forests

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Performance of Iron(II)-Sulphate-Treated Norway Spruce and Siberian Larch in Laboratory and Outdoor Tests

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Abstract: Wood in outdoor applications is exposed to various environmental factors that cause weathering. Weathering is important, primarily from an aesthetic standpoint and predominantly in wooden claddings. However, not all parts of claddings are equally exposed to weathering. Sections exposed to UV radiation and moisture discolour faster than less exposed sections, such as wood under roof overhangs. Architects and owners seek a uniform appearance in buildings. To achieve fast and uniform greying, a surface treatment with iron(II) sulphate can be used. Such a treatment results in an appearance that is similar to that resulting from natural greying. However, iron compounds do not exert a biocidal effect; therefore, it is desirable to upgrade iron(II) sulphate aqueous solution with boric acid and quarterly ammonium compounds. To this end, spruce and larch samples were treated with varying concentrations of iron(II) sulphate and biocides. After treatment, the inherent durability, water performance and resistance dose (D_{Rd}) were determined according to the Meyer-Veltrup model. The samples were also exposed outdoor conditions. During exposure, colour changes and iron leaching were monitored. The results show that the addition of biocides does not affect the rate of colour change and the final colour, which is similar to natural greying after 36 weeks of outdoor exposure. The addition of biocides exerted a positive effect on the durability of treated wood, despite the low retention of preservative solutions. The water behaviour of the treated wood had little effect on the resistance dose, with a more considerable influence on inherent durability. The addition of biocides can increase the resistance dose up to 2.4 (Fe5B0.2Q0.2). On all spruce and larch samples treated with iron(II) sulphate and exposed to outdoor conditions, the colour change in the first week was roughly comparable to the final state. However, 40% of the iron had leached from the surface after only one week of exposure.

Keywords: iron(II) sulphate; wood staining; boric acid; quarterly ammonium compounds; wood decay; wetting ability; outdoor performance; *Picea abies*; *Siberian larch*

Citation: Lesar, B.; Humar, M. Performance of Iron(II)-Sulphate-Treated Norway Spruce and Siberian Larch in Laboratory and Outdoor Tests. *Forests* **2022**, *13*, 1497. https://doi.org/10.3390/f13091497

Academic Editor: Samuel L. Zelinka

Received: 4 August 2022
Accepted: 13 September 2022
Published: 15 September 2022

1. Introduction

Wood in outdoor applications is subject to biotic and abiotic degradation processes [1]. These are natural and necessary processes that are undesirable in commercial applications; therefore, attempts are made to slow down the decomposition as much as possible. When wood is used outdoors in aboveground applications, several environmental factors degrade the main wood constituents [2]. These processes are referred to as weathering [3]. Weathering of wood includes colour changes, loss of surface fibres, surface roughening and cracking and changes in chemical composition [3–5]. The main factors causing surface degradation are solar radiation and water. Wood changes colour rapidly after exposure to environmental factors because it absorbs ultraviolet light [6]. The colour change of wood exposed to outdoor conditions is also influenced by disfiguring fungi and other factors mentioned above [7]. Mould growth on coated or uncoated exterior facades is an undesirable element and often shortens aesthetic service life.

From an aesthetic point of view, it is important to consider the influence of exposure on weathering of wood. For example, the direction of exposure and design details play crucial roles. For example, sections exposed to rainfall change colour faster than sections under roof overhangs [8]. In addition, the colour changes of facades show a seasonally fluctuating pattern [5]. Additionally, only biocides can limit fungal discolouration after severe weathering [5]. Another possible solution to limit greying of wood in outdoor applications is the use of pigmented coatings or clear wood coatings with UV absorbers [9]. However, coatings are subject to one major disadvantage: they require regular maintenance [9,10], which is expensive and time-consuming. A higher maintenance requirement compared to other materials is also one of the main reasons for negative experiences with the use of wood in outdoor applications [11]. Uncoated wood is becoming more popular for exterior applications, frequently resulting in an uneven colour of wood facades [12], which is relevant because consumers and architects prefer a uniform colour over the entire surface [13].

One possible solutions to achieve a homogeneous grey colour is to produce stains with a grey colour that corresponds to the natural grey of weathered wood [14]. There are several alternative stains currently available on the market. Another option for the artificial greying of wood is a single treatment based on iron(II) sulphate, which catalyses the greying [15]. Treatment of wood with iron(II) sulphate results in a complex reaction between iron and phenolic wood extracts, if present. Staining proceeds even in the absence of phenolic extractives, possibly due to the promotion of iron(II) oxidation by photo-induced phenoxyl and ketyl radicals from photolysis of the ether linkages of lignin [15].

There is a scarcity of information available about the synergistic effects of iron(II) sulphate and biocides. With such a combination, greying of wood can be stimulated to protect against fungal infestation. The aim of this study was to test the compatibility iron(II) sulphate with two frequently used biocides (boric acid (B) and quaternary ammonium compounds (Q)). Special attention will be given to the properties wood treated with the above solutions. In addition, the durability of the treated wood, as well as colour changes and iron leaching, will be determined. Iron leaching should be considered when treated wood is exposed to rain over other building structures, as iron can cause colour changes in the underlaying mineral materials [12].

2. Materials and Methods

2.1. Sample Preparation and Treatment

The study included four sets of samples made of Norway spruce wood treated with iron(II) sulphate. Four main properties were assessed in this study: resistance to wood decay fungi (1), hydrophobic properties (2), and leaching in laboratory (3) and field tests (4) (Table 1). For each experiment, wood samples made of Norway spruce (*Picea abies* (L.) Karst.) and Siberian larch heartwood (*Larix sibirica* Ledeb.) (only for field tests) were prepared. Wood samples were made of mature wood without growth anomalies and signs of fungal infestations. Nine aqueous solutions were used for the treatment. Two biocides (boric acid and quaternary ammonium compounds) in two concentrations were added to the treatment solutions based on iron(II) sulphate. Only 5% iron(II) sulphate was used in combination with biocides. The concentration was chosen based on preliminary research, which revealed that a 5% iron(II) sulphate concentration is optimal for rapid colour change, final appearance of the wood and the cost of treatment (data not published). The exact compositions of the solutions are shown in Table 1. All treated samples were immersed in the prepared aqueous solution for 10 min. After treatment, all samples were dried and stored at 20 °C/65% RH for one week. The uptake of treatment solutions was determined gravimetrically.

Table 1. Experimental design.

Treatment				Type of Test			
Mark	**$FeSO_4$ Conc.% (wt/wt)**	**Boric Acid Conc.% (wt/wt)**	**QUAT * Conc.% (wt/wt)**	**Durability**	**Water Performance**	**Leaching**	**Field Test**
Fe2.5	2.5			x	x	x	x
Fe5	5			x	x	x	x
Fe5B0.1	5	0.1		x	x		
Fe5Q0.1	5		0.1	x	x		
Fe5B0.1Q0.1	5	0.1	0.1	x	x		x
Fe5Ba0.2	5	0.2		x	x		x
Fe5Q0.2	5		0.2	x	x		x
Fe5B0.2Q0.2	5	0.2	0.2	x	x		x
Fe10	10			x	x	x	
Control				x	x		x

* QUAT—quaternary ammonium compounds.

2.2. Laboratory Experiments

2.2.1. Durability Test against Wood-Destroying Basidiomycetes

A decay test was performed according to the modified CEN/TS 15083-1 [16]. Conditioned, treated and control specimens with dimensions of 1.5 × 2.5 × 5 cm^3 made of Norway spruce were steam-sterilised in an autoclave before exposure to wood decay fungi (350 mL experimental jars with aluminium).

Covers and cotton wool with 50 mL of 4% potato dextrose agar (DIFCO) were prepared and inoculated with two brown-rot fungi (*Gloeophyllum trabeum* (Pers.) Murrill (ZIM L018) and *Fibroporia vaillantii* (DC.) Parmasto (ZIM L037)). Brown-rot fungi were chosen because they are the predominant decomposers of softwoods in aboveground applications. The fungal isolates used in the present study originated from the fungal collection of the Biotechnical Faculty of the University of Ljubljana and are made available to research institutions upon request [17]. Information on the origin of fungal isolates and identification details are available in a corresponding catalogue. One week after inoculation, the samples were placed on HDPE plastic mesh to avoid direct contact between the samples and the medium. The assembled test glasses were incubated at 25 °C under 80% relative humidity (RH). After incubation (16 weeks), specimens were cleaned of adhering fungal mycelia, and mass loss was determined gravimetrically after drying at 103 ± 2 °C for 24 h, weighing to the nearest 0.0001 g, oven drying at 103 ± 2 °C and weighing again to the nearest 0.0001 g to determine mass loss due to wood-destroying basidiomycetes. Five specimens per treatment/fungi were used in this test.

2.2.2. Water Performance Studies

To test the hydrophobic properties of iron(II)-sulphate-treated wood, short- and long-term water absorption and surface contact angle were determined. All hydrophobic tests were performed on Norway spruce (*Picea abies* Karst.) specimens with dimensions of 1.5 × 2.5 × 5.0 cm^3 and annual ring orientation of 45° ± 15°. Ten specimens were used per treatment. The same samples were used for all water performance studies.

2.2.3. Short-Term Water Uptake

Measurements were performed at a room temperature of 20 °C and an RH of 50 ± 5% on a Krüss K100MK2 processor tensiometer. The axial surfaces of the samples were positioned in such a way that they were in contact with the deionised water, and their masses were then measured continuously every 2 s for 200 s. Other parameters were set as follows: precontact velocity, 6 mm/min; contact sensitivity, 0.005 g; and immersion depth, 1.0 mm.

2.2.4. Long-Term Water Uptake Test

Long-term water uptake was based on the ENV 1250-2 [18] leaching procedure. Before testing, samples were oven-dried at 60 ± 2 °C until they had a constant mass and weighed

to determine the oven-dried mass. The dry wood blocks were placed in a plastic box and weighted with weights to prevent floating. Then, 100 g of distilled water was added per specimen. The mass of the specimens was determined after 1 h, 24 h and 48 h, and the moisture content of the samples was calculated.

2.2.5. Water Vapour Uptake in a Water-Saturated Atmosphere

In addition to liquid water uptake, wood also absorbs water from the air. An experiment was conducted to determine the performance of wood in a climate with high relative humidity. Samples were oven-dried at 60 ± 2 °C until they had a constant mass and weighed to determine the oven-dried mass. Samples were stacked in a glass climate chamber with a fan over distilled water. The samples were positioned on a plastic net over the water. After 24 h of exposure, they were reweighed, and their moisture content was calculated. The samples were left in the same chamber for an additional four weeks until a constant mass was reached. In addition to wetting, outdoor performance is also affected by drying. Wood that dries faster performs better than slow-drying wood. The wet samples were therefore stored in a closed container over freshly activated silica gel for 24 h, and the moisture content of the samples was calculated.

2.2.6. Contact Angle of Water

The change in contact angle (CA) with time (dynamic contact angle) of distilled water was determined by the sessile drop method on the surfaces of the five test specimens with dimensions of 1.5 × 2.5 × 5.0 cm^3 using a Theta optical tensiometer (Biolin Scientific Oy, Finland). Before measurement, the test specimens were conditioned for one week at 23 ± 2 °C and a relative humidity of 50% ± 5%. A steel ball with a precise diameter of 4.000 mm was used to calibrate the goniometer microscope. Droplets of 4 µL were applied to the radial surface at three different locations on each specimen at 10 mm intervals (regardless of earlywood or latewood). Image recording was set to 65 s (7.6 frames per second, FPS); recording began when the droplet formed. CAs were determined by computer-aided analysis (OneAttension, Version 2.4 (r4931), Biolin Scientific, Finland, using Young–Laplace CA analysis mode) of the shapes of the distilled water droplets as observed by an optical goniometer and recorded by a digital camera installed in an axial bias of the objective. CA measurements began with the first image of a self-supporting droplet on the substrate. CA was calculated as the average of 15 CA measurements on the sample with the same treatment. CA was measured on Norway spruce samples only.

2.3. Factor Approach to Quantifying the Resistance Dose

A model approach was applied as proposed by Meyer-Veltrup and colleagues [19] and Isaksson and colleagues [20]. The applied model aims to predict aboveground performance. Because the method is well described in the abovementioned literature, it has not been described in detail in this publication. The wetting ability factor (k_{wa}) was calculated based on the water performance tests described in this article. The methodology for calculating the wetting ability factors followed the approach described by Meyer-Veltrup [19], except that the size of the samples differed. The original model provides for thinner samples (0.5 × 1.0 × 10.0 cm^3) than those used in the current study (1.5 × 2.5 × 5.0 cm^3). Because the approach is based on relative values, the sample size has an insignificant effect on the assay result. The results of agar block tests with pure fungal cultures evaluated the inherent resistance factor (k_{inh}). Both factors were used to calculate the resistance dose (D_{Rd}) of the treated and control Norway spruce samples. However, only brown-rot basidiomycetes were used to determine inherent resistance in this study. Terrestrial microcosm tests, exposure to white-rot fungi and in-ground soil tests were not performed, as suggested by the original Meyer-Veltrup model [19]. Resistance dose was calculated for Norway spruce samples.

2.4. Outdoor Exposure

For outdoor exposure, special cylinder specimens were made from Norway spruce (*Picea abies*) and Siberian larch (*Larix sibirica*) wood. First, boards with dimensions of $3 \times 20 \times 100$ cm^3 were made. Cylinder specimens with a diameter of 3.0 cm and a height of 3.0 cm were drilled from the board. After drilling, the specimens were cleaned, marked, conditioned and immersed in preservative solutions for 10 min (Table 1). Then, the specimens were conditioned under laboratory conditions at 20 ± 2 °C and 60% RH for one week. Before exposure, the round wooden surfaces of the specimens were sealed with an elastic one-component sealant based on a polyurethane hybrid compound (Sikaflex-251 UV). Special boards with screws were prepared for outdoor exposure (Figure 1). 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; 293 m above sea level; Scheffer climate index, 55.3). The samples were exposed in use class three according to EN 335:2013 [21]. The exposure angle was 45° to the south. Specimens were exposed to outdoor conditions on 1 April 2019. Ten specimens per treatment/wood species were prepared.

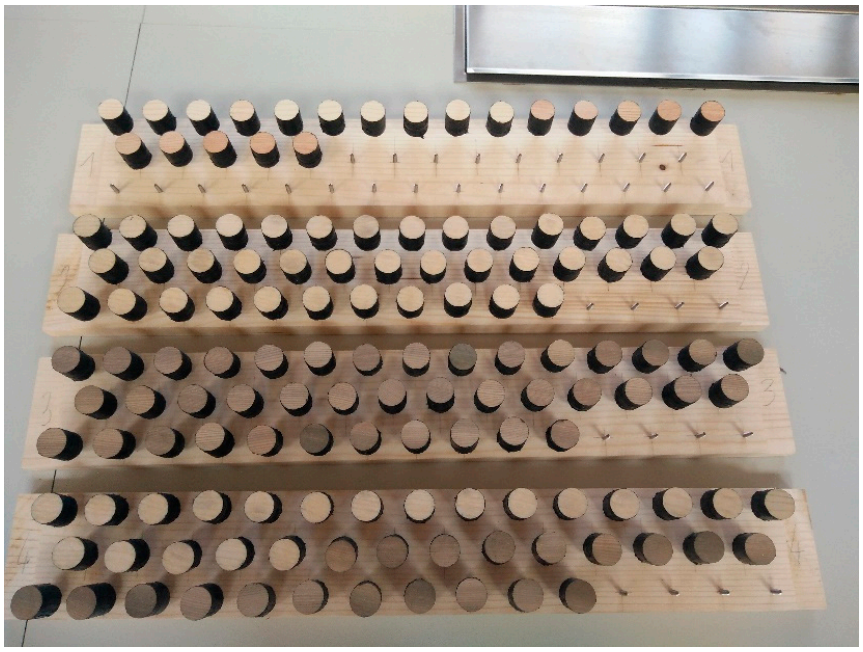

Figure 1. Cylindrical samples prepared for outdoor testing.

Before exposure and during exposure, specimens were scanned, and colour was determined. Specimens were scanned using an A3 2400S flatbed scanner, and colours were determined using Corel Photo PAINT 8 CIE Lab colour space. Microsoft Excel was used to calculate the colour difference. The total colour difference (ΔE) (Equation (1)) between a reference colour, i.e., a colour before outdoor exposure (L × 0, a × 0, b × 0), and a target colour, i.e., current colour on the day of measurement (L × 1, a × 1, b × 1), in the CIE Lab colour space was calculated by determining the Euclidean distance between two colours, which is expressed as:

$$\Delta E = \sqrt{([\Delta L]^{*\wedge *})\wedge 2 + ([\Delta a^*]\wedge *)\wedge 2 + ([\Delta b^*]\wedge *)\wedge 2)} \quad (1)$$

Colour measurements were performed after treatment and conditioning before exposure and after 1, 2, 4, 8, 36 and 172 weeks of exposure.

Furthermore, the colour and leaching of iron were measured during outdoor exposure. The amount of iron ions on the surface of the exposed samples was measured using a TwinX XRF instrument (Oxford Instruments, England). The amount of iron was measured with a PIN detector (U = 26 kV, I = 115 μA, t = 300 s), with a detection limit of 2–5 ppm.

Initial measurements were taken after conditioning and just before outdoor exposure. The amount of iron leached during exposure was determined as the ratio between the amount of iron before and after a given duration of outdoor exposure.

At the end of outdoor exposure, i.e., after 172 weeks, the exposed surfaces of the cylindric samples were evaluated for the presence of blue stain and mould fungi. Microscopic analysis was performed with a digital microscope (Olympus DSX1000, Tokyo, Japan). The moisture content of the wood samples was approximately 12%.

2.5. Statistical Evaluation

Statistical analysis of the data was performed with Microsoft Excel (Microsoft, 2019, Redmond, WA, USA) and GraphPad Prism (GraphPad Software, 9.0, San Diego, CA, USA). The test determined the significance of differences between the mean values at a 5% significance level.

3. Results and Discussion

For precise application of preservative solution, all the samples were subjected to treatment solutions for 10 min to simulate brushing, which is one of the most common treatment options for iron(II) sulphate or similar staining solutions in practice. This results in relatively low retention of treatment solutions. The retention in Norway spruce specimens ranged between 32 and 40 kg/m^3 (Table 2) (comparable to classical wood preservatives [22]). The average application rate for all treatments was 145 g/m^2, which is comparable with literature data for superficial application of iron(II) sulphate on spruce wood [15]. Higher retention was determined in cylindrical samples made of Norway spruce prepared for outdoor testing, with retention ranging from 58 kg/m^3 for Fe2.5 solution to 67 kg/m^3 (Fe5B0.2 and Fe5B0.2Q0.2 solutions). The higher retention of cylindrically shaped specimens can be explained by the higher ratio of axial surfaces compared to samples prepared for laboratory tests. On the other hand, Siberian larch wood specimens for outdoor testing exhibited lower uptake of treatment solution (from 16 kg/m^3 (Fe5B0.1Q0.1 and Fe5B0.2Q0.2) to 19 kg/m^3 (Fe5 and Fe5B0.2) (Table 3), as result of the relatively lower permeability of Siberian larch wood [23]. The combination of iron with respective biocides exerted a positive effect on the uptake of the preservative solutions. The predominant factor that affects penetration of the treatment solutions is the presence of quaternary ammonium compounds, which are well-known surfactants that affect surface tension and enable improved penetration into wood.

Table 2. Properties of iron(II)-sulphate-based solution for treatment of Norway spruce wood. ($p > 0.05$).

		Mark	Control	Fe2.5	Fe5	Fe5B0.1	Fe5Q0.1	Fe5B0.1Q0.1	Fe5B0.2	Fe5Q0.2	Fe5B0.2Q0.2	Fe10
Solution uptake	(kg/m^3)	Avg.	0 ^{c}	32 ^{a}	35 ^{a}	32 ^{a}	36 ^{a}	32 ^{a}	40 ^{b}	37 ^{b}	37 ^{b}	34 ^{a}
		Std. dev.	0.0	6.1	10.6	6.1	6.6	4.8	8.5	10.0	7.8	6.2
	Wood Decay Fungi											
Mass loss (%)	*G. trabeum*	Avg.	39.8 ^{a}	31.3 ^{b}	32.3 ^{b}	31.0 ^{b}	32.4 ^{b}	21.5 ^{c}	29.3 ^{b}	19.5 ^{d}	21.0 ^{d}	29.4 ^{b}
		Std. dev.	8.0	10.0	4.2	4.0	6.6	9.0	3.5	5.2	3.5	7.3
	F. vaillanti	Avg.	12.3 ^{a}	7.5 ^{b}	4.7 ^{b}	5.4 ^{b}	6.0 ^{b}	6.8 ^{b}	4.8 ^{b}	5.5 ^{b}	6.1 ^{b}	4.9 ^{b}
		Std. dev.	3.7	2.8	1.7	1.4	1.7	2.6	2.0	2.1	2.2	2.3
Durability class			5	4	5	5	5	4	4	4	4	4
	Time of Contact											
Contact angle (°)	1 s	Avg.	57 ^{a}	91 ^{c}	78 ^{b}	63 ^{a}	40 ^{d}	39 ^{d}	90 ^{c}	24 ^{e}	22 ^{e}	52 ^{a}
		Std. dev.	10	11	15	15	19	7	22	10	6	15
	5 s	Avg.	52 ^{a}	86 ^{c}	73 ^{b}	58 ^{a}	26 ^{d}	27 ^{d}	83 ^{c}	12 ^{e}	14 ^{e}	47 ^{a}
		Std. dev.	12	10	15	15	17	7	24	7	5	15
	30 s	Avg.	47 ^{a}	75 ^{c}	62 ^{b}	49 ^{a}	15 ^{d}	11	71 ^{c}	N.A.	N.A.	44 ^{a}
		Std. dev.	12	10	13	16	8	10	26	N.A.	N.A.	14
	60 s	Avg.	40 ^{a}	72 ^{c}	53 ^{b}	39 ^{a}	12 ^{d}	N.A.	47 ^{b}	N.A.	N.A.	39 ^{a}
		Std. dev.	10	1	12	10	5	N.A.	N.A.	N.A.	N.A.	14
	Time of immersion											
Short-term water uptake (g/cm^2)	50 s	Avg.	0.083 ^{a}	0.122 ^{c}	0.084 ^{a}	0.117 ^{c}	0.054 ^{b}	0.063 ^{b}	0.104 ^{c}	0.052 ^{b}	0.042 ^{d}	0.079 ^{a}
		Std. dev.	0.020	0.017	0.010	0.047	0.031	0.031	0.051	0.028	0.023	0.024
	100 s	Avg.	0.096 ^{a}	0.139 ^{c}	0.099 ^{a}	0.135 ^{c}	0.067 ^{b}	0.075 ^{b}	0.126 ^{c}	0.069 ^{b}	0.052 ^{d}	0.099 ^{a}
		Std. dev.	0.023	0.018	0.013	0.052	0.034	0.036	0.059	0.034	0.029	0.031
	200 s	Avg.	0.109 ^{a}	0.153 ^{c}	0.113 ^{a}	0.150 ^{c}	0.084 ^{b}	0.092 ^{b}	0.152 ^{c}	0.092 ^{b}	0.067 ^{d}	0.118 ^{a}
		Std. dev.	0.026	0.018	0.016	0.057	0.037	0.041	0.069	0.041	0.035	0.039
	Time of immersion											
Long-term water uptake (%)	1 h	Avg.	20.6 ^{a}	14.0 ^{a}	15.6 ^{a}	21.2 ^{a}	16.3 ^{a}	16.0 ^{a}	22.0 ^{a}	20.3 ^{a}	15.5 ^{a}	26.5 ^{b}
		Std. dev.	1.6	1.4	1.1	6.7	2.0	5.0	9.8	7.3	1.9	8.6
	24 h	Avg.	45.2 ^{a}	42.0 ^{a}	44.0^{a}	50.8 ^{b}	44.9 ^{a}	43.7 ^{a}	50.5 ^{b}	49.4 ^{b}	40.9 ^{a}	58.0 ^{c}
		Std. dev.	2.4	1.9	1.7	8.6	3.1	6.7	9.2	7.3	2.5	8.1
	48 h	Avg.	51.1 ^{a}	48.7 ^{a}	50.7 ^{a}	56.1 ^{b}	51.5 ^{a}	50.7 ^{a}	55.7 ^{b}	55.9 ^{b}	47.6 ^{a}	62.8 ^{c}
		Std. dev.	1.9	1.6	1.5	7.7	2.5	5.0	7.4	6.6	2.0	6.5

Table 2. *Cont.*

		Mark	Control	Fe2.5		Fe5	Fe5B0.1	Fe5Q0.1	Fe5B0.1Q0.1	Fe5B0.2	Fe5Q0.2	Fe5B0.2Q0.2	Fe10
	Time of condition												
Water vapour uptake (%)	24 h	Avg.	13.5 [a]	14.4 [b]	14.0 [b]	14.1 [b]	14.3 [b]	14.3 [b]	13.5 [a]	14.0 [b]	14.3 [b]	13.7 [b]	14.0 [b]
		Std. dev.	0.13	0.35	0.42	0.82	0.81	0.75	0.41	0.45	0.54	0.43	0.42
	4 w	Avg.	25.5 [a]	26.4 [b]	26.5 [b]	26.9 [b]	26.7 [b]	26.1 [b]	25.7 [b]	26.1 [b]	26.2 [b]	25.6 [a]	26.5 [b]
		Std. dev.	0.95	0.22	0.41	0.25	0.22	0.62	0.53	0.39	0.31	0.14	0.41
	Time of condition												
Drying above silica gel (%)	24 h	Avg.	17.0 [a]	16.9 [a]		17.3 [a]	18.0 [b]	16.8 [a]	16.9 [a]	17.5 [a]	16.7 [a]	17.4 [a]	17.4 [a]
		Std. dev.	0.66	0.41		0.41	0.67	0.22	0.50	0.40	0.56	0.60	0.45
Factors that determine the service life of wood*	k_{inh}		1	1.5		1.9	1.8	1.6	1.8	2.0	2.1	2.0	1.9
	k_{wa}		1	1.1		1.1	0.9	1.2	1.1	0.9	1.1	1.2	0.9
	D_{Rd} (d)		325	502		682	531	613	672	580	739	781	586
	$D_{rd\ rel}$		1	1.5		2.1	1.6	1.9	2.1	1.8	2.3	2.4	1.8

Different letters indicate a statistically significant difference ($p > 0.05$) between different materials tested.

Table 3. Solution uptake in cylindrical samples used for outdoor testing.

	Wood		Fe2.5	Fe5	Fe5B0.1Q1	Fe5B0.2	Fe5Q0.2	Fe5B0.2Q0.2
Solution uptake (kg/m^3)	Norway spruce	Avg.	58 ^{a}	61 ^{a}	59 ^{a}	67 ^{b}	63 ^{a}	67 ^{b}
		Std. Dev.	3.7	3.2	6.1	5.2	2.6	5.0
	Siberian larch	Avg.	18 ^{a}	19 ^{a}	16 ^{b}	19 ^{a}	18 ^{a}	16 ^{b}
		Std. Dev.	1.0	2.2	1.6	1.1	1.5	1.2

Different letters indicate a statistically significant difference ($p > 0.05$) between different materials tested.

3.1. Durability Test against Wood-Destroying Basidiomycetes

Durability is one of the most important properties that determines whether a wood species is suitable for outdoor use. Wood samples were exposed to brown-rot decay fungi for 16 weeks. The mass loss of the control Norway spruce was 12.3% in samples exposed to *F. vaillanti* and 39.8% in samples exposed to *G. trabeum*. The data show that the wood was susceptible to fungal degradation. The mass loss of treated specimens exposed to *G. trabeum* was also much higher than that of *F. vaillanti*. All treated specimens exposed to *F. vaillanti* exhibited lower mass loss than the untreated controls. However, there was no statistically significant difference between the treatments in specimens exposed to *F. vaillanti*. On the other hand, the results show that iron(II) sulphate already partially reduced the mass loss of treated specimens exposed to *G. trabeum*. Still, the concentration of iron(II) sulphate in the treatment solution did not significantly affect the mass loss of the specimens. This was effective, although iron ions can stimulate the degradation of lignin or cellulose by fungi via a Fenton reaction at low concentrations [24,25]. Samples treated with boric acid at both concentrations and quaternary ammonium compound at lower concentrations with iron(II) sulphate solutions resulted in similar mass losses as in specimens treated with iron(II) sulphate only (Table 2). In particular, samples treated with Fe5B0.11Q0.1 lost 24.5% of their initial mass, Fe5Q0.2 spruce wood lost 19.5% of its initial mass and Fe5B0.1Q0.1 lost 21.0% of its initial mass. If the principle of durability classification according to EN 350 is applied, the treated wood samples can be classified as durability class 3 (Fe5Q0.2) and 4. The minimal effect of the treatment solutions in response to brown-rot fungi can be ascribed to the low retention of the preservative solutions, as the samples were superficially treated [26,27].

3.2. Water Performance Studies

3.2.1. Contact Angle of Water

The contact angle of water on wood is an important factor with respect to performance. If the surface is hydrophobic and the contact angle is above 90°, water will run off the surface faster than on hydrophilic surfaces, where absorption of water is faster. Therefore, the goal is to obtain a hydrophobic surface or a contact angle on the treated samples higher than that of the controls. After 1 s of contact between water and wood, the samples treated with Fe2.5 (91°) and Fe5B0.2 (90°) showed hydrophobic properties. However, after only 5 s, these two sample types lost their hydrophobic effect and became hydrophilic. After 60 s, Fe2.5-treated samples had the highest contact angle (72°). QUAT had the most significant effect on the hydrophilic nature of the wood. On the wood samples treated with a solution containing QUAT in high concentrations (Fe5Q0.2 and FeB0.2Q0.2), the droplets penetrated into the wood after 30 s (Table 2). Such a result is a consequence of the fact that these compounds are used as surfactants in several industrial applications [28]. Samples treated only with iron(II) sulphate solutions at all concentrations exhibited increased contact angles compared to control samples during 60 s of measurement. A higher contact angle indicates that less water will be absorbed through the exposed surface. However, contact angle is a surface phenomenon, so the data are not fully in line with short- or long-term water uptake.

3.2.2. Short- and Long-Term Water Uptake

Short-term water uptake was measured with a tensiometer by immersing the axial surfaces of the specimens in water at a depth of 1 mm for 200 s. The untreated controls

absorbed 0.109 g/cm^2 of water (Table 2). Samples treated with Fe2.5 exhibited 40% higher uptake compared to the control samples. Boric-acid-treated samples (Fe5B0.1 and Fe5B0.2) exhibited a similar uptake to that of Fe2.5-treated samples. In contrast to the results determined through contact angle analysis, all samples treated with QUATs exhibited lower water uptake than the control samples. After 200 s, the Fe5B0.2Q0.2 samples exhibited the lowest water uptake (39% lower than the control samples). However, this experiment was performed on axial planes with morphologies that differed from those of longitudinal planes. Penetration into axial planes was determined because axial planes are a weal point for fungal colonization.

The lowest water uptake after 24 h of long-term water exposure (40.9%) was determined in the same samples. The results showed a statistically significantly lower moisture content than that determined in the specimens treated with Fe10, Fe5B0.1, Fe5B0.2 and Fe5Q0.2. The moisture content of Fe5B0.2Q0.2 treated wood was slightly lower (40.9%) than the average moisture content of the control samples (45.2), but the difference was not statistically significant. Significantly higher moisture contents than those determined in the control samples after 24 h of long-term water uptake were measured in the Fe10-only samples. The same samples also had significantly higher moisture content ($p > 0.05$) than the other samples after one hour of immersion. These results indicate that iron(II) sulphate at the highest concentration (10%) affected moisture content after long-term water uptake. The results indicate that the addition of boric acid and QUATs at higher concentrations in the treated samples resulted in increased capillary water uptake [29].

3.2.3. Water Vapour Uptake

The moisture content of samples stored in a conditioning container over liquid water was measured after 24 h and after four weeks, when the samples reached their equilibrium moisture content. The moisture content of the control samples was 13.5% after 24 h. Fe5B0.1Q0.1-treated samples had the same MC (13.5%). All other samples had higher MC. Fe2-treated specimens reached the highest MC after 24 h (14.4%). After four weeks of conditioning, the lowest MC was determined in control samples (25.5%) (Table 2). All iron-sulphate-treated samples had a higher MC than control spruce wood, with a maximum value of 26.9% for the samples treated with Fe5 solution. This result shows that all treatments resulted in an increase in MC in samples with high moisture content, which is in line with literature data showing that preservative solutions likely increase equilibrium moisture content [30,31].

From a practical standpoint, the release of water from moist wood is an important factor. Rapid drying of wood results in conditions favourable to fungal attack in the short term. After 24 h of drying, the above silica gel samples dried at a rate of 8.2% (Fe5B0.2Q0.2) to 9.6% (Fe2.5 and Fe5) (Table 2). All treated samples, except Fe5B0.2Q0.2, dried faster than the untreated control samples, indicating that treating wood with iron(II) sulphate and adding boric acid and QUATs do not slow down the drying of treated wood.

3.3. Predicting Aboveground Performance

Based on the durability and moisture performance tests discussed in previous sections, factors related to inherent durability (k_{inh}) and wetting ability (k_{wa}) were calculated for treated wood, using Norway spruce as the reference material [19,32]. Based on the procedure proposed in [19], the material resistance dose (D_{Rd}) was calculated, assuming a critical dose, independent of wood species (D_{crit} = 325 d). This number corresponds to the number of days with optimal conditions for fungal attack before the first signs of deterioration.

As shown in Table 2, all treated samples had a higher resistance dose (from $D_{Rd\ rel}$ = 1.5 (Fe2.5) to 2.4 (Fe5B0.2Q0.2)) than the control Norway spruce samples (DRd rel = 1). These results can be attributed to higher durability reflected by high inherent durability (from k_{inh} = 1.5 (Fe2.5) to 2.1 (Fe5Q0.2)). Moisture behaviour of treated samples had a minimal effect on resistance dose. Samples FeQ1 and Fe5B0.2Q0.2 had the highest wetting ability factor (k_{wa} = 1.2). For three types of treated samples (Fe10, Fe5B0.1 and Fe5B0.2), this

factor was even lower than for the untreated controls (k_{wa} = 0.9). As expected, the highest resistance dose was found in the samples treated with a solution of iron(II) sulphate and the two biocides at higher concentrations ($D_{Rd\ rel}$ = 2.4) (Table 2). This is still lower than expected for the treated wood [32]. However, we must consider that our samples were only immersed in the treated solution for 10 min, resulting in low uptake of the treated solution compared to traditional preservatives. In contrast to the traditional durability classification, the dosimeter-based resistance model applied here demonstrated the excellent performance of wood treated with Fe5B0.2Q0.2, indicating that this material can be used for exterior applications.

3.4. Outdoor Exposure

Sample specimens were exposed at an angle of 45° to the south, about 1.5 m above ground level in the use class three according to EN 335:2013 [21]. This exposure enables the most severe exposure to sunlight and rain. The outdoor exposure samples were cylindrical so that the iron ion concentration could be measured directly on the surface with an XRF instrument.

The treatment resulted in an average colour change (ΔE) of 14 units compared to the untreated controls. The treated samples were darker than the controls, even before outdoor weathering (Figures 2 and 3). There was no statistically significant difference between the treatments applied to Norway spruce and Siberian larch wood samples. The only difference between the treated wood species was that the Siberian larch wood samples were darker (L* = 37.3) than the spruce wood samples (L* = 47.4). Iron(II) sulphate caused an immediate reaction with wood, darkening the samples [33,34]. The most continuous pattern of change was observed in the untreated control samples, in which the colour change (ΔE) increased with time for 40 weeks of outdoor exposure (Figures 4 and 5). From the 25th week of exposure to the end of the experiment, the total colour change (ΔE) was highest in the control samples for both wood species studied. After 172 weeks of exposure, there were minor differences in colour between treated and untreated samples. Between the fourth and eighth weeks, ΔE was slightly slower for Fe2.5-treated wood than for the other treatments. For all other treatments, the change in the first week was roughly comparable to the final change, indicating that the iron concentration was insufficient in the samples treated with Fe2.5 solution. Analysis shows that all other samples treated with iron(II) sulphate were darker after one week than untreated samples after nine months. Similar results were reported by Hundhausen and colleagues [15]. When treated with iron(II) sulphate, such a rapid change in colour is expected and desirable. When treated with various preparations, the differences in final colour are on the order of one unit. The course of the colour change was not affected by the biocide additives. From an application point of view, these are promising results, as the treatments provided additional protection to the wood without affecting greying. With exposure extended to 172 weeks, all samples became darker by five points, on average. This darkening was likely due to the growth of blue stain fungi on the surface (Figures 6 and 7). In addition, this darkening could be related to seasonal variation in the colour of wood [35].

Leaching of iron can cause stains on building products that are under wood treated with iron(II) sulphate [8], which inspired our analysis of iron concentration on the surface of wood samples before and after weathering. Before exposure, the iron concentration on the surface of the samples ranged from 459 (Fe2.5) to 1209 ppm (Fe5). After the first week of exposure, the iron concentration on the surface was reduced by between 38% (Fe2.5) and 51% (Fe5). At the end of exposure, the average concentration of iron was only 80 ppm, indicating that between 85% (Fe2.5) and 93% (Fe5 and Fe5B0.2) iron was leached from the wood in 172 weeks (Figure 8). Alternatively, part of the iron may have been diffused to the central part of the samples. Therefore, we can conclude that effect of leaching was very pronounced. These results also indicate that iron(II) sulphate did not chemically bond to the wood components as would be the case with copper-based wood preservatives [36].

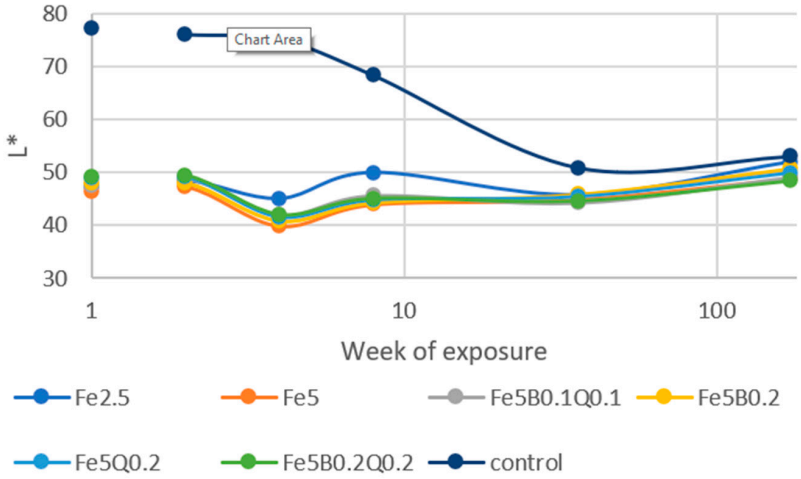

Figure 2. Mean L* values of control and treated Norway spruce samples following outdoor exposure. The compositions of treatments are listed in Table 1. The *x*-axis is a logarithmic scale.

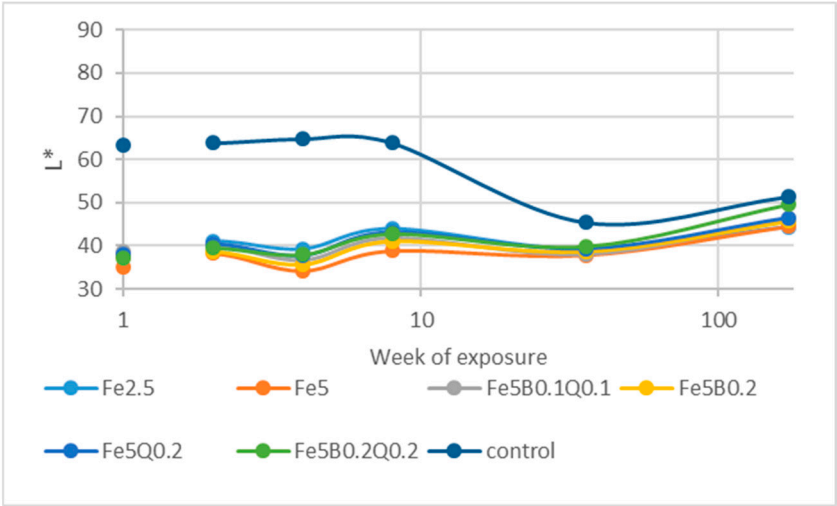

Figure 3. Mean L* values of control and treated Siberian larch samples following outdoor exposure. The compositions of treatments are presented in Table 1. The *x*-axis is a logarithmic scale.

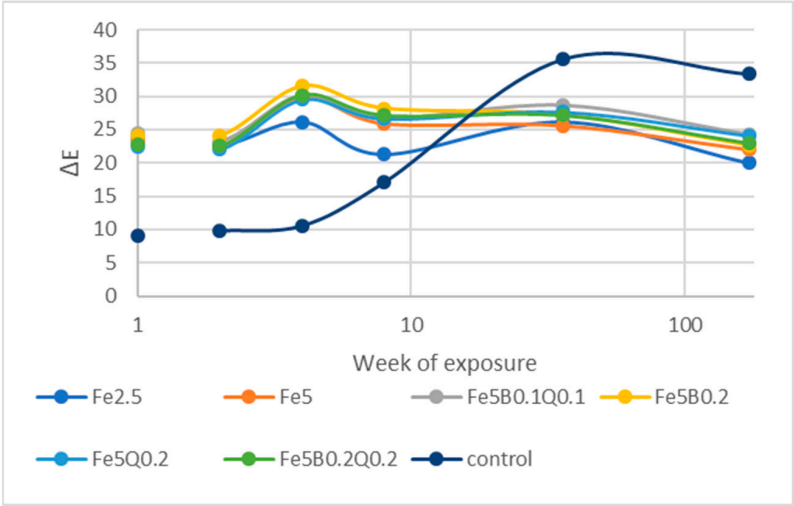

Figure 4. Mean colour change (ΔE) of control and treated Norway spruce samples following outdoor exposure. The compositions of treatments are presented in Table 1. The *x*-axis is a logarithmic scale.

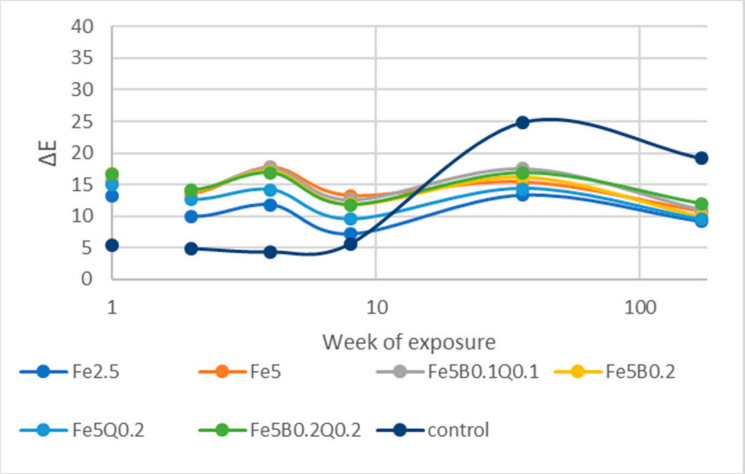

Figure 5. Mean colour change (ΔE) of control and treated Siberian larch samples following outdoor exposure. The compositions of treatments are presented in Table 1. The *x*-axis is a logarithmic scale.

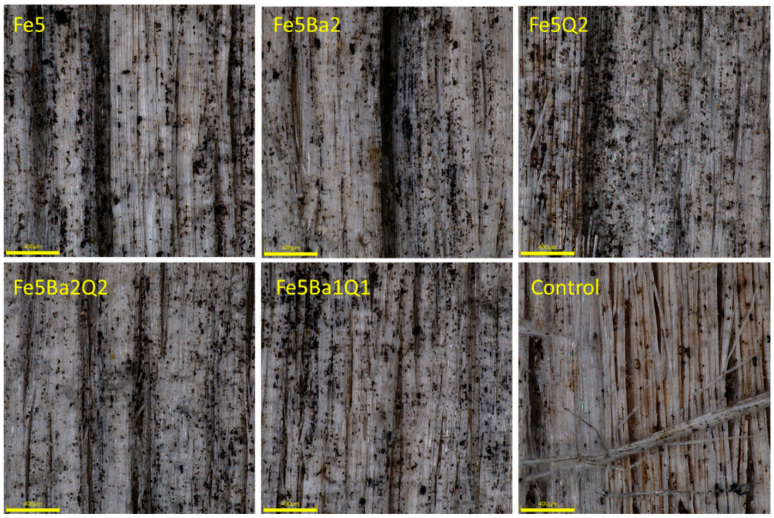

Figure 6. Surface of control and treated Norway spruce samples after 172 weeks of outdoor exposure. Control bars are 400 µm in length.

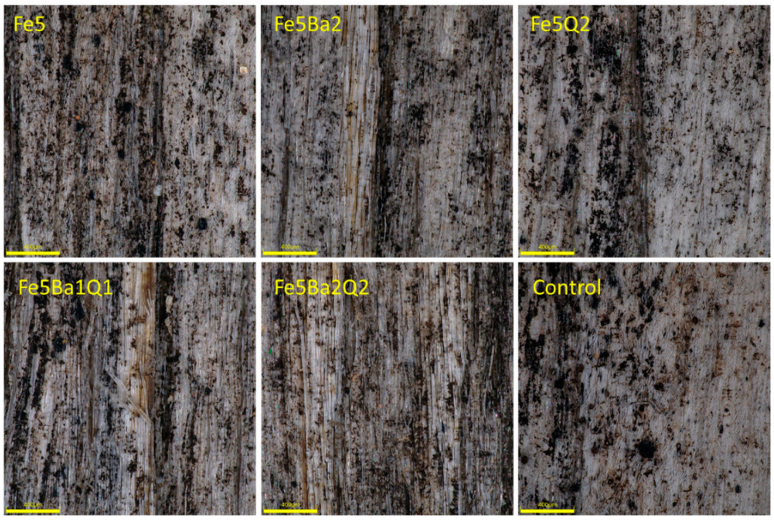

Figure 7. Surface of control and treated Siberian larch samples after 172 weeks of outdoor exposure. Control bars are 400 µm in length.

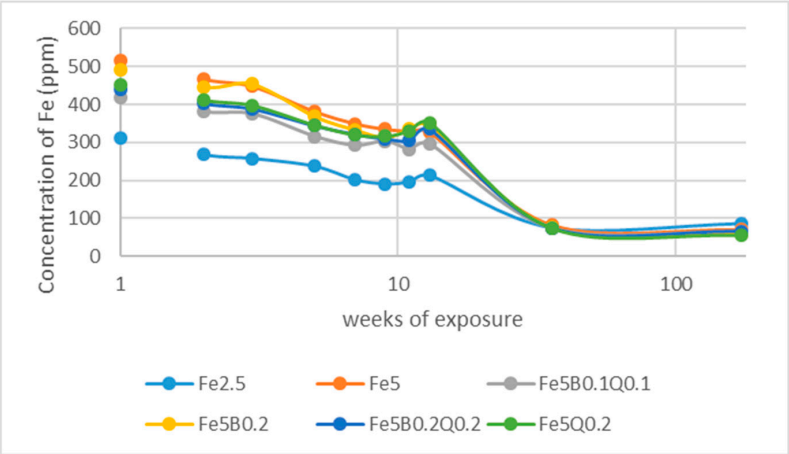

Figure 8. Mean concentrations of iron on the surface of iron(II)-sulphate-treated Norway spruce samples following outdoor exposure. The compositions of treatments are presented in Table 1. The *x*-axis is a logarithmic scale.

Besides iron, boron [32] and quat [33] can also be leached from wood, meaning that the wood was protected only for a limited time only if exposed to rainfall. After 172 weeks of outdoor weathering, blue stain fungi grew on all treated and untreated samples (Figures 6 and 7). However, none of the samples was decayed, as the samples were too small and dried-out too quickly. Microscopic images show that the surface of the control samples was much more damaged than that of the iron-treated samples, with more cracks and lose fibres observed on the surface of untreated wood than on treated samples. This is particularly evident in Norway spruce wood and only to a lesser extent in Siberian larch wood. The reason for the less damaged surface of the treated samples compared to the untreated control samples should be investigated in future research.

4. Conclusions

Treatment of wood with solutions based on iron(II) sulphate and biocides (boric acid and quaternary ammonium compounds) proved to be effective for chemical staining and to prolong the service life of Norway spruce wood. Spruce and Siberian larch wood treated with iron(II) sulphate reached the final colour change after only four weeks, whereas the colour change of the Norway spruce and Siberian larch control samples reached their final colour after approximately 36 weeks outdoors. The effect of iron(II) sulphate on greying is predominant in the initial phases. Biocides (boric acid and quaternary ammonium compounds) had no effect on the colour of iron(II)-sulphate-treated wood nor on iron leaching from treated wood under outdoor conditions. However, biocides exerted a positive effect on the resistance dose of the treated Norway spruce wood. Even when the wood was only superficially treated, the samples treated with Fe5B0.2Q0.2 reached a resistance dose of 2.4, which is comparable to Scots pine heartwood, whereas the control Norway spruce samples had a relative resistance dose of 1.0. The main influence on resistance dose indicated the inherent durability of treated samples. On the other hand, the moisture behaviour of treated samples had minimal effect on resistance dose. Blue stain fungi were observed on the surface of the treated and untreated Norway spruce and Siberian larch samples after longer periods of weathering. The results show that Norway spruce and Siberian larch wood treated with iron(II) sulphate with the addition of boric acid and QUAT can be used for exterior applications for class three use.

Author Contributions: Conceptualization, B.L.; methodology, B.L.; investigation, B.L: resources, M.H.; data curation, M.H.; writing—original draft preparation, B.L.; writing—review and editing, M.H.; visualization, B.L.; supervision, M.H.; project administration, M.H.; funding acquisition, M.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Slovenian Research Agency (ARRS) grant number P4-0015, and IC LES PST 0481-09. Part of research was founded Ministry of Education, Science and Sport grant number C3330-16-529003 and grant number C3330-18-952001, Ministry of Agriculture, Forestry and Food as part of project grant number V4-2017.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

Acknowledgments: The authors extend their thanks to Marko Škamlec for his technical support in conducting the experiments.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zabel, R.A.; Morrell, J.J. Changes in the strength and physical properties of wood caused by decay fungi. In *Wood Microbiology*; Academic Press: San Diego, CA, USA, 2020; pp. 271–291.
2. Williams, R.S. Weathering of Wood. In *Handbook of Wood Chemistry and Wood Composites*; Rowell, R.M., Ed.; CRC PR ESS Boca: London, UK, 2005; pp. 155–202, ISBN 0849315883.
3. Feist, W.C. Outdoor Wood Weathering and Protection. In *Archaeological Wood: Properties, Chemistry, and Preservation. Proceedings of 196th Meeting of the American Chemical Society*; Barbour, R.J., Rowell, R.M., Eds.; Advances in Chemistry Series 225; American Chemical Society: Los Angeles, CA, USA, 1988.
4. George, B.; Suttie, E.; Merlin, A.; Deglise, X. Photodegradation and photostabilisation of wood—The state of the art. *Polym. Degrad. Stab.* **2005**, *88*, 268–274. [CrossRef]
5. Kržišnik, D.; Lesar, B.; Thaler, N.; Humar, M. Micro and material climate monitoring in wooden buildings in sub-Alpine environments. *Constr. Build. Mater.* **2018**, *166*, 188–195. [CrossRef]
6. Evans, P.D.; Thay, P.D.; Schmalzl, K.J. Degradation of wood surfaces during natural weathering. Effects on lignin and cellulose and on the adhesion of acrylic latex primers. *Wood Sci. Technol.* **1996**, *30*, 411–422. [CrossRef]
7. Gobakken, L.R.; Høibø, O.A. Aesthetic service life of coated and uncoated wooden cladding—Influencing factors and modelling. In Proceedings of the 42nd Annual Meeting of the International Research Group on Wood Protection, Queenstown, New Zealand, 8–12 May 2011.
8. Zimmer, K.; Gobakken, L.R.; Flindall, O.; Nygaard, M. Colour changes in unpainted wooden façades—Fifty Shades of Grey Colour changes in unpainted wooden façades—Fifty Shades of Grey. In Proceedings of the IRG/WP 49th IRG Annual Meeting, Johannesburg, South Africa, 29 April–3 May 2018.
9. Aloui, F.; Ahajji, A.; Irmouli, Y.; George, B.; Charrier, B.; Merlin, A. Inorganic UV absorbers for the photostabilisation of wood-clearcoating systems: Comparison with organic UV absorbers. *Appl. Surf. Sci.* **2007**, *253*, 3737–3745. [CrossRef]
10. Nejad, M.; Cooper, P. Exterior Wood Coatings. In *Wood in Civil Engineering*; IntechOpen: Vienna, Austria, 2017; pp. 111–129. [CrossRef]
11. Markström, E.; Kitek Kuzman, M.; Bystedt, A.; Sandberg, D. Use of wood products in multi-storey residential buildings: Views of Swedish actors and suggested measures for an increased use. *Wood Mater. Sci. Eng.* **2019**, *14*, 404–419. [CrossRef]
12. Zimmer, K.; Flindall, O.; Ross Gobakken, L.; Nygaard, M. *Weathering of un Painted Wooden Façades—Experience and Examples*; NIBIO Report; Norwegian Institute of Bioeconomy Research: Oslo, Norway, 2020.
13. Høibø, O.; Nyrud, A.Q. Consumer perception of wood surfaces: The relationship between stated preferences and visual homogeneity. *J. Wood Sci.* **2010**, *56*, 276–283. [CrossRef]
14. Podgorski, L.; Georges, V.; Garmendia, I.; Sarachu, B.S. A fast and economic method to produce grey wooden surfaces for decking and cladding: Preliminary results. In Proceedings of the RG/WP 40th IRG Anual Meeting, Beijing, China, 24–28 May 2009.
15. Hundhausen, U.; Mai, C.; Slabohm, M.; Gschweidl, F.; Schwarzenbrunner, R. The staining effect of iron(II) Sulfate on nine different wooden substrates. *Forests* **2020**, *11*, 658. [CrossRef]
16. *CEN/TS 15083-1*; Durability of wood and wood-based products—Determination of the natural durability of solid wood against wood-destroying fungi, test methods—Part 1: Basidiomycetes. European Committee for Standardization: Brussels, Belgium, 2005.
17. Raspor, P.; Smole-Možina, S.; Podjavoršek, J.; Pohleven, F.; Gogala, N.; Nekrep, F.V.H. *ZIM: Collection of Industrial Microorganisms. Catalogue of Cultures*; University of Ljubljana, Biotechnical Faculty: Ljubljana, Slovenia, 1995.
18. *ENV 1250-2:1994*; Wood Preservatives—Methods of Measuring Losses of Active Ingredients and Other Preservative Ingredients from Treated Timber Part 2: Laboratory Method for Obtaining Samples for Analysis to Measure Losses by Leaching into Water or Synthetic Sea Water. European Committee for Standardization: Brussels, Belgium, 1994.
19. Meyer-Veltrup, L.; Brischke, C.; Alfredsen, G.; Humar, M.; Flæte, P.O.; Isaksson, T.; Brelid, P.L.; Westin, M.; Jermer, J. The combined effect of wetting ability and durability on outdoor performance of wood: Development and verification of a new prediction approach. *Wood Sci. Technol.* **2017**, *51*, 615–637. [CrossRef]
20. Isaksson, T.; Brischke, C.; Thelandersson, S. Development of decay performance models for outdoor timber structures. *Mater. Struct. Constr.* **2013**, *46*, 1209–1225. [CrossRef]

21. *CEN EN 335*; Durability of wood and wood-based products—Use classes: Definitions, application to solid wood and wood-based products. European Committee for Standardization: Brussels, Belgium, 2013.
22. Archer, K.; Lebow, S. Wood preservation. *Prim. Wood Process. Princ. Pract.* **2006**, *9781402043*, 297–338. [CrossRef]
23. *EN 350:2016*; Durability of wood and wood-based products—Testing and classification of the resistance to biological agents, the permeability to water and the performance of wood and wood- based materials. European Committee for Standardization: Brussels, Belgium, 2016.
24. Jung, Y.H.; Kim, H.K.; Park, H.M.; Park, Y.C.; Park, K.; Seo, J.H.; Kim, K.H. Mimicking the Fenton reaction-induced wood decay by fungi for pretreatment of lignocellulose. *Bioresour. Technol.* **2015**, *179*, 467–472. [CrossRef] [PubMed]
25. Seesuriyachan, P.; Kuntiya, A.; Kawee-ai, A.; Techapun, C.; Chaiyaso, T.; Leksawasdi, N. Improvement in efficiency of lignin degradation by Fenton reaction using synergistic catalytic action. *Ecol. Eng.* **2015**, *85*, 283–287. [CrossRef]
26. Reinprecht, L.; Panek, M. Fungicide efficacy of boron in the wood preservative containing ammonium salts. *Acta Fac. Xylologiae TU Zvolen* **2007**, *49*, 53–62.
27. Lesar, B.; Kralj, P.; Humar, M. Montan wax improves performance of boron-based wood preservatives. *Int. Biodeterior. Biodegrad.* **2009**, *63*, 306–310. [CrossRef]
28. Mckeen, L. Quaternary Ammonium Compound Introduction to Food Irradiation and Medical Sterilization. In *The Effect of Sterilization on Plastics and Elastomers*; Studies in Natural Products Chemistry; Elsevier Science: Amsterdam, The Netherlands, 2012.
29. Ramos, A.M.; Jorge, F.C.; Botelho, C. Boron fixation in wood: Studies of fixation mechanisms using model compounds and maritime pine. *Holz Roh-und Werkst.* **2006**, *64*, 445–450. [CrossRef]
30. Lesar, B.; Gorišek, Ž.; Humar, M. Sorption properties of wood impregnated with boron compounds, sodium chloride and glucose. *Dry. Technol.* **2009**, *27*, 94–102. [CrossRef]
31. Zelinka, S.L.; Glass, S.V. Water vapor sorption isotherms for southern pine treated with several waterborne preservatives. *J. Test. Eval.* **2010**, *38*, 5. [CrossRef]
32. Humar, M.; Kržišnik, D.; Lesar, B.; Brischke, C. The performance of wood decking after five years of exposure: Verification of the combined effect of wetting ability and durability. *Forests* **2019**, *10*, 903. [CrossRef]
33. Uzunovic, A.; Byrne, T.; Gignac, M.; Yang, D.Q. *Wood Discolourations and Their Prevention with an Emphasis on Bluestain. Special Publication SP-50*; FPInnovations: Quebec City, QU, Canada, 2008; pp. 5–15.
34. Krpat, M.; Hubbe, M.A.; Laleicke, F. Natural, Accelerated, and Simulated Weathering of Wood: A Review. *Bioresurces* **2020**, *15*, 9998–10062. [CrossRef]
35. Kržišnik, D.; Lesar, B.; Thaler, N.; Humar, M. Influence of natural and artificial weathering on the colour change of different wood and wood-based materials. *Forests* **2018**, *9*, 488. [CrossRef]
36. Richardson, H.W. *Handbook of Copper Compounds and Applications*; Marcel Dekker: New York, NY, USA, 1997; ISBN 0-8247-8998-9.