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ANALYSIS OF COPPER AND CHROMIUM IN LEACHATES FROM WOOD TREATED WITH THE CCB AND CB PRESERVATIVES[1]

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The objective of the study was determination of the amount of active ions included in the CCB and CB preservatives diffusing from wood to water in individual stages of leaching. Wood in the form of samples applied in testing fungicidal properties with the agar-block method were treated with tested preservatives and then leached according to the standard EN 84. Moreover, there was investigated the influence of the initial water soaking of treated wooden samples on leaching dynamics of copper and chromium ions.

Key words: leachability; CCB and CB preservatives; AAS analysis; active ions; EN 84

INTRODUCTION

The majority of works on durability of wood treated with chemical preservatives aims at simulating the phenomenon of leaching which takes place in practice during wood utilisation. An attention should be drawn to a number of factors significantly influencing the real emission of components of a preservative from treated wood and therefore influencing results of testing. Among different factors there should be mentioned quality of water as a leaching agent, volume of samples, ratio of water amount to wood volume, number of leaching stages and duration, method of inducing extraction etc. (Cockroft and Laidlaw 1978, Cooper and Ung 1993, Lee, Grafton and Tainter 1993, Willeitner and Peek 1998). In order to determine the degree of leaching of a

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given preservative there is applied the biological method consisting in the comparison of the limiting fungicidal value determined before and after leaching. The EN 84 standard applies the full-cell impregantion of wooden samples with water before beginning leaching. The procedure aims to speed up diffusion of salts from wooden cells to a solution and therefore to increase of the effect of leaching salts from wood.

During the research on leachability of active ions from middle-size wood treated with the CCB and CB preservatives there was observed migration of some components far into wood (Mazela 2000). Therefore, arises a question on the influence of the initial water soaking on the effect of leaching of active components of the CCB and CB preservatives during testing fungicidal properties of wood treated with preservatives.

The objective of the work was determination of the amount of active ions contained in the CCB and CB preservatives and diffusing from wood to water in individual stages of leaching during laboratory tests according to the standard EN 84. There was also determined the influence of the initial water soaking of treated wooden samples on the effect of leaching of active metals.

MATERIALS

Preservatives:

Two preservatives were used during studies. The first one preservative was of the CCB type containing 36% of $CuSO_4$, 40% of $K_2Cr_2O_7$, 24% of H_3BO_3. The second of the CB type consisted of 15% of CuO, 5% of H_3BO_3 and ca. 0.5% of Tebuconazol (α-[2-(4-chlorophenyl) ethyl]-α-(1,1-dimethylethyl)-1H-1,2,4-triazolyl-1-ethanol).

Solutions of preservatives have the following concentrations: 0.1; 0.16; 0.25; 0.4; 0.63; 1.0 1.6; 2.5% for the CCB preservative and 0.16; 0.25; 0.4; 0.63; 1.0 1.6; 2.5; 4.0; 6.3% for the CB preservative.

METHODS

The procedure of leaching was made by the two methods:

– strictly according to the EN 84 standard,

– according to the EN 84 standard with passing over initial water soaking of samples.

The amount of active ions of copper and chromium in water extracts obtained extracts from consecutive stages of leaching was determined with the use of an atom absorption spectrometer (type Varian AA20). The conditions of spectrophotometric tests are presented in Table 1.

The standard solutions for preparing calibration curves were made of ready standards of metals Cu (1000 ppm) and Cr (1000 ppm). The atomisation of samples was made with the use of an oxy-acetylene blowpipe.

Table 1

Tabela 1

Conditions spectrophotometric tests

Warunki oznaczeń spektrofotometrycznych

Conditions Warunki	Investigated element Badany pierwiastek	
	Cu	Cr
Wave length (nm) Długość fali (nm)	327.4	357.9
Gap width (nm) Szerokość szczeliny (nm)	0.2	0.2
Range of measurements (µg/ml) Zakres oznaczeń (µg/ml)	0.1 ÷ 24	0.06 ÷ 15
Source of radiation (mA) Źródło promieniowania (mA)	4	7

RESULTS

The content of copper and chromium ions in the CCB preservative depending on the concentration of the preservative was equal to 0.4÷2.9 and 0.6÷4.5 g/l respectively. For the non-chromium preservative the concentration of copper was 0.4÷13.2 g/l. The results of the tests are presented in Tables 2-4. The summary amount of leached ions from wood as well as the percentage loss of ions for every concentration of impregnating solution was determined with the use of the atomic absorption spectrophotometric (AAS) analysis.

Table 2

Tabela 2

The leaching degree of the CCB preservative from wood determined as copper ion loss from wood

Stopień wymycia preparatu CCB z drewna wyrażony ubytkiem jonów miedzi

Solution concentration Stężenie roztworu [%]	Cu content in a solution Zawartość Cu w roztworze [g/l]	Preservative absorption Wchłonięcie preparatu [kg/m^3]	Cu absorption Wchłonięcie Cu [kg/m^3]	Cu content in a sample Zawartość Cu w próbce [ppm]	Total content of Cu in water extracts Suma zawartości Cu w ekstrakcie [ppm]	Leaching degree Stopień wymycia [%]
0.25	0.37	1.90	0.28	550	83.8	15.1
0.40	0.51	2.97	0.43	870	101.8	11.7
0.63	0.80	4.82	0.70	1410	158.8	11.3

1.00	1.29	7.65	1.12	2230	331.2	14.8
1.60	1.99	12.55	1.83	3660	431.7	11.8
2.50	2.89	19.62	2.86	5730	537.1	9.4

Table 3

Tabela 3

The leaching degree of the CCB preservative from wood determined as chromium ion loss from wood

Stopień wymycia preparatu CCB z drewna wyrażony ubytkiem jonów chromu

Solution concentration Stężenie roztworu [%]	Cr content in a solution Zawartość Cr w roztworze [g/l]	Preservative absorption Wchłonięcie preparatu [kg/m^3]	Cr absorption Wchłonięcie Cr [kg/m^3]	Cr content in a sample Zawartość Cr w próbce [ppm]	Total content of Cr in water extracts Suma zawartości Cr w ekstrakcie [ppm]	Leaching degree Stopień wymycia [%]
0.25	0.57	1.90	0.30	600	88.4	14.7
0.40	0.79	2.97	0.47	940	88.7	9.5
0.63	1.25	4.82	0.76	1520	103.2	6.8
1.00	1.91	7.65	1.21	2420	135.2	5.6
1.60	2.88	12.55	1.98	3970	95.5	2.4
2.50	4.47	19.62	3.10	6200	48.3	0.8

Table 4

Tabela 4

The leaching degree of the CB preservative from wood determined as copper ion loss from wood

Stopień wymycia preparatu CB z drewna wyrażony ubytkiem jonów miedzi

Solution concentration Stężenie roztworu [%]	Cu content in a solution Zawartość Cu w roztworze [g/l]	Preservative absorption Wchłonięcie preparatu [kg/m^3]	Cu absorption Wchłonięcie Cu [kg/m^3]	Cu content in a sample Zawartość Cu w próbce [ppm]	Total content of Cu in water extracts Suma zawartości Cu w ekstrakcie [ppm]	Leaching degree Stopień wymycia [%]
0.40	0.41	2.97	0.43	870	113.9	13.1
0.63	0.64	4.75	0.69	1390	169.2	12.2
1.00	1.05	7.36	1.07	2150	197.1	9.2
1.60	1.75	11.80	1.72	3450	200.9	5.8

2.50	2.55	18.25	2.66	5330	326.0	6.1
4.00	4.24	29.76	4.34	8690	557.3	6.4
6.30	13.25	48.28	7.05	14100	1013.9	7.2

The total amount of extracted chromium from wood treated with the CCB preservative of solutions concentration changing from 0.25 to 2.5% was varying from 0.8 to 14.7% of chromium total amount in a sample. On the first day there was extracted 7.1 to 30.6 ppm. During the next days the amount of leached chromium decreased gradually.

The amount of copper coming from extraction of wood treated with the CCB preservative was varying from 9.4 to 15.1% while for wood treated with the CB preservative from 7.2 to 13.1% and depended on a concentration of a solution.

The amount of copper ions leached in individual stages was increasing with the increase of concentration of impregnation solutions of both preservatives. Only in the case of the CCB preservative leaching of chromium was lower than the amount of leached copper and was decreasing with the increase of concentration of the solution from 0.63 to 2.5%. For samples treated with the CCB preservative the degree of leaching of copper from wood of the similar absorption was bigger than for wood treated with the CB preservative (Table 3).

Comparison of metal ions loss from samples leached after initial water treatment and without that activity.

On the basis of the obtained results there was observed the higher copper and chromium ions loss from treated samples leached without their previous water soaking. As it results from earlier studies (Mazela 2000) water forcing into wood at lowered pressure during predicting treatment aiming to intensify leaching causes relocation of components of impregnating salts into deeper layers of wood. Therefore, the outer layers of wood of preliminary higher concentration of salt indicate now lower leaching of components of the preservative in comparison to samples, which were not subjected to the full-cell water soaking. Thus, there was carried out detailed comparative analysis of the two methods of leaching samples treated with the CCB preservative (Fig. 1 and 2) as well as with non-chromium preservative (Fig. 3). Plots present both relationships of leaching degree of metal ions depending on concentration of preservative.

The difference of the both methods consisted in the omitting before leaching water soaking of samples in one of the cases. The samples were grouped according to concentration of preservative (6 samples in each series).

For each series of samples of the same concentration there was determined the significance level of differences between amounts of leached ions during the process according to the EN 84 standard and the modified method without the preliminary water soaking. Differences of mean losses of metal ions resulting from different procedures of leaching are not proved statistically. However, the detailed analysis of the amount of leached ions indicates significant differences in the first stage of leaching. For the number of concentrations of the applied working solutions (i.e. 0.25, 0.40, and 0.63%)

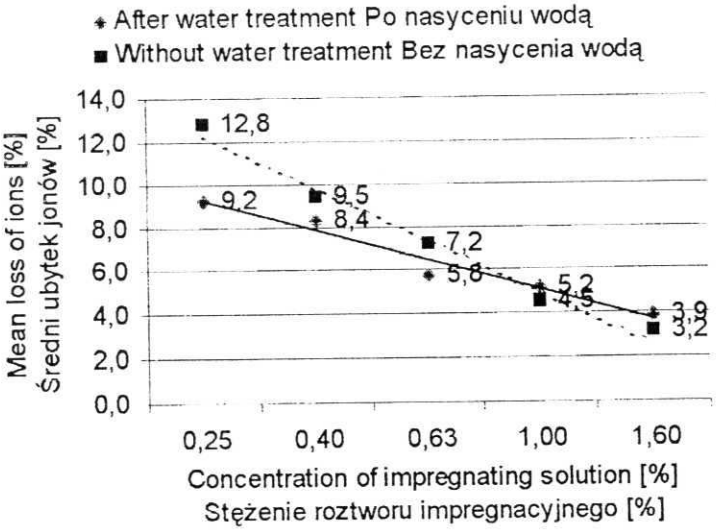

Fig. 1. Leaching degree of copper ions from wood treated with the CCB preservative
Rys. 1. Stopień wymycia jonów miedzi z drewna nasyconego preparatem typu CCB

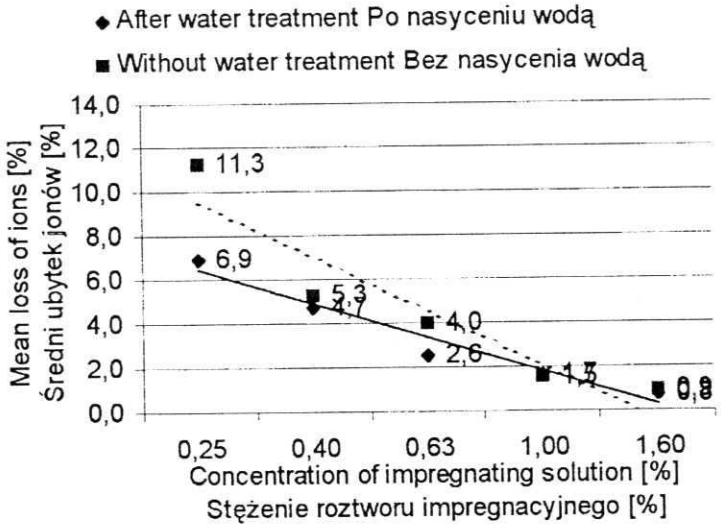

Fig. 2. Leaching degree of chromium ions from wood treated with the CCB preservative
Rys. 2. Stopień wymycia jonów chromu z drewna nasyconego preparatem typu CCB

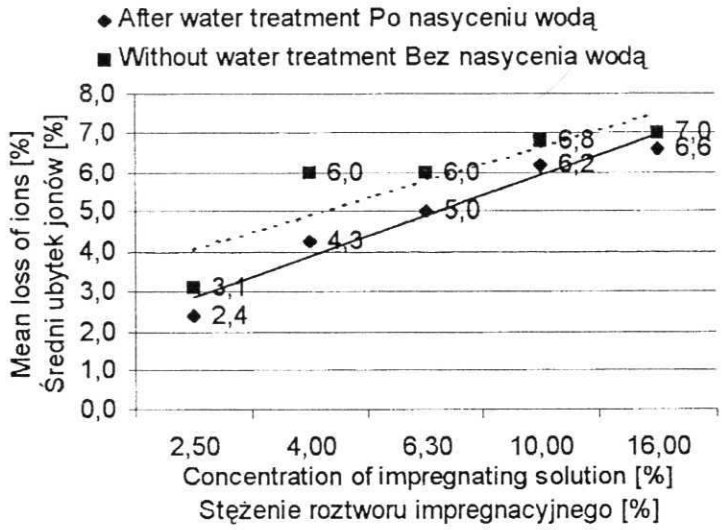

Fig. 3. Leaching degree of copper ions from wood treated with the CB preservative
Rys. 3. Stopień wymycia jonów miedzi z drewna nasyconego preparatem typu CB

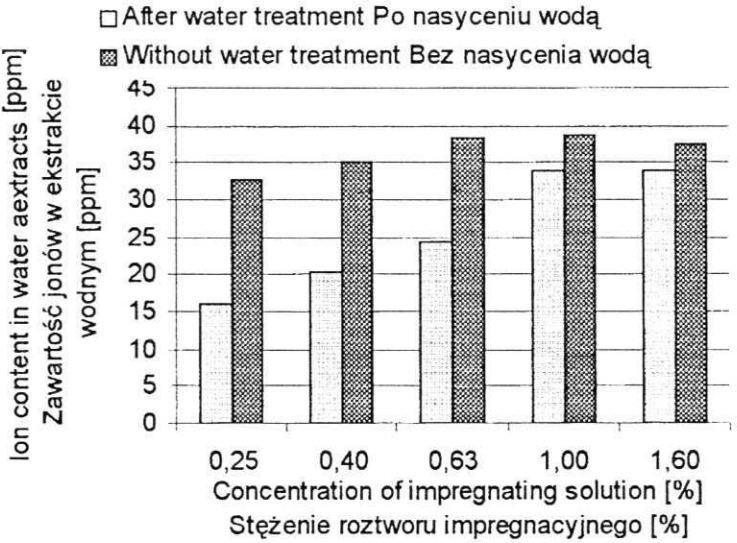

Fig. 4. Amount of leached copper ions from wood treated with the CCB
Rys. 4. Ilość wymytych jonów miedzi z drewna nasyconego preparatem typu CCB

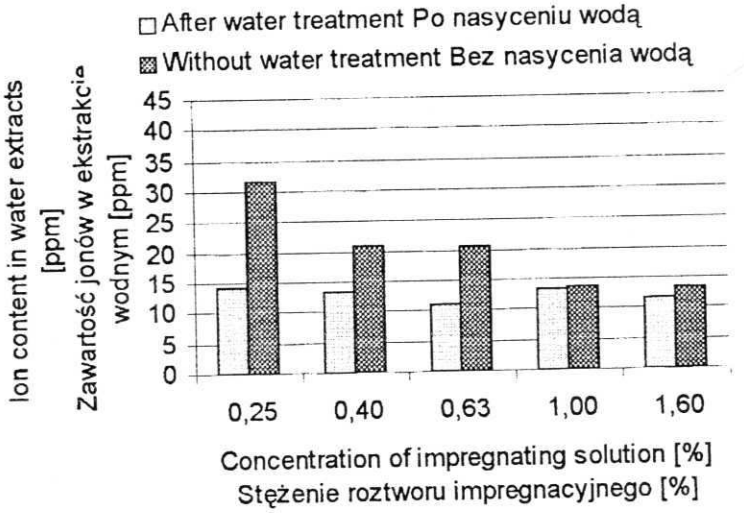

Fig. 5. Amount of leached chromium ions from wood treated with the CCB
Rys. 5. Ilość wymytych jonów chromu z drewna nasyconego preparatem typu CCB

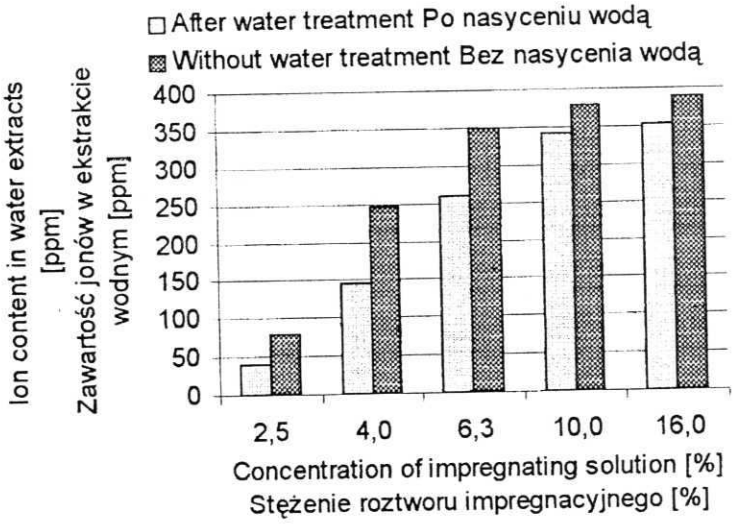

Fig. 6. Amount of leached copper ions from wood treated with the CB
Rys. 6. Ilość wymytych jonów miedzi z drewna nasyconego preparatem typu CB

the significance level of differences of copper ion losses from wood treated with the CCB preservative was in the first stage of leaching equal to 3.36, 2.98, 2.80 respectively. For chromium the differences are significant only for the smallest investigated concentration i.e. 0.25% and the level was equal to 3.46. The analogous comparative analysis was performed for copper leached from wood treated with the non-chromium preservative indicated significance of differences at every concentration. The significance level of differences was equal 7.66, 20.10, 17.90, 7.18, and 7.56 respectively.

Leaching of preservatives' components was the most intensive during the initial phase of the process regardless of leaching preceded with the full-cell water soaking or leaching started from the air-dry moisture content. Fig. 4-6 present differences of leached copper and chromium ions from wood after the first day of leaching with the both methods.

Leaching of samples, which were not previously soaked with water, was more intensive than for samples subjected to soaking. The difference in results of parallel tests was decreasing with the increase of solution concentration especially for wood treated with the CCB preservative.

DISCUSSION

The results of copper and chromium content in water extracts coming from leaching were compared to results of other authors. Illner (1988) investigated leachability of the CCB preservative from using different pH values varying from 3.7 to 5.8. After the 14 days cycle of leaching samples treated with the solution of 4% concentration wood indicated the following losses: copper – 25%, chromium – 40% and boron – 15%. Comparing to results from this work and taking into account the highest concentration of impregnating solution (i.e. 2.5%) it can be stated that the leaching level of copper was much lower i.e. of ca. 9.4% and for chromium 0.8%.

It was stated that the described earlier method of leaching wooden samples, also applied for testing fungicidal value of preservatives, gives after leaching significantly lower results of amounts of leached components compared to the use as a leaching agent water of the similar pH as rain water.

Yamamoto, Motegi and Inai (1999) presented the results similar to that obtained in this work. Among others they also investigated leachability of copper and chromium contained in the BAAC (boric acid + didecyldimethylammoniumchloride), ACQ (CuO + benzalkoniumchloride) and CCA (CrO_3 + CuO + As_2O_5) wood preservatives. The block shape samples of dimensions of 2 x 2 x 1 cm were subjected to speeded up leaching according to JIS K 1571: 1998. The process lasted 10 days. The contend of individual metals was investigated by the AES ICP (Plasma Emission Atomic Spectroscopy). Table 5 presents the comparison of some of results.

Table 5

Tabela 5

Leaching degree of metals from wood treated with different preservatives

Stopień wymycia metali z drewna impregnowanego różnymi preparatami

Type of Preservative Typ preparatu	Salt absorption Wchłonięcie soli [kg/m^3]	Absorption Wchłonięcie [kg/m^3]		Leaching degree Stopień wymycia [%]	
		Cu	Cr	Cu	Cr
CCA[a]	3.3	0.39	0.45	10.5	3.3
	6.6	0.77	0.91	50.7	2.0
ACQ[a]	2.7	0.19	-	98.4	-
	5.7	0.41	-	97.5	-
CCB[b]	2.9	0.43	0.47	11.7	9.5
	7.6	1.12	1.21	14.8	5.6
CB[b]	2.9	0.43	-	13.1	-
	7.3	1.07	-	9.2	-

[a] Acc. to Yamamoto, Motegi and Inai (1999)

[a] Wg Yamamoto, Motegi i Inai (1999)

[b] Acc. to own investigations

[b] Wg badań własnych

As it results from the Table the highest degree of leaching from wood was obtained for copper compounds contained in the ACQ preservative in the form of CuO compound combined with benzalkoniumchloride (98.4 to 97.5%). The second highest leaching degree indicated CCA and CCB preservatives in which copper is present in the form of CuO and $CuSO_4$ combined with CrO_3 and As_2O_5 as well as with $K_2Cr_2O_7$ and H_3BO_3 (10.5÷50.7 and 11.7÷14.8%). The lowest degree of copper leaching was reported for the CB preservative (9.2÷13.1%). For that preservative the percentage amount of leached copper was decreasing with the increase of the preservative concentration in wood.

The application of wood small-size samples of rectangular prism shape and strictly defined dimensions let for precise determination of amounts of extracted copper and chromium ions from wood. It allowed us to observe differences in leaching dynamics of copper and chromium from wood previously water soaked and not subjected to preprocessing. The differences were especially evident on the beginning of leaching.

RECAPITULATION

Full-cell water soaking of wood as a preprocessing treatment of leaching causes significant delay of diffusion of preservative components contained in wood from

near-surface layers to the exterior. It especially concerns the beginning of the process.

Vacuum water soaking of wood treated with CCB and CB preservatives does not cause the increase of leaching of preservative components from wood but in the initial phase it slows down the process. The above observations suggest that during laboratory tests on leachability of preservatives from wood according to the standard EN 84 the initial water soaking preceding mycological tests may be omitted. However, it requires verification with the use of other preservatives.

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REFERENCES

Cockcroft R., Laidlaw R.A. (1978): Factors effecting leaching of preservatives in practice. The Int. Res. Group on Wood Pres. Doc. IRG/WP/3113.

Cooper P.A., Ung Y.T. (1993): A simple quantitative measure of CCA fixation. For. Prod. J. (46)5: 19-20.

Illner H.M. (1988): Unterschungen zur Verminderung einer moglichen Umweltbelasung im Tränkwerk bei Beregnung salzimprägnierter Holzer. Dissertation. Universität Hamburg. Fachbereich Biologie. 226 S.

Lee A. W. C., Grafton III J. C.; Tainter, F. H. (1993): Effect of rapid redrying shortly after treatment on leachability of CCA- treated southern pine. For. Prod. J. 43(2): 37-40.

Mazela B. (2000): Changes of copper and chromium content after leaching in wood impregnated with the CCB and CB preservatives. The Int. Res. Group on Wood Pres. 31 IRG/WP/00-50147.

Willeitner H., Peek R.-D. (1998): How to determine what is a realistic emission from treated wood. The Int. Res. Group on Wood Pres. Doc. IRG/WP/98-50105.

Yamamoto K., Motegi S., Inai A. (1999): Comparative study on the leaching of wood preservatives between natural exposure and accelerating laboratory conditions. The Int. Res. Group on Wood Pres. Doc. IRG/WP/99-50134.

ANALIZA ZAWARTOŚCI MIEDZI I CHROMU W WYCIĄGACH WODNYCH POCHODZĄCYCH Z WYMYWANIA DREWNA NASYCONEGO PREPARATAMI TYPU CCB I CB

Streszczenie

Przedmiotem badań było określenie ilości jonów aktywnych zawartych w preparatach typu CCB i CB dyfundujących z drewna do wody w poszczególnych etapach wymywania. Drewno w postaci próbek stosowanych do badania właściwości grzybobójczych metodą agarowo-klockową, po uprzednim nasyceniu badanymi preparatami, wymywano wg procedury opisanej w normie EN 84. Ponadto określono wpływ wstępnego nasycania wodą próbek drewna impregnowanego na dynamikę wymywania jonów miedzi i chromu.Otrzymane wyniki wskazują, że wstępne nasycenie drewna wodą "na pełno" przed procesem wymywania, zdecydowanie opóźnia zjawisko dyfuzji składników preparatu zawartego w drewnie z warstw przypowierzchniowych na zewnątrz. Dotyczy to zwłaszcza początkowego okresu wymywania. Próżniowe nasycenie wodą drewna impregnowanego preparatami typu CCB i CB nie zwiększa efektu wymycia składników preparatu z drewna, lecz w początkowym okresie hamuje ten proces.

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