Boštjan Lesar*, Miha Humar, Florjan Osvald[1]

Colour Changes of Weathered Wood Surfaces Before and After Treatment with Iron (II) Sulphate

Promjena boje površina drva izloženih vremenskim utjecajima prije i nakon tretmana željezovim (II) sulfatom

ORIGINAL SCIENTIFIC PAPER
Izvorni znanstveni rad
Received – prispjelo: 10. 8. 2023.
Accepted – prihvaćeno: 8. 11. 2023.
UDK: 674.07
https://doi.org/10.5552/drvind.2024.0148

ABSTRACT • *Outdoor wood is exposed to various factors that can be described as weathering and cause the wood to grey. The ageing processes can vary greatly depending on the exposure. Parts of wood that are not exposed to external factors, e.g. under the overhanging, are less exposed, and the weathering process is therefore slower. This can be accelerated by solutions based on iron ions. In this way, the wood greys quickly and evenly. However, after iron treatment, the colour also depends on the previous exposure of wood to weathering. In our study, the colour change was observed as a function of weathering time. Before treatment, the samples were exposed to outdoor weathering for different periods of time and then treated with a 5 % solution of pure iron (II) sulphate and commercial iron (II) sulphate. It was determined that the pre-weathering time affected the final colour change, as the samples exposed for five weeks before treatment have comparable colour to naturally weathered wood. At the beginning of exposure, iron (II) sulphate limits mould growth, but after two months, staining fungi develop on the treated samples as well. The growth of blue stain fungi on the treated samples did not significantly affect the colour and visual appearance of the wood treated with iron-based solutions.*

KEYWORDS: *ageing; weathering; iron (II) sulphate; colour change; blue stain fungi*

SAŽETAK • *Drvo za vanjsku uporabu izloženo je različitim čimbenicima koji se mogu opisati kao vremenski utjecaji, a uzrokuju sivljenje drva. Procesi starenja mogu uvelike varirati ovisno o izloženosti drva tim utjecajima. Na dijelovima drva koji nisu izravno izloženi vanjskim čimbenicima, npr. ispod prevjesa, proces starenja je sporiji. Taj se proces starenja može ubrzati otopinama na bazi iona željeza tako da drvo brzo i ravnomjerno posivi. Međutim, boja nakon tretmana željezom također ovisi o prethodnoj izloženosti drva vremenskim utjecajima. U ovom smo istraživanju promatrali promjenu boje kao funkciju trajanja izloženosti drva vremenskim utjecajima. Uzorci su prije tretmana različito vrijeme bili izloženi vremenskim utjecajima, a zatim su tretirani 5 %-tnom otopinom čistog željezova (II) sulfata i komercijalnog željezova (II) sulfata. Utvrdili smo da je prvotna izloženost vremenskim uvjetima utjecala na konačnu promjenu boje jer su uzorci koji su bili pet tjedana izloženi vremenskim utjecajima prije tretmana imali sličnu boju kao i prirodno drvo izloženo vremenskim utjecajima. Na početku izlaganja željezov (II)*

* Corresponding author
[1] Authors are researchers at University of Ljubljana, Biotechnical Faculty, Department of Wood Science and Technology, Ljubljana Slovenia. https://orcid.org/0000-0003-3965-3458; https://orcid.org/0000-0001-9963-5011

sulfat ograničavao je razvoj plijesni, ali su se nakon dva mjeseca izlaganja i na tretiranim uzorcima drva razvile gljive promjene boje. Razvoj gljiva plavila na tretiranim uzorcima nije znatnije utjecao na boju i vizualni izgled drva tretiranog otopinama na bazi željeza.

KLJUČNE RIJEČI: *starenje; izlaganje vremenskim utjecajima; željezov (II) sulfat; promjena boje; gljive plavila*

1 INTRODUCTION
1. UVOD

Outdoor wood is exposed to various weather conditions that cause the wood to turn grey (Feist, 1988; Williams, 2005; Humar *et al*., 2020; Kropat *et al*., 2020; Zabel and Morrell, 2020; Altay, 2023). The weathering processes can vary greatly depending on the exposure (Nejad and Cooper, 2017). Parts of wood that are not exposed to wetting, e.g. under overhang, are much less exposed to weathering factors. Therefore, the weathering processes are slower (Zimmer *et al*., 2018), which results in an uneven colour of wooden facades. Many customers do not like such an uneven visual appearance of wooden façades and other vertical surfaces (Zimmer *et al.* 2018). Uneven greying affects the aesthetic properties of buildings with wooden facades or other wooden objects exposed outdoors. This is a common reason for choosing other materials such as polymers and minerals that maintain a uniform colour over a longer period of time. Such material changes have an impact on lower wood consumption and the entire wood supply chain. One of the possible solutions for a more even colour is the use of pigmented coatings or wood-transparent coatings with UV absorbers. However, a coating has one major disadvantage: it requires regular maintenance (Nejad and Cooper, 2017), which is expensive and time-consuming. On the other hand, it was already proven that treatment of wooden facades, with an ion-based solution, results in more even and faster greying and prevents uneven discolouration of the building claddings (Hundhausen *et al*., 2020; Lesar and Humar, 2022). Iron-treated wood is also suitable for mimicking ancient wood (Høibø and Nyrud, 2010; Sun *et al*., 2023). However, the colour of wood treated with iron ions also depends on whether the wood has previously been exposed to weathering or has been aged by UV light (Nejad and Cooper, 2017; Zimmer *et al*., 2018). In the case of spruce wood, for example, wood freshly treated with iron (II) ions takes on a slightly greener hue compared to naturally aged spruce surface. The colour can even turn brown, if the wood is exposed only to solar radiation and not precipitation or condensation of surface water (Hundhausen *et al*., 2020). The finding of Hundhausen and co-workers in 2020 show that staining proceeds also on wood without the presence of wood extractives, possibly due to the oxidization of iron (II) that is promoted by photo-induced phenoxyl and ketyl radicals from photolysis of lignin ether bonds. Respective findings explain colour differences of iron (II) sulphate-treated façades that are partly protected by, for instance, a roof overhang.

The effect of iron (II) sulphate on greying is most notable in the initial phases after treatment (Lesar and Humar, 2022). The presence of transparent biocides (e.g. boric acid, quaternary ammonium compounds) had no effect on the colour of wood treated with iron (II) sulphate, nor on iron leaching from treated wood outdoors. However, the biocides positively affect the durability of the treated wood (Lesar and Humar, 2022). Positive effects on decay resistance and mould growth were also confirmed during hydrothermal treatment with different iron compounds (Aleinikovas *et al*., 2021). However, after several months of outdoor exposure, blue stain fungi develop on the surface of wood treated with iron (II) sulphate as well. On the other hand, iron (II) sulphate protects the wood surface exposed to weathering. The surface of the control samples was much more damaged than that of the treated samples (Lesar and Humar, 2022). Long-term outdoor weathering also shows that iron-treated wood is not damaged by wasps as untreated wood (Lesar *et al*., unpublished results) (Figure 1).

This study is a follow up of the paper: Performance of Iron (II)-Sulphate-Treated Norway Spruce and Siberian Larch in Laboratory and Outdoor Tests (Lesar and Humar, 2022). The aim of this work is to elucidate the importance of the pre-treatment prior to iron (II) sulphate impregnation. The key objective is to ensure that the colour of the treated wood is comparable to the colour of naturally weathered wood. In this study, untreated wood was exposed to outdoor weathering for various periods of time. Then the samples were treated with 5 % solution of iron (II)sulphate. Afterwards, the samples were exposed to the weathering again, and the colour changes, mould growth and other surface properties were assessed.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

2.1.1 Wooden material
2.1.1. Drvni materijal

The specimens used for the study were made of Norway spruce (*Picea abies* (L.) H. Karst) and European larch (*Larix decidua* Mill.). The dimensions of

Figure 1 Model façades exposed outdoors for 5 years. Above red line control samples, below iron (II) sulphate treated wood. Left façade exposed to nord, right façade exposed to south. Surface damage by wasps is clearly visible on control samples.
Slika 1. Modeli fasada pet godina izloženih vanjskim utjecajima. Iznad crvene crte nalaze se kontrolni uzorci, a ispod nje je drvo tretirano željezovim (II) sulfatom. Lijeva fasada bila je izložena prema sjeveru, a desna prema jugu. Na kontrolnim su uzorcima jasno vidljiva oštećenja površine, uzrokovane osama.

the specimens were 40 mm × 110 mm × 10 mm, with the radial orientation of the fibres in the radial direction (45±15)°. In total, 85 specimens were prepared. Of these, 45 were spruce samples, and 40 larch samples.

2.1.2 Treatment solutions
2.1.2. Otopine za tretiranje

The Norway spruce and larch specimens were treated with a 5 % iron (II) sulphate solution in distilled water. Two different sources of iron (II) sulphate were used. The concentration of the iron (II) sulphate solution was chosen based on previous studies (Lesar and Humar, 2022). Initially, iron (II) sulphate heptahydrate ($FeSO_4 \times 7H_2O$) (IS) for laboratory purposes in the form of blue-green crystals prepared by Carlo Erba was used. For comparison with the laboratory-grade iron (II) sulphate, a solution was also prepared with commercial, iron (II) sulphate with purity > 98 % and an iron (Fe) content of 20 %. (Agrolit, Slovenia). For commercial purposes, the name green vitriol (GV) was used. The green vitriol was in the form of granules. A solution of the commercial green vitriol (GV) was prepared according to the same procedure as the iron (II) sulphate solution.

2.2 Methods
2.2. Metode

2.2.1 Treatment
2.2.1. Tretman

The test specimens were treated by immersing each specimen in a solution of laboratory grade iron (II)sulphate or green vitriol for 10 seconds. After the treatment, the uptake of the solution was determined gravimetrically. The samples were then dried for 24 hours under laboratory conditions. The samples were then exposed outdoors.

2.2.2 Outdoor exposure
2.2.2. Vanjsko izlaganje

After conditioning, the samples were exposed outdoors at the test field site on special stands. The samples were exposed on the premises of the Department of Wood Science and Technology in Ljubljana, Slovenia (46°02'55.7 "N 14°28'47.3 "E, height above sea level 293 m).

2.2.3 Pre-weathering before iron (II) sulphate treatment
2.2.3. Predizlaganje vremenskim utjecajima prije tretmana željezovim (II) sulfatom

The Norway spruce and larch test specimens were placed on a stand at an angle of 45° and oriented towards the south (Figure 2). On 3 May 2022, the test specimens were exposed to outdoor weathering for 1 to 5 weeks. Each week, five samples of each species were isolated from the test plot and stored in a dark dry space. After the ageing was completed (after five weeks), the samples were scanned with an A3 2400S flatbed scanner. The colour was determined on scanner pictures with the programme Corel Photo PAINT 8 in the CIE Lab colour space. In the figure, the entire surface of each sample was selected, and the colour was measured using the tool in the software and all three CIE Lab components (L^*, a^*, b^*) were extracted. The samples were then treated with solutions of iron (II) sulphate or green vitriol as described in chapter 2.2.1, conditioned for 24 hours and exposed to the test field for a further 21 weeks. At this time, untreated control

Figure 2 Stand with samples facing south at exposure angle of 45°
Slika 2. Stalak s uzorcima izloženima prema jugu pod kutom od 45°

samples of both wood species, which had previously been kept in the dark, were also exposed outdoors alongside other treated samples.

Before and during exposure, the samples were scanned, and the colour was determined as described. Microsoft Excel was used to calculate the colour difference. The total colour difference Δ*E* (Eq. 1) between a reference colour (L^*0, a^*0, b^*0) and a target colour (L^*1, a^*1, b^*1) in the CIE Lab colour space is calculated by determining the Euclidean distance between two colours.

In addition to UV radiation, blue stain and mould fungi also contribute significantly to the discolouration of wood in outdoor applications. Therefore, as part of the study, the presence of blue stain and mould fungi on the samples using an Olympus DSX1000 digital microscope was determined as well. The study was conducted by scanning 1 to 2 representative samples of each treatment after 4, 8, 12, 21 weeks of weathering. The presence of blue stain fungi was assessed in both tests.

2.2.4 Weather data
2.2.4. Podatci o vremenu

The weather also influences the colour change of wood that lies outdoors. For this purpose, weather data were obtained from the archives of the Slovenian Environment Agency (ARSO, 2022). The data came from the ARSO monitoring station, Bežigrad, near the field test site. The amount of precipitation per day, the average temperature in °C and sunshine hours per day were the focus of our interest. For this purpose, archived data from the website of the Slovenian Environmental Agency (ARSO) were obtained for the duration of our experiment between 1 May 2022 and 3 November 2022.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Solution uptake
3.1. Upijanje otopine

The treatment was carried out by immersing each sample in the solution for 10 seconds and then placing the sample on a grid where the excess solution was drained off before weighing. The Norway spruce samples have an average uptake of 32.9 kg/m^3. Pre-weathering has a positive influence on the solution uptake. The highest uptakes were observed at the samples treated, aged for 2 and 4 weeks. On the other hand, the lowest uptake was recorded in spruce samples treated with iron (II) sulphate and aged for 1 week. It should be noted that the differences were not very prominent. However, the positive effect of the weathering on solution uptake is mainly a result of the microcracks on the surface, as reported by (Keržič and Humar, 2022). The larch samples had approximately 10 kg/m^3 lower up-

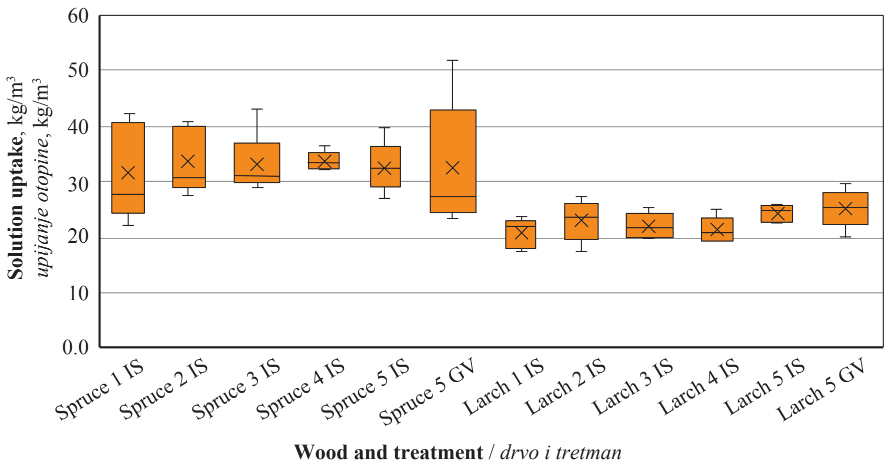

Figure 3 Influence of pre-weathering on solution uptake of spruce and larch wood (IS- iron (II) sulphate; GV- green vitriol). Numbers are weeks of pre-weathering.
Slika 3. Utjecaj predizlaganja smrekovine i ariševine vremenskim uvjetima na upijanje otopine (IS – željezov (II) sulfat; GV – zeleni vitriol). Brojevi označavaju tjedne predizlaganja vremenskim utjecajima.

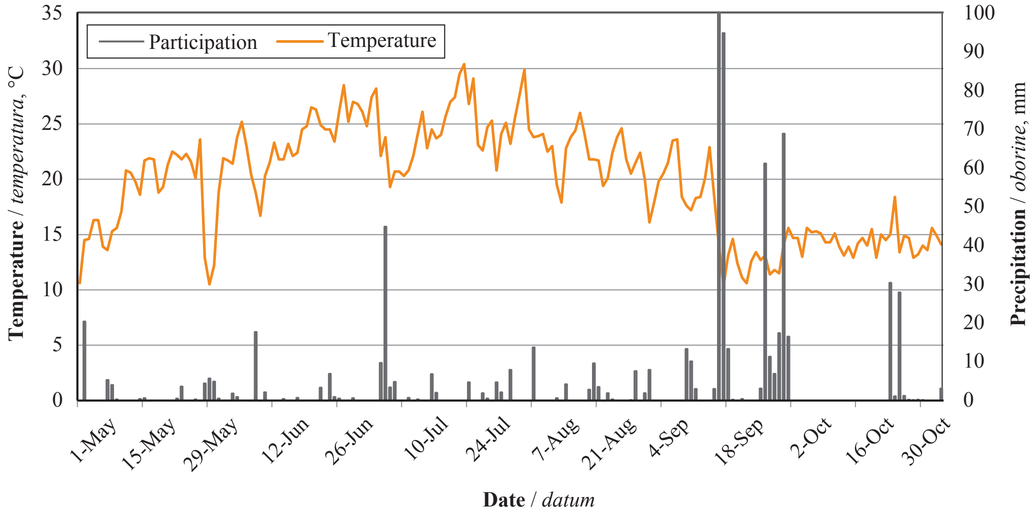

Figure 4 Average daily temperature and daily amount of precipitation from 1 May to 3 November 2022
Slika 4. Prosječna dnevna temperatura i dnevna količina oborina od 1. svibnja do 3. studenog 2022.

take than Norway spruce samples with an average uptake of 22.8 kg/m^3 (Figure 3). This can be mainly attributed to the different densities of the wood (larch has a higher density), as well as porosity and water-permeability of wood. The solution uptakes of various specimens are comparable, although the wood is weathered for different periods of time. The differences are believed to be merely due to the variability of the wood and described microcracks. Similar solution uptakes were reported in previous studies (Lesar and Humar, 2022; Lesar *et al*., 2022).

3.2 Weather data
3.2. Vremenski podatci

As already reported, weather conditions influence the weathering of wood (Feist, 1988; Evans *et al*., 1996; Williams, 2005; Gobakken and Høibø, 2011). Samples were exposed to weathering between 3 May and 3 November 2022. In this period, the average temperature was 19.8 °C, and average precipitation 4.2 mm and average daily solar radiation 7.7. hours (Figure 4 and Figure 5). In the observed period, there were 75 days with precipitation higher then 0.1 mm and the total rainfall in the respective period was 779.9 mm. The highest daily precipitation of 156.9 mm was reported on 16 September.

3.3 Pre-weathering before iron (II) sulphate treatment
3.3. Predizlaganje vremenskim utjecajima prije tretmana željezovim (II) sulfatom

Untreated samples were pre-weathered from 1 to 5 weeks before iron treatment. Total colour change increased with increasing weathering duration for both

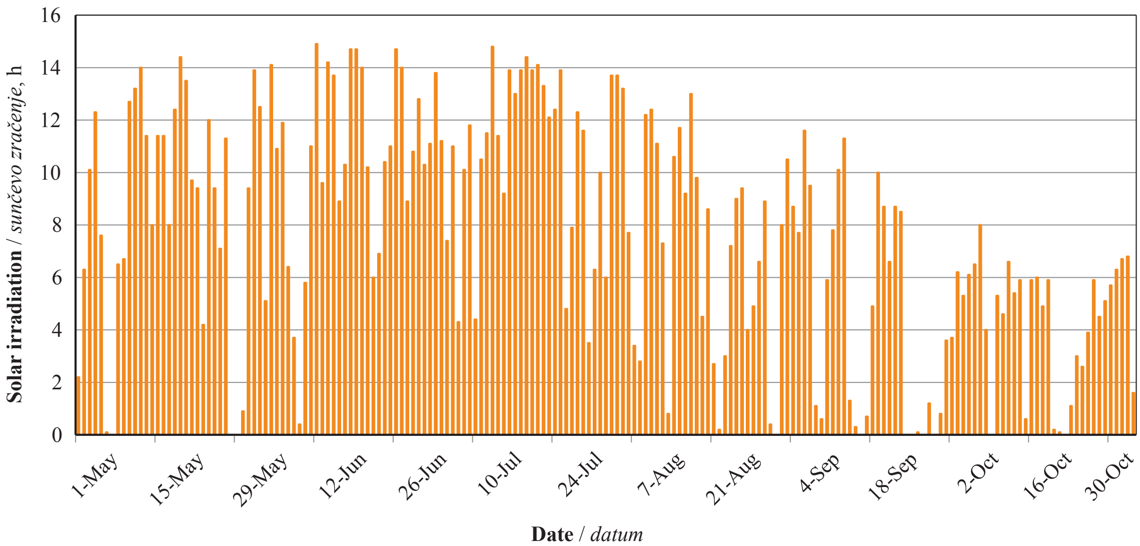

Figure 5 Duration of solar irradiation from 1 May to 3 November 2022
Slika 5. Trajanje Sunčeva zračenja od 1. svibnja do 3. studenog 2022.

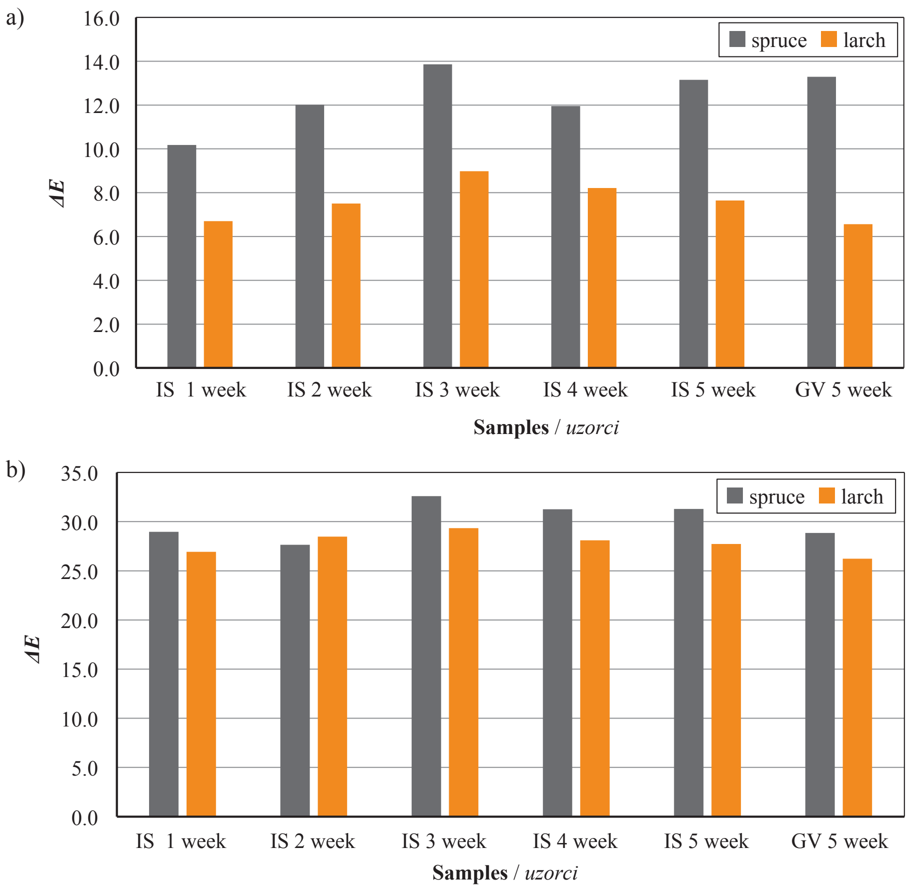

Figure 6 Colour change of Norway spruce and larch samples (a) exposed to weathering from one to five weeks (b) after weathering and treatment with iron (II) sulphate (IS) and green vitriol GV)
Slika 6. Promjena boje uzoraka obične smrekovine i ariševine (a) izloženih vremenskim utjecajima od jednog do pet tjedana i (b) nakon izlaganja vremenskim utjecajima i tretmana željezovim (II) sulfatom (IS) i zelenim vitriolom (GV)

wood species. In general, higher colour changes were determined on Norway spruce wood than on larch wood, predominately as the initial colour of spruce wood was lighter. The most prominent colour change appeared after the first week of outdoor exposure. Namely, colour change (ΔE^*) measured on Norway spruce samples was 10.2, and 6.7 on larch wood (Figure 6a). Pre-weathering of spruce samples and only minor differences for larch samples, exposed to weathering for 5 weeks and later treated with iron (II) sulphate or green vitriol, were observed. Results are in line with previous studies (George *et al*., 2005; Niklewski *et al*., 2022; Podgorski *et al*., 2009).

The most prominent colour changes occurred after treatment with iron (II) sulphate and green vitriol. Colour measurement was performed only one day after the treatment, when the samples were dried. For Norway spruce samples, ΔE^* was 27.6 to 32.6. and for larch wood from 26.2 to 29.3 (Figure 6b). As already observed in a previous study (Lesar and Humar, 2022), colour change of larch samples was higher compared to Norway spruce samples. Larch samples become darker than spruce ones.

However, when the samples are exposed to outdoor weathering, the colour change is the most prominent between the first and second week for both wood species used. This phenomenon was not affected by pre-weathering and iron solution used; it can rather be attributed to the action of iron (II) sulphate on the wood (Figure 7 and 8). Similar patterns of colour change were observed in Norway spruce and larch samples. Comparing Norway spruce and larch samples, it can be seen that the colour change of Norway spruce samples is, on average, 4 units higher than that of larch samples. This can be attributed to the fact that larch is inherently darker compared to spruce, which lowers the colour change. After the third week, the colour change is more uniform. This shows that the most apparent change in colour occurs in the first two weeks of exposure after the iron ion treatment. The samples aged for one week and treated with iron (II) sulphate had the highest colour change, which can be attributed to pre-exposure to UV and rain for the shortest time. On average, the colour change of samples pre-weathered for 5 weeks is 8 units lower compared to samples pre-weathered for 1 week. This can be attributed to the fact that the more the samples have been pre-weathered, the more prominent colour change occurs before treatment with IS and GV solutions, respectively. The colour changes of the samples pre-weathered for 5 weeks are very uniform

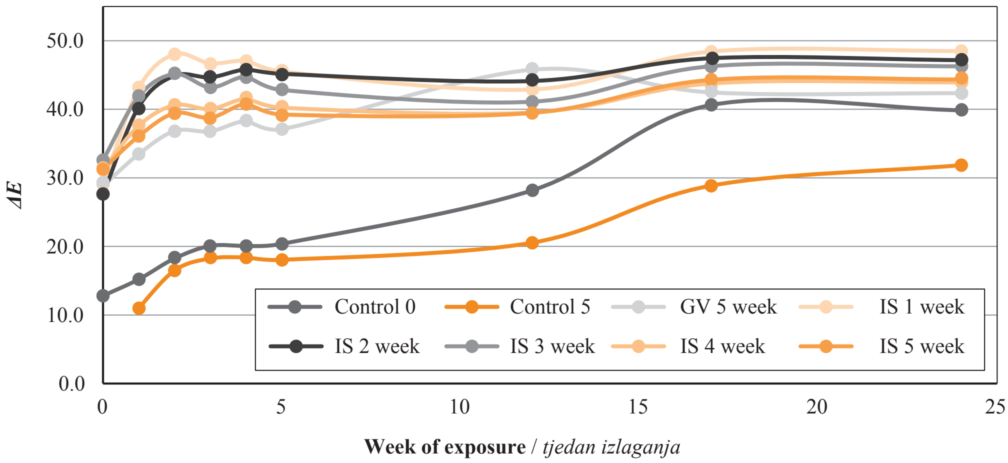

Figure 7 Colour change (Δ*E**) of control and iron (II) sulphate and green vitriol treated Norway spruce wood samples, exposed outdoor at 45° to south
Slika 7. Promjena boje (Δ*E**) kontrolnih uzoraka smrekovine tretiranih željezovim (II) sulfatom i zelenim vitriolom izloženih na otvorenome i prema jugu pod kutom od 45°

after the third week of exposure, as the additional colour change varies only by two units. The colour change of the control samples also shows a maximum colour change in the first three week of exposure, followed by a slight increase of colour change till the end of the experiment. However, none of the control samples exposed at the beginning of May or 5 weeks later did not reach the exact colour change as the treated samples. Untreated samples would require additional time to reach the final appearance.

3.4 Visual appearance of weathered control and treated samples
3.4. Vizualni izgled izloženih kontrolnih i tretiranih uzoraka

Figures 9 and 10 show the visual changes in Norway spruce and larch samples exposed outdoors. In the first row there is an untreated control sample of Norway spruce or larch that has been pre-weathered for 5 weeks. This is followed by the samples pre-weathered for 1 week and treated with a 5 % iron (II) sulphate solution, the samples pre-weathered for 3 weeks and treated with a 5 % IS solution, and the samples pre-weathered for 5 weeks and treated with the same 5 % IS solution, and the sample treated with 5 % (GV) green vitriol is in the last row. All samples were exposed for 21 weeks after treatment.

Figures 9 and 10 confirm the results of the colour change measurements. The control sample shows a distinct colour change until the second week of exposure, after which the colour remains fairly uniform until the 12th week when further distinct colour changes occur. However, for the samples that were pre-weathered and treated with iron-containing solutions, a visible colour change was observed shortly after treatment. The one-week-pre-weathered sample is darker and browner than the three- or five-weeks pre-weathered samples. The five-week pre-weathered samples show even shades of grey. It was established that the one-week pre-weathered samples become

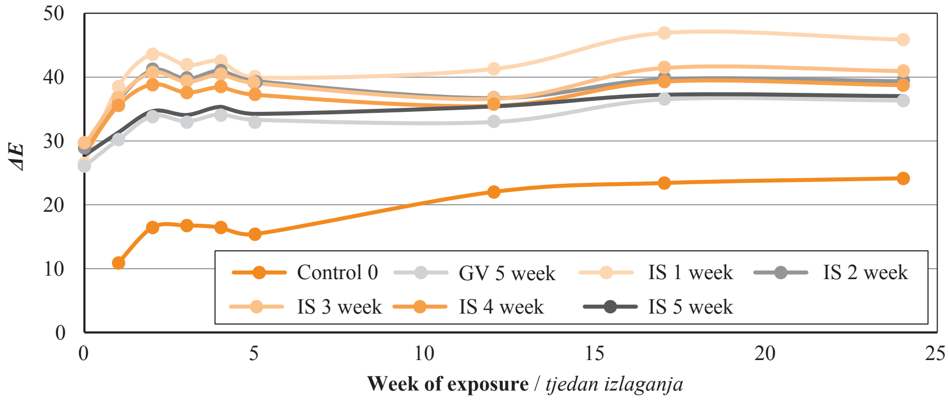

Figure 8 Colour change (Δ*E**) of control and iron (II) sulphate and green vitriol treated larch wood samples, exposed outdoor at 45° to south
Slika 8. Promjena boje (Δ*E**) kontrolnih uzoraka ariševine tretiranih željezovim (II) sulfatom i zelenim vitriolom, izloženih na otvorenome i prema jugu pod kutom od 45°

Figure 9 Visual appearance of control and iron treated Norway spruce wood samples. The first column shows wood samples before the test, the second column shows samples aged outdoors for 1, 3 and 5 weeks, the third column shows samples immediately after treatment with iron (II) sulphate (IS) and green vitriol (GV), the fourth to eleventh columns show colour changes during outdoor exposure from week 1 to week 24.

Slika 9. Vizualni izgled kontrolnih uzoraka i uzoraka smrekovine tretiranih željezom. Prvi stupac prikazuje uzorke drva prije ispitivanja, u drugom su stupcu uzorci izloženi na otvorenome jedan, tri i pet tjedana, treći stupac predočuje uzorke neposredno nakon tretiranja željezovim (II) sulfatom (IS) i zelenim vitriolom (GV), a uzorci od četvrtog do jedanaestog stupca pokazuju promjene boje tijekom vanjskog izlaganja od 1. do 24. tjedna.

browner, while the five-week pre-weathered samples become grey. This indicates that the UV-induced radical changes continue long after initiation, although wood was stored in a dark place. The five-week pre-weathered sample achieves a better approximation to the colour of naturally aged wood. For the five-week pre-weathered samples, there was only a slight difference in colour between IS and GV treatment. For

Figure 10 Visual appearance of control and iron treated larch wood samples. The first column shows wood samples before the test, the second column shows samples aged outdoors for 1, 3 and 5 weeks, the third column shows samples immediately after treatment with iron (II) sulphate (IS) and green vitriol (GV), the fourth to eleventh columns show colour changes during outdoor exposure from week 1 to week 24.

Slika 10. Vizualni izgled kontrolnih uzoraka i uzoraka ariševine tretiranih željezom. Prvi stupac prikazuje uzorke drva prije ispitivanja, drugi stupac uzorke izložene u vanjskom prostoru jedan, tri i pet tjedana, u trećem su stupcu uzorci neposredno nakon tretiranja željezovim (II) sulfatom (IS) i zelenim vitriolom (GV), a uzorci od četvrtog do jedanaestog stupca pokazuju promjene boje tijekom vanjskog izlaganja od 1. do 24. tjedna.

larch wood, the difference was slightly more prominent. It is believed that this difference is mainly related to the more prominent colour variations in fresh wood samples.

If the samples of spruce and larch are compared, the relation between colour and ageing can be seen in both species. Although larch samples are clearly darker than spruce samples, there is a clear correlation between ageing and colour change in both species analysed. This can be observed in specimens that have been pre-weathered for one week showing more browning and those pre-weathered for five- weeks showing more greying. Another reason for the darker colour of larch samples is that they have a higher proportion of extractives that react with iron (Hundhausen, 2020).

3.5 Observation of blue stain fungi
3.5. Promatranje gljiva plavila

During the experiment, the presence of blue stain fungi and moulds on the surface was monitored. The analysis was performed on the exposed control, IS-treated and GV-treated samples. The sample surfaces were observed with a digital microscope. The measure-

Figure 11 Observation of mould growth on Norway spruce wood samples. Columns show wood samples exposed outdoors for 4, 8, 12 and 21 weeks after treatment. The first raw control samples (0) were exposed at the same time as the treated samples, the second raw control samples were exposed for 5 weeks before treatment, raw samples 3, 4, 5 were aged for 1, 3 and 5 weeks before treatment with iron (II) sulphate (IS) and raw samples 6 for five weeks before treatment with green vitriol (GV). The bar is 400 µm long.
Slika 11. Promatranje razvoja plijesni na uzorcima obične smrekovine. Stupci prikazuju uzorke drva izložene na otvorenome 4, 8, 12 i 21 tjedan nakon tretmana. Prvi netretirani kontrolni uzorci (0) izloženi su u isto vrijeme kad i tretirani uzorci, drugi netretirani kontrolni uzorci izloženi su pet tjedana prije tretmana, netretirani uzorci 3., 4. i 5. izlagani su jedan, tri i pet tjedana prije tretmana željezovim (II) sulfatom (IS), a netretirani uzorci 6. izlagani su pet tjedana prije tretmana zelenim vitriolom (GV). Žuta je linija dugačka 400 µm.

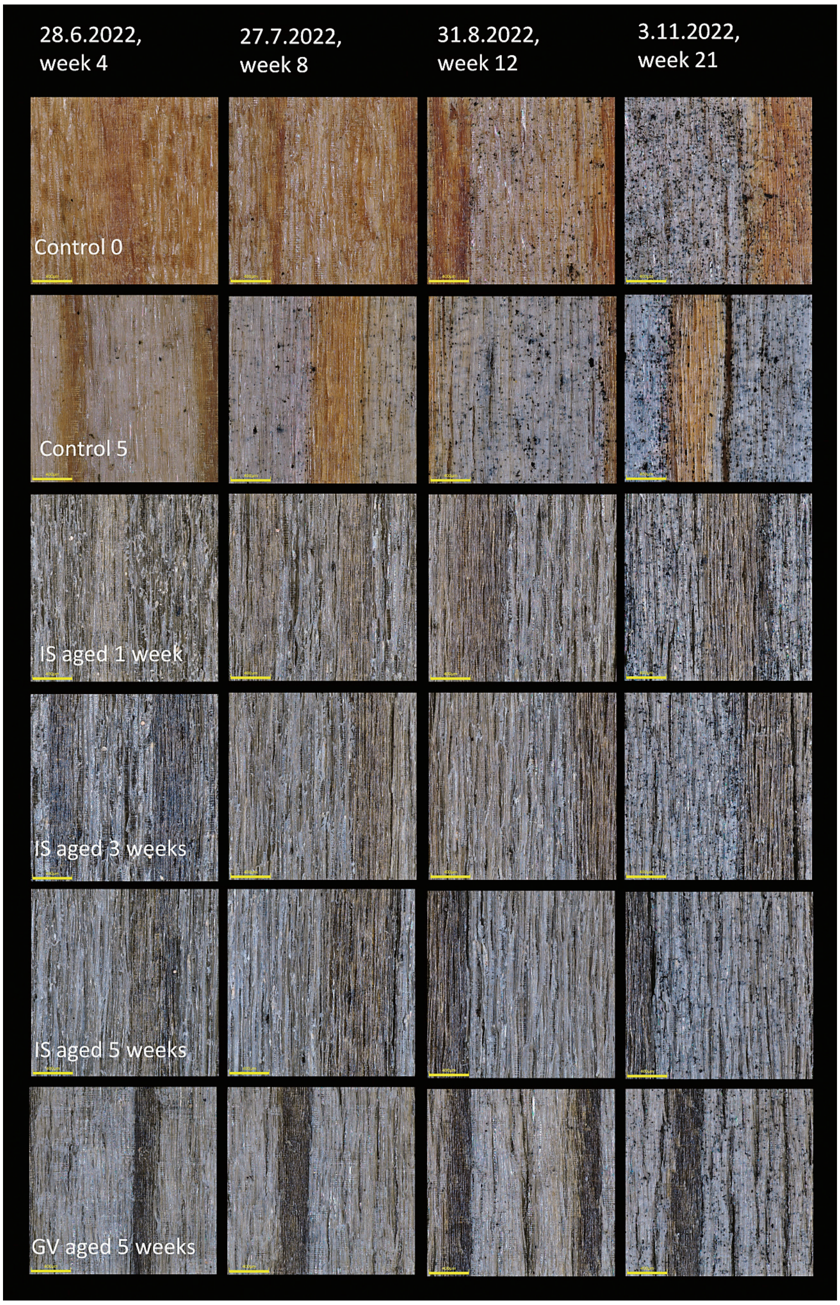

Figure 12 Observation of mould growth on larch wood samples. Columns show wood samples exposed outdoors for 4, 8, 12 and 21 weeks after treatment. The first raw control samples (0) were exposed at the same time as the treated samples, the second raw control samples were exposed for 5 weeks before treatment, raw samples 3, 4, 5 were aged for 1, 3 and 5 weeks before treatment with iron (II) sulphate (IS) and raw samples 6 for five weeks before treatment with green vitriol (GV). The bar is 400 µm long.

Slika 12. Promatranje razvoja plijesni na uzorcima ariševine. Stupci prikazuju uzorke drva izložene na otvorenome 4, 8, 12 i 21 tjedan nakon tretmana. Prvi netretirani kontrolni uzorci (0) izloženi su u isto vrijeme kad i tretirani uzorci, drugi netretirani kontrolni uzorci izloženi su pet tjedana prije tretmana, netretirani uzorci 3., 4. i 5. izlagani su jedan, tri i pet tjedana prije tretmana željezovim (II) sulfatom (IS), a netretirani uzorci 6. izlagani su pet tjedana prije tretmana zelenim vitriolom (GV). Žuta je linija dugačka 400 µm.

ments were performed after 4, 8, 12 and 21 weeks of outdoor exposure.

The figures (Figure 11 and 12) show the presence of blue stain fungi on the aged samples of Norway spruce and larch. The samples that were pre-weathered before treatment, control-5 and control-0 were exposed at the test site on the same day as the treated samples. The samples of control-5 showed the first signs of blue stain fungi already after nine weeks (5 weeks pre-weathering + 4 weeks of weathering), in both wood species. After 8 weeks, the first signs of blue stain fungi were also observed on the control-0 larch samples, that were not pre-weathered, which is comparable to control-5 samples weathered for 4 weeks. On the other hand, the first signs of blue stain fungi were observed on the control-0 Norway spruce samples after 12 weeks of weathering. The strongest growth of blue stain fungi occurred between week 12 and 21 for both wood species. These changes on the surface were also detected by colour measurements (Figure 7 and 8) and the visual appearance of the surfaces (Figure 9 and 10). Such pronounced growth was to be expected as it occurred during the autumn months with a lot of rain (Figure 4). This is in line with other research stating that the colour of the wood fluctuates due to the stronger growth of blue stain fungi in the autumn months (Kržišnik *et al*., 2018). The growth of blue stain fungi was more intense in the early wood than in the late wood. This can be observed especially in the control and treated larch samples (Figure 12).

The presence of blue stain fungi on the treated samples was influenced by the pre-weathering duration before treatment. All samples were treated on the same day with the same concentration (5 %) of iron (II)sulphate solution. The first signs of blue stain can be observed already four weeks after treatment (IS-treated samples were 5 weeks pre-weathered before treatment), just like control 5. This can be observed in Norway spruce and larch samples. These are only small patches of blue-stain fungi predominately due to inoculation of the samples during pre-weathering. On other iron-treated samples, no signs of blue stain fungi were found until week 12. Like the control samples, the most prominent growth of blue stain fungi was observed on both wood species used between 12 and 21 weeks after exposure. Nevertheless, the surface area covered by blue stain fungi was lower in the treated samples than in the untreated control samples. The biocidal activity of iron can only be observed at the beginning of the exposure; later, the iron was leached from the wood (Lesar and Humar, 2022; Lesar *et al*., 2022; Zimmer *et al*., 2020), and its biological activity was insignificant. At the end of the exposure, there was no statistically significant difference in the growth of blue stain fungi between the different ageing times of the samples before treatment. Figures 13 and 14 show that there was no difference between IS and GV treatment. The growth of blue stain fungi on the treated samples has no significant influence on the colour and visual appearance of the wood treated with iron.

4 CONCLUSIONS
4. ZAKLJUČAK

For the treatment, it was sufficient to immerse the samples in the iron aqueous solution for 10 seconds to obtain the desired effect. The solution uptake is different for spruce and larch since larch wood is denser and less permeable. It was noted that the pre-weathering has an influence on the higher uptake of iron-based solutions in both wood species. As expected, pre-weathering of the wood affects the colour change, and the changes are visible faster after continuous exposure. The most prominent colour changes occur in the first few weeks of outdoor exposure. Lower solution uptake of iron-based solutions in larch wood specimens had no effect on the colour change. It is believed that this is due to the higher proportion of extractives in larch that react with iron ions compared to Norway spruce.

During a 21-week observation period of aged samples treated with iron-containing solutions, the colour of larch and Norway spruce wood samples changed significantly during the first two weeks of exposure. After that, the colour changes are less prominent. In addition, samples that were pre-weathered for 1 week before treatment show a stronger colour change than those that were exposed to outdoor weathering for 5 weeks. This is also confirmed when analysing the visual appearance, for both the Norway spruce and larch samples: The samples pre-weathered for 1 week are browner than those weathered for 5 weeks. This indicates that the UV induced changes continue long after the exposure. However, samples pre-weathered for only 5 weeks are more similar to naturally aged wood, i.e. they have a brownish-grey colour. Blue stain fungi are the main cause of wood discolouration, along with UV light and rain. It was found that they are present in all samples but in varying amounts. The growth of blue stain fungi on the treated samples had no significant effect the colour and visual appearance of the wood treated with iron-based solutions. There was no difference in colour change and mould growth between pure iron (II) sulphate and green vitriol solutions prepared from industrial-grade iron sulphate. It can be concluded that it makes sense to use industrial green vitriol for the commercial application for accelerated greying of wood, as it is much cheaper than that for laboratory analysis. Further research is needed to investigate the possibility of artificially ageing or otherwise pre-treating the wood prior to treatment with iron (II) sulphate to achieve a uniform grey colour similar to that of naturally aged wood. This could be a good basis for the commercialisation of the whole process of wood ageing with iron (II) sulphate.

Acknowledgements – Zahvala

The authors acknowledge the financial support of Slovenian Research Agency (ARRS) within research programme P4-0015 (Wood and lignocellulosic composites), and the Infrastructure Centre (IC LES PST 0481-09). The Ministry of Agriculture, Forestry and Food, under the V4-2017 project, also supported part of the published research.

5 REFERENCES
5. LITERATURA

1. Aleinikovas, M.; Varnagirytė-Kabašinskienė, I.; Povilaitienė, A.; Šilinskas, B.; Škėma, M.; Beniušienė, L., 2021: Resistance of wood treated with iron compounds against wood-destroying decay and mould fungi. Forests, 12 (5): 645. https://doi.org/10.3390/f12050645
2. Altay, Ç., 2023: Weathering performance of oriental beech (*Fagus orientalis* L.) wood impregnated with glycerol and glyoxal. Drvna industrija, 74 (2): 213-221. https://doi.org/10.5552/drvind.2023.0054
3. Evans, P. D.; Thay, P. D.; Schmalzl, K. J., 1996: Degradation of wood surfaces during natural weathering. Effects on lignin and cellulose and on the adhesion of acrylic latex primers. Wood Science and Technology, 30 (6): 411-422. https://doi.org/10.1007/BF00244437
4. Feist, W. C., 1988: Outdoor Wood Weathering and Protection. In: Proceedings of 196th meeting of the American Chemical Society, Archaeological wood: properties, chemistry, and preservation. American Chemical Society, Advances in Chemistry Series 225, Los Angeles.
5. George, B.; Suttie, E.; Merlin, A.; Deglise, X., 2005: Photodegradation and photostabilisation of wood – The state of the art. Polymer Degradation and Stability, 88 (2): 268-274. https://doi.org/10.1016/j.polymdegradstab.2004.10.018
6. Gobakken, L. R.; Høibø, O. A., 2011: Aesthetic service life of coated and uncoated wooden cladding – influencing factors and modelling. In: Proceedings of 42nd Annual Meeting IRG/WP 11-20470, The international research group on wood protection, Queens Town, New Zealand.
7. Høibø, O.; Nyrud, A. Q., 2010: Consumer perception of wood surfaces: The relationship between stated preferences and visual homogeneity. Journal of Wood Science, 56 (4): 276-283. https://doi.org/10.1007/s10086-009-1104-7
8. Humar, M.; Lesar, B.; Kržišnik, D., 2020: Tehnična in estetska življenjska doba lesa. Acta Silvae et Ligni, 121: 33-48. https://doi.org/10.20315/asetl.121.3
9. Hundhausen, U.; Mai, C.; Slabohm, M.; Gschweidl, F.; Schwarzenbrunner, R., 2020: The staining effect of iron (II) sulfate on nine different wooden substrates. Forests, 11 (6): 658. https://doi.org/10.3390/f11060658
10. Keržič, E.; Humar, M., 2022: Studies on the material resistance and moisture dynamics of wood after artificial and natural weathering. Wood Material Science and Engineering, 17 (6): 551-557. https://doi.org/10.1080/17480272.2021.1902388
11. Kropat, M.; Hubbe, M. A.; Laleicke, F., 2020: Natural, accelerated and simulated weathering of wood: A Review. BioResources, 15 (4): 9998-10062. https://doi.org/10.15376/biores.15.4.Kropat
12. Lesar, B.; Humar, M., 2022: Performance of iron (II)-sulphate-treated Norway spruce and siberian larch in laboratory and outdoor tests. Forests, 13 (9): 1497. https://doi.org/10.3390/f13091497
13. Lesar, B.; Humar, M.; Škamlec, M., 2022: Properties of iron (II) sulphate treated Norway spruce. In: Proceedings of IRG53 Scientific Conference on Wood Protection Bled, The international research group on wood protection, Slovenia, IRG/WP 22-30765.
14. Nejad, M.; Cooper, P., 2017: Exterior Wood Coatings. In: Wood in Civil Engineering, In Tech. https://doi.org/10.5772/67170
15. Niklewski, J.; van Niekerk, P. B.; Marais, B. N., 2022: The effect of weathering on the surface moisture conditions of Norway spruce under outdoor exposure. Wood Material Science and Engineering, 18 (4): 1394-1404. https://doi.org/10.1080/17480272.2022.2144444
16. Podgorski, L.; Georges, V.; Garmendia, I.; Sarachu, B. S., 2009: A fast and economic method to produce grey wooden surfaces for decking and cladding: preliminary results. In: IRG /WP 40th IRG Anual meeting, Beijing, China.
17. Sun, M.; Zhao, C.; Cai, L.; Yu, Y., 2023: Antique wood preparation by inorganic salts treatment and its performance. Maderas. Ciencia y Tecnología, 25: 1-10. http://dx.doi.org/10.4067/s0718-221x2023000100423
18. Williams, R. S., 2005: Weathering of Wood. In: Handbook of Wood Chemistry and Wood Composites. London: CRC PRESS Boca, pp. 155-202. https://doi.org/10.1201/9780203492437-11
19. Zabel, R. A.; Morrell, J. J., 2020: Wood deterioration agents. In: Wood Microbiology (2nd ed.). Decay and Its Prevention, pp. 19-54. https://doi.org/10.1016/b978-0-12-819465-2.00002-4
20. Zimmer, K.; Flindall, O.; Ross Gobakken, L.; Nygaard, M., 2020: Weathering of un painted wooden façades – Experience and examples. Wood Be Better, NIBIO, Norwegian Institute of Bioeconomy Research 6.
21. Zimmer, K.; Gobakken, L. R.; Flindall, O.; Nygaard, M., 2018: Colour changes in unpainted wooden façades – Fifty Shades of Grey Colour changes in unpainted wooden façades – Fifty Shades of Grey. In: Proceedings of IRG49 Scientific Conference on Wood Protection, The international research group on wood protection, Johannesburg, South Africa, IRG/WP 18-10903, pp. 1-23.

Corresponding address:

BOŠTJAN LESAR
University of Ljubljana, Biotechnical Faculty, Department of Wood Science and Technology, Jamnikarjeva 101, SI-1000, Ljubljana, SLOVENIA, e-mail: bostjan.lesar@bf.uni-lj.si