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Research Article

THE EFFECTS OF PRE-OZONE TREATMENT ON RETENTION LEVELS AND THE COMPRESSION STRENGTH OF SPRUCE WOOD TREATED WITH ACQ AND CCA

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ABSTRACT

In this study, ozone pre-treatment was applied to spruce wood samples. Spruce wood samples at equilibrium moisture content (EMC) were pre-treated using ozone for 30 and 60 min, respectively. The intensity of ozone was kept constant at 15 g/h for all variations. The ozone pre-treated spruce wood samples were then impregnated with 2.5 % Alkaline copper quat ((Celcure AC500) (ACQ)) and 1% copper chromium arsenic (CCA) solution by applying initial vacuum for 20 min and then free-pressure for 30 min. The retention levels and penetration depths were determined for each variation and control sample. The ozone pre-treatment increased the retention levels and penetration depths. It was found that the retention levels were 5.03 and 5.27 kg/m^3 for the ozone pre-treated (30 and 60 min) spruce for wood samples treated with 2.5% ACQ, while the retention level for control wood samples was 3.84 kg/m^3. The results showed that ozone pre-treatment enhanced the impregnation properties of spruce wood. In addition, the applied ozone pre-treatment increased compression strength parallel to grain values (CS).
Keywords: Spruce, ozone treatment, penetration depths, retention, mechanical properties.

1. INTRODUCTION

Spruce wood is one of the most important species in Turkey. However, spruce wood is difficult to impregnate with wood preservatives [1]. Spruce wood is mostly used in the furniture industry and building sector. However, it has limited usages in the wood preservation industry because of its difficult impregnability. Investigations showed that high surface tension during the wood drying process causes the displacement of membranes as well as sealing off the pit aperture which is called pit aspiration [2, 3]. Different pre-treatment methods were applied to improve the impregnation properties of such refractory wood species such as steaming, mechanical incising, drilling techniques and bio-incising [4-10].

Investigations showed that drilling techniques [11,12], bio-treatment [8, 13-15], chemical-treatment [16] and microwave-treatment [10,17] increased the retention levels and penetration depth. However, these pre-treatment methods decreased mechanical properties. The pre-

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treatments effects on retention levels, penetration depth and/or mechanical properties were summarized in Table 1.

Table 1. Effect of the pre-treatment on some wood species

Pre-Treatment	**Wood Species**	**Ret. Levels**	**P.D**	**Mechanical Strength % Decrease**			**References**
		% Increase		**MOE**	**MOR**	**CS**	
Bio-Treatment	Spruce Wood	-	-	9.3	17		[13]
Bio-Treatment	Spruce Wood	55	-	-	-	-	[14]
Drilling Tech.	Fir	95	-	-	-	-	[11]
Drilling Tech.	*Tsuga canadensis*	50	49-98	-	-	-	[12]
Chemical	Spruce Wood	48.6	-	-	-	12-31	[16]
Bio-Treatment	Spruce Wood	-	-	15.2-29.9 (Brinell hardness)			[15]
Bio-Treatment	Spruce Wood	103	-	-	-	14.4	[8]
Microwave-Treatment	*Abies alba* L.	612	-	-	-	-	[17]
Microwave-Treatment	Douglas Fir	123	-	2.5	14.5	-	[10]

Ozone is a gaseous unstable molecule composed of three oxygen (O_3) atoms. The disinfecting effect of the ozone is due to its strong oxidizing property. Ozone is the third most powerful oxidant known to carry fluorine and persulfate, along with its radical nature, due to its chemical structure [18]. In addition, ozone is also used in the bleaching process in pulp and paper production [19, 20]. In this study, it was aimed that impregnation properties could be improved by pre-treating spruce wood samples with ozone without decreasing mechanical properties.
The main objective of the present research was to increase the penetration depth and retention levels of ozone pre-treated spruce wood impregnated with CCA and ACQ wood preservatives.

2. MATERIAL AND METHODs

2.1. Preparation of wood specimens

Spruce wood obtained from the Maçka in Trabzon province of Turkey was used in this study. Planks of 25 mm thickness with full log width and length were prepared. Planks were converted into longitudinal specimens of size 30 x 15 x 15 mm (L/W/T). The spruce wood samples were divided into nine groups (Table 2). The test spruce wood samples were conditioned in equilibrium moisture content until wood samples reached to 12% moisture content prior to ozone pre-treatment.

Table 2. Experimental design

Groups	Time of Ozone application [min]	Preservative Type	Concentration of preservative [%]
C	-	-	-
CQ	-	ACQ	2.5
CA	-	CCA	1
O1C	30	-	-
O1Q	30	ACQ	2.5
O1A	30	CCA	1
O2C	60	-	-
O2Q	60	ACQ	2.5
O2A	60	CCA	1

In this study, Chromated copper arsenate (CCA) type C was used, which is composed of 18.5% copper oxide (CuO), 34.0% arsenic pentoxide (As_2O_5) and 47.5% chromium trioxide (CrO_3). Solution of CCA (1%) was prepared for impregnation procedure. The Alkaline copper quat (ACQ) contains copper and a quaternary ammonium compound. The ACQ treatment solution was type Celcure AC 500 manufactured by Osmose company. Celcure AC 500 is composed of 16.63% basic copper carbonate, 5% 2-aminoethanol, 4.8% benzylammonium chloride. Solutions of ACQ (2.5%) were prepared for impregnation procedure (Table 2).

2.2. Ozone Treatment

Ozone (model: Enaly) with 15 g/h was used for the experiment and the ozone intensity was kept constant for all groups Ten replicates were used for each group. The spruce wood samples (O1C, O1Q, O1A, and O2C, O2Q, O2A) which had 12% initial moisture content (MC) were pre-treated with ozone for 30 and 60 min respectively, for all test groups.

2.3. Determination of preservative retention

2.3.1. Impregnation method

Before impregnation with wood preservatives, cross sections of the ozone pre-treated test samples were coated using two layers of paraffin to prevent the preservative flow through the longitudinal direction. Samples were then impregnated with either CCA or ACQ according to AWPA E10-01 [21]. Test specimens in solution were subjected to a pre-vacuum of 685 mmHg for 20 minutes followed by for 30 minutes kept under atmospheric condition.

After the impregnation the preservative retention was calculated as follows;

$$R = \frac{GXCX10}{V} \quad (kg/m^3) \qquad (1)$$

Where R (retention) is the amount of wood preservative remained in the wood specimen (kg of preservative per m^3 of wood), G is the weight of the preservative solution absorbed by the block (W2-W1) g. C is the Grams of preservative in 100 g of treating solution, and V is the volume of the specimen (cm^3).

2.3.2. Measurement of penetration

The depth of preservative penetration was determined using Chrome Azurol S (color index No.43825, also known as mordant blue 29) reagent according to AWPA-A3-08 standard [22]. To prepare this reagent, 0.5 g Chrome Azurol S and 5 g sodium acetate were dissolved in 80 ml

distilled water and the solution was diluted to a volume of 300 mL. Then, this reagent was sprayed on the cross section of impregnated specimens. As a result, ACQ and CCA-impregnated areas appeared in blue color and untreated surfaces changed to red color. Depth of penetration was measured at eight different points in each specimen with a digital caliper with 0.1 mm precision. The maximum and minimum depths of penetration were then determined. In addition, the impregnation area (%) on the wood cross section was calculated by the aid of the software Image J program [23].

2.4. Mechanical Properties

2.4.1 The Compression Strength

The compression strength parallel to grain values for control samples (untreated) and test samples were recorded at Losenhausen and Mohr & Federhaff Universal Test Machine according to the Turkish Standards 2595 [24].

The compression strength (CS) parallel to grain was calculated from the following formula;

$$CS = \frac{F_{max}}{A \times b} \quad (kg/cm^2) \qquad (2)$$

Where: F*max* is the force applied on wood specimen (kg); A is the width of the sample (cm); and b is the height of the sample (cm).

2.5. Statistical Analyses

Statistical analyses were conducted using SPSS 22 software [25]. The retention levels and mechanical properties results of spruce wood were compared using the Duncan homogeneity test at 95 % confidence level.

3. RESULTS AND DISCUSSION

The retention levels for the samples with and without the ozone pre-treatment and the Duncan test results homogeneity groups are given in Table 3. The ozone pre-treatment increased the retention levels up to 44.66%. The lowest increase in retention level (10.07%) was obtained in O1A while the highest increase was obtained in O2A groups (Table 3 and Figure 1).

Table 3. Retention levels ($kg.m^{-3}$) and penetration (%) of ACQ and CCA

	Retention [$kg.m^{-3}$]			**Impregnated area*** [%]**			**Penetration Depth[mm]**		
Groups	**means**	**HG***	**Std. dev.**	**means**	**HG***	**Std. dev.**	**means**	**HG***	**Std. dev.**
CA	1.91	(A)**	0.23	28.32	(A)	0.98	2.19	(A)	0.17
O1A	2.10	(AB)	0.56	43.44	(B)	2.78	3.66	(AB)	0.92
O2A	2.76	(B)	0.28	69.07	(C)	8.12	7.39	(D)	1.34
CQ	3.84	(C)	0.66	26.88	(A)	2.37	1.90	(A)	0.59
O1Q	5.03	(D)	0.49	75.16	(C)	2.59	5.79	(CD)	1.50
O2Q	5.27	(D)	0.32	71.06	(C)	0.97	4.97	(BC)	1.42

*: Homogeneity groups

** : Means with the same letter are not significantly different at $p < 0.05$. Comparisons were done within the each wood species group.

***: The impregnation area (%) on the wood cross section was calculated by the aid of the software Image J.

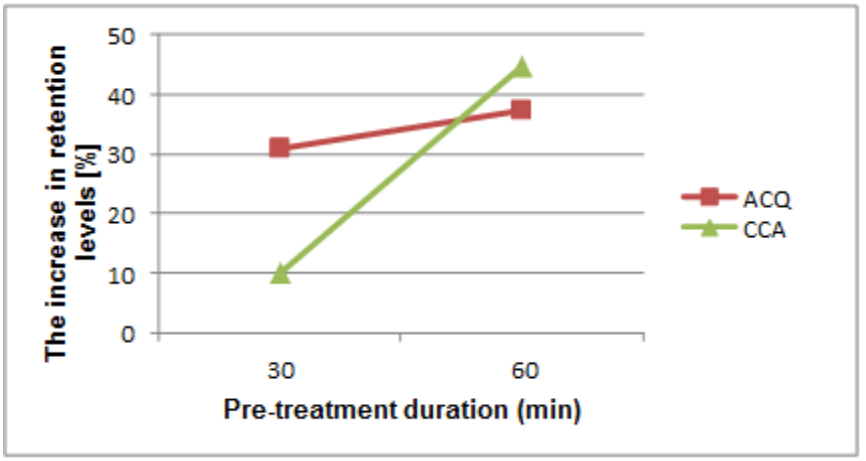

Figure 1. The increase in retention levels for the ozone pretreated wood samples treated with either CCA or ACQ compared to control samples

The impregnated areas of the samples with and without the ozone pre-treatment are given in Table 4. The ozone pre-treatment increased the impregnation area from 26.88 % to 75.16 % for the wood samples treated with 2.5% ACQ. The lowest treated area (43.44 %) was obtained in O1A while the highest impregnated area (75.16 %) was obtained in O1Q group (Figure 2).

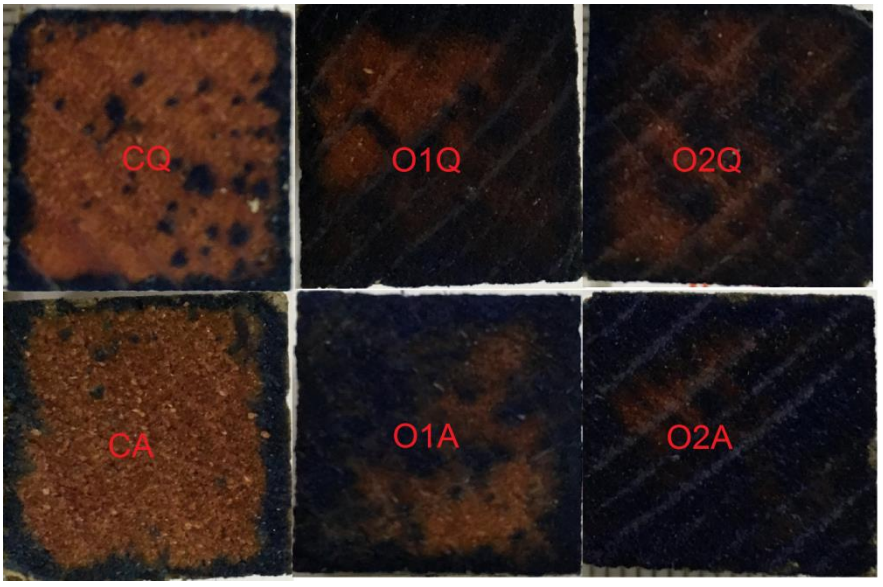

Figure 2. Cross-section of impregnated samples

The penetration depth of the samples with and without the ozone pre-treatment is given in Table 3. The ozone pre-treatment increased the penetration depth from 2.19 mm to 7.39 mm in O2A. The lowest penetration depth (3.66 mm) was obtained in O1A while the highest was

obtained in O2A groups. The results showed that duration of ozone pre-treatment enhanced the impregnated area and penetration depth significantly for the wood samples treated with 1% CCA. However, there was no significant effect of ozone pre-treatment duration on the impregnated area and penetration depth for wood samples treated with 2.5% ACQ.
The data were statistically evaluated by one-way ANOVA to demonstrate the effect of ozone pre-treatment and wood samples without pre-treatment on retention levels (Table 4).

Table 4. ANOVA results on differences of retention levels

Variation Source	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	32.792	5	6.558	31.716	.000
Within Groups	2.895	14	.207		
Total	35.687	19			

Table 5 summarizes the effect of ozone pre-treatment at different durations on compression strength as compared to control groups. Ozone pretreatment (O1C and O2C) did not adversely affect the compression strength compared to the control samples(C). The results showed that ozone pretreatment had no significant effect on the compression strength of the wood samples compared to the control samples. However, wood preservatives both CCA and ACQ used in this study significantly increased the compression strength of the treated wood samples compared to the control samples. Different pre-treatment methods decreased the wood mechanical properties (Table 1). However, ozone pre-treatment did not adversely affect on wood mechanical properties.

Table 5. Compression strength values.

Groups	Compression Strength [Kg.cm^{-2}]		
	means	**HG***	**Std. dev.**
C	318.08	(A)**	11.91
O1C	322.28	(A)	15.03
O2C	319.86	(A)	23.46
CA	397.04	(B)	28.60
O1A	414.07	(BC)	18.42
O2A	427.58	(C)	13.78
CQ	426.63	(C)	24.50
O1Q	418.00	(BC)	6.70
O2Q	421.19	(BC)	21.95

*: Homogeneity groups

** : Means with the same letter are not significantly different at $p < 0.05$. Comparisons were done within the each wood species group

The data were statistically evaluated by one-way ANOVA to demonstrate the effect of ozone pre-treatment and untreated wood samples on compression strength. Differences between test and control groups were statistically significant at 0.05 level (Table 6).

Table 6. ANOVA results on differences of compression strength

Variation Source	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	91169.613	8	11396.202	30.900	.000
Within Groups	11432.909	31	368.804		
Total	102602.522	39			

4. CONCLUSION

The results of this study indicated that the ozone pre-treatment increased the retention levels, penetration depth and compression strength. The reason for the increase in retention levels and penetration depth could be explained that the pit aspiration of spruce wood might cause deformation by ozone pre-treatment. However, further studies are needed to confirm the effects of ozone pre-treatment on wood porosity using SEM (Scanning Electron Microscope) and mercury porosity meter. Ozone pre-treatment could be a very good option to treat refractory wood species with wood preservation not only because of enhancing penetration depth, retention levels but also because of no adverse effect on wood mechanical properties.

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