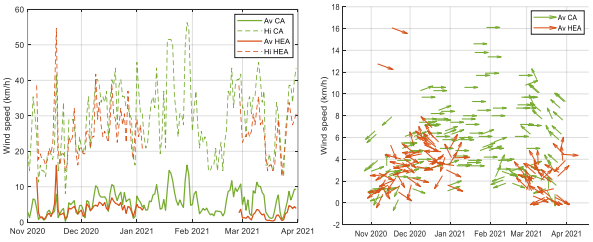

Figure 9*. Wind speed profile (km/h). I.HEA, II. IEA and III. CA. to evaluate acidic atmosphere for six months period.*

The relative humidity profile showed significant daily humidity fluctuations 13-100%. (Figure 10). Average maximum was 93.5% and average minimum 56.5 % in HEA. The month with the lowest relative humidity was March (56.5%).

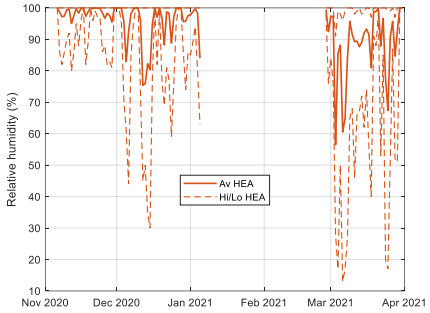

Figure 10. *Relative humidity average RH profile (%). HEA to evaluate acidic atmosphere for six months period.*

Besides, it was found that for both HEA and CA that acidity fog values were higher than rain values (Figure 11). In HAE the pH values of acid rain were 3.92±0.33 and acid fog 3.84±0.21 in IEA the pH values of acid rain were 5.80±1.87 and acid fog 4.84±1.38. In CA acid rain pH values were 4.67±0.51 which is an expected value since the normal pH of rainwater is approximately 4.5. Thus, it is anticipated the potential influence of the volcanic environment that can act in the wood materials.

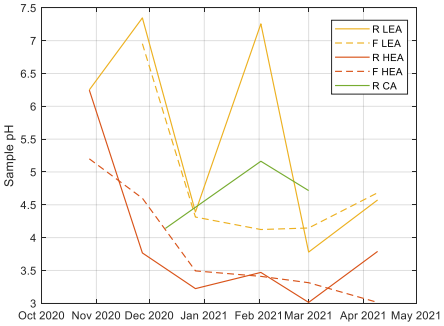

Figure 11. *pH profile (0-14). I.HEA and II. IEA to evaluate acidic atmosphere for six months period.*

Given the micro eruptions present in volcano areas, it was observed that the anions analysis revealed the presence of chloride and sulphate as showed in Figure 12, and the nitrate and fluoride had less concentration

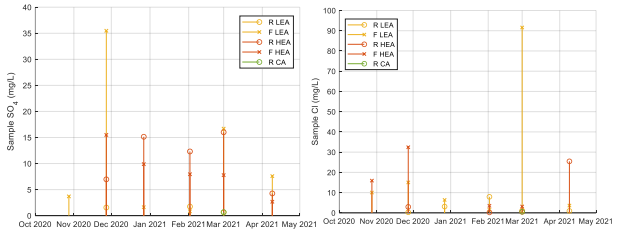

Figure 12*. Anion's profile (mg/L). I.HEA and II. IEA to evaluate acidic atmosphere for six months period.*

Comparatively, the acid gas had been reported as the main pollutant in acidic atmosphere. Figure 13 illustrates the gas profile of SO_2 and H_2S, where it can be observed that there were some concentration peaks that might affect the wood fibres.

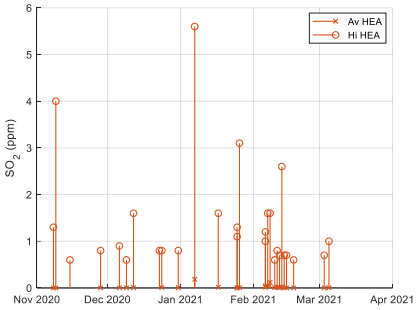

Figure 14. *SO_2 gas emission profile (ppm). I.HEA to evaluate acidic atmosphere for six months period.*

Due to variability in environmental conditions, it must be considered the challenges from of the different degrading agents contribution cannot be isolated, and obtained results are different according to the campaigns [49]. Hence, it is essential to compliment the wood mechanical performance with a cross-correlation analysis considering these parameters for a longer period.

3.2 VARIATIONS IN MOISTURE CONTENT AND DENSITY

Moisture content (MC) and density initial parameters before the exposure were MC 13 ± 0.51 % for Teak and 12.5± 1.03% for Cypress, according to previous reported results and density was 0.84 ± 0.09 g/cm^3 and 0.63 ± 0.05 g/cm^3 respectably. These experimental values were according to previous results [29]. On the other hand, based on the first measurements, both species presented a loss of density in the three exposure sites between day 90 and day 180 (Figure 14). The apparent loss of density in the softwood (≈8%) was higher than in Teak (≈4%), and the same line, in horizontal position was more noticeable than in vertical position. Eventhoug is expected to have a minor value for Cypress, the degradation rate was the double. It could be a consequence of the permeability and the mean path available for water desorption between fibres, due to MC variations shown extensive fluctuations (12.41% – 22.04% for Teak and 13.53% – 22.31% for Cypress). In Figure 16 an example for Cypress, according to weather conditions and on-site measurements results is shown.

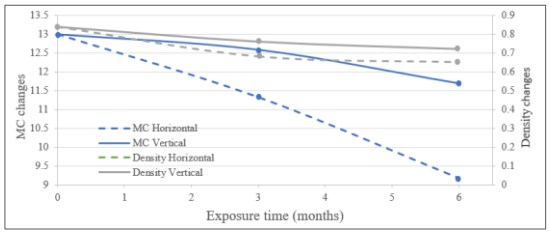

Figure 14. *Moisture Content and Density changes in HEA during 180 study period for Cypress.*

As is documented in the literature, the MC and density influence on the mechanical properties. This result can be notice in the ultrasonic wave velocity variations whereas it is clear that at higher moisture content, less wave velocity is obtained. Also, the inverse behavior described.

It seems to occur to a lesser extent in the case of the vertical position based on lower MC percentages. Additionally it should be considered that outdoor exposure leads to the depolymerization of cellulose and the loss of hemicellulose and lignin content due to oxygen and humidity, as well as the effect of UV light, which induces photochemical reactions in wood [50].
Generally, weathering causes wood to become more hydrophilic because the extractives are leached from the surface, causing the wood to become less water-repellent [51]. MC also influences in the diffusion rate of acids in the wood [52]–[58]. These aspects should be considered in future discussions when more data are available.

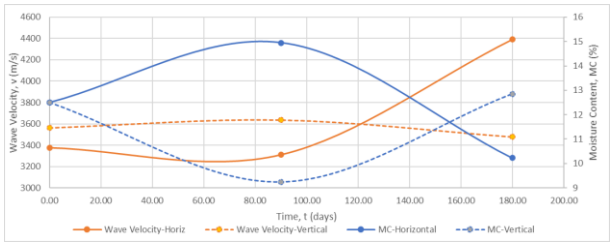

Figure 15. *Moisture Content and Wave Velocity in Acidic High Exposure Areas (HEA) during 180 study period for Cypress.*

3.3 MECHANICAL PROPERTIES EVALUATION

Since the wood presents natural intrinsic variation of its fibres, it is expected that the mechanical performance would change depending on the individual trials. To minimize this condition, several assays were performed.
Considering initial parameters at beginning of the research were E_{app} 11.17± 0.67Gpa for Cypress, and 14.78± 0.79 GPa for Teak; and E_{dyn} 10.21± 0.34 GPa for Cypress and 15.88±0.55 GPa for Teak.
For both species, an appreciable decreasing in the E_{app}, and E_{dyn} values at 90 days and then at 180 days was observed. Cypress E_{dyn} decreased in average 2.2±0.68 GPa and 2.1±0.31 GPa for Teak (Figure 16).
Whereby an estimated decline rate of 5-7% in E_{dyn} and 8-11% in E_{app} was found. A tendency of 3% more decrease in Cypress than in Teak was documented. The ultrasonic wave velocity and E_{dyn} were sensitive to environmental conditions and changed as a function of species and exposure time as it was previously shown in Figure 15.

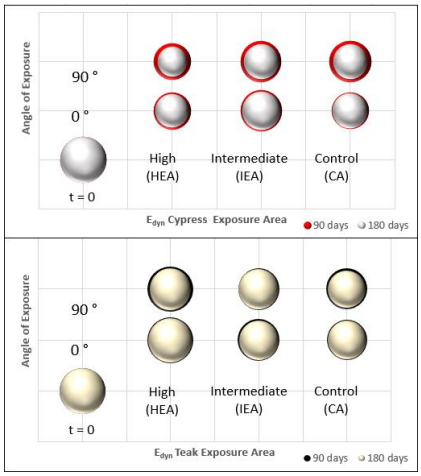

Figure 16. *E_{dyn} decreased of Cypress and Teak during 180 day of exposure in 3 exposure sites.*

Figure 17 illustrates the stronger decreasing in HEA than in intermediate and non-acidic atmospheres.
Regarding the exposure position, a slight variation was observed, this decreasing was higher in horizontal position than in vertical position, which can be attributed to the fact that the specimens in the horizontal position remain wet for longer period, and in vertical position fibers orientation allows drainage with less non-ligate water.
It was found that Cypress E_{app} in average decreased even 2.7 Gpa in HEA, while Teak E_{app} 2.6 Gpa (Figure 17), contrary that IEA and CA whereas the decreasing occurred with minor incidence.

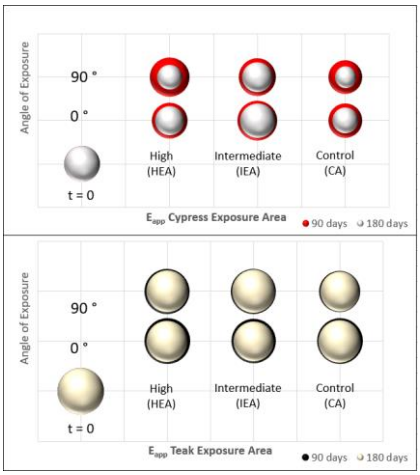

Figure 17. *E_{app} decreased of Cypress and Teak during 180 day of exposure in 3 exposure sites.*

In this regard, it is essential to mention that for the HEA, the SO_2 acid pollutant was detected in less than 0.5 ppm during a significant part of the period. However, an important acid exposition was detected during the study time. This acidic atmosphere remained between 0.5ppm and 1 ppm of SO_2 concentration, which can be express as an acid accumulation in the material of this pollutant during 1.26 days of continuous exposure (Figure 14).
It should also be noted that there were values as maximum data quantified up to 4.0 ppm in several measurements near the volcano.
Even though the reduction in the elastic modulus is appreciable in both species, it is clear that Teak is more resistant to the environment than the softwood, Cypress, unless so far this report had been carried out. Therefore, the degradation impact shall be more noticeable in three years to comply with this methodology.

3.4 CHEMICAL COMPOSITION

The results of the fiber chemical characterization after 90 days of exposure are reported in Table 4. It was found that Cypress has more lignin than Teak and contains more hemicellulose. The hemicellulose content has been reported as one of the sensitive carbohydrates to degradation by UV radiation [59]. The oxidation can increase due to acid environments, contributing to a lower mechanical performance of the material.

Table 4: *Preliminary results of fiber content. Specimens before be exposed.*

Wood Type	Holocell. (%)	Lignin (%)
Cypress	65.10 ±0.21	28.80±0.23
Teak	56.80±0.12	23.50±0.27

On the hand, the fiber characterization was carried out using a different technique base on the carbohydrate degradation. As reported in the literature it was found that TGA is faster and easier method to implement and less expensive than wet traditional analyzes and allows the determination of hemicelluloses and α-cellulose content of biomass samples with similar or improved precision [60]. Due to these advantageous features, it is recommended to perform assays using this technique as a compliment to this methodology. An example of this result can be observed in Figure 18.

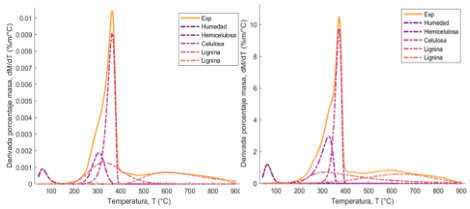

Figure 18: *Derivative curves DTGA of Teak. and Cypress.*

3.5 COLOR CHANGES EVALUATION

Regarding the color composition analysis, in both species during the first two months of exposure in HEA, an increase in color parameter of lightness (L*) was observed. While in the following months a decrease (darkening) was appreciated. In Cypress, specimens exposed in horizontal position a linear tendency was detected. Whilst color change behavior in specimens exposed in vertical position appears to be oscillatory, this behavior seems to be maintained over time.

Teak specimens had a linear darkening from month 2 to 4, then a trend towards a slight increase in luminosity was observed in month 5 and it decreases again in month 6.

Both species showed a more significant color change in horizontal position than in vertical position, which is consistent with the microscopic changes in the material.

In literature color change chance perception is categorized in 5 levels: 1) not perceived ($0<\Delta E^*<1.5$); 2) barely perceived ($1.5<\Delta E^*<3.0$); 3) perceived ($3.0<\Delta E^*<6.0$); 4) quite noticeable ($6<\Delta E^*<12.0$); and 5) completely changed ($\Delta E>12.0$) [61].

According to that categorization. In Cypress the color change in vertical position completely changed at month 2 and in vertical position at month 4. Teak for the color completely changed in both positions at month 2. It is important to consider that month 2 (of exposure) corresponded to October and November, and October was the rainiest month of the year.

It was noted that in Teak (considered as a dark wood) it tended to lighten in month 3 and Cypress (light wood) it tended to darken in month 4. After month 4 the color changes were less abrupt and the wood coloration turned gray in both species and three exposure areas. In Figure 19 an oscillating color change between month 4 and 6 can be noticed.

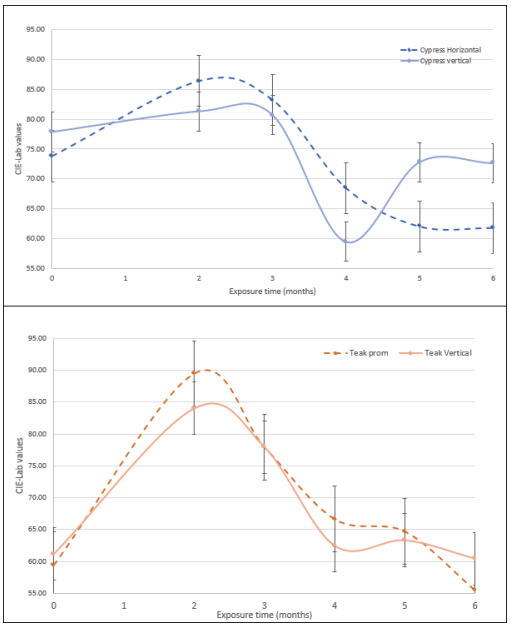

Figure 19: *CIE-Lab color composition and color change during initial 6 months of exposure. Before exposure month 0 to month 6 Cypress (up) and Teak (down).*

Figure 20: *Color change appearance during initial 6 months of exposure. From month 0 to month 6 Teak (left) and Cypress (right). (e), day month 6 (f) for Teak (left) and Cypress (right).*

It must be considered that the average irradiation was 312.4976 W/m^2 and maximum average was 542.2500 W/m^2 average low was 73.2941 W/m^2 in HEA (figure 22, left), and according to historical data months with the lowest UV index were May, August and November (UV Index 5). The rest of the months of the year correspond to the highest UV index (UV Index 6) as[62].

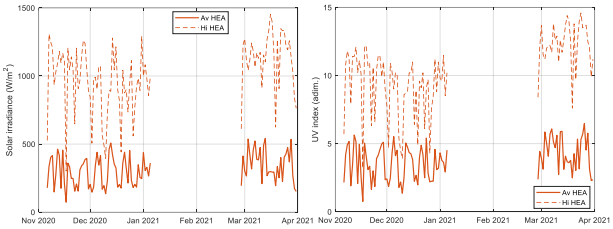

Figure 22. *Irradiation (W/m2) and UV Index respectably in HEA to evaluate acidic atmosphere for six months period.*

The Teak color change associated with changes in dynamic E_{dyn} and ultrasonic wave velocity evaluation had been studied by other authors and agreement with preliminary reports was found [63]. In the case of

Cypress, no references have been found allowing comparisons.

Due to surveys and consultations that have been made to experts on this subject and to local residents and visitor, this study also confirmed that color changes measurements are important due to the impact of perceptual factors on the reliability of the material [64].

4 CONCLUSIONS

- A methodology to analyze the degradation and performance of structural timber in acidic atmospheres was successfully established.
- It was obtained a decline rate of 5-7% approximately in E_{dyn} and 8-11% in E_{app}, respectively, due to timber degradation in acidic atmospheres.
- E_{app} decreased 2.43% more than E_{dyn} in horizontal position than vertical position, and 2.71% more in Cypress than in Teak. Both modules significantly decreased in HEA compared to IEA and CA.
- The acidic atmosphere remained between 0.5ppm and 1 ppm of SO_2 gas concentration, with some higher concentration points during the study period. It affected the rain, dropping-down the pH to 3.92. Thus, it is anticipated the potential influence of the volcanic environment that can act in the wood materials.
- Significant modification of color changes on average ΔE 12.67 for Cypress and ΔE 17.24 for Teak were registered; further analysis is required to understand the correlation of color changes with other factors.
- The challenge of not isolating degrading agents' contributions must be considered since they are according to the campaigns (exposure periods) with the expected environmental conditions variability. For that reason, research data leading to aging, weathering, degradation, or decay, from this research cannot be easily compared to another context. Consequently, more control to complement with essays in a degradation chamber for further investigation dynamic mechanical analysis DMA may be considered.

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