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Migrations of chromium compound in pine wood samples (*Pinus sylvestris* L.)

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Abstract: The aim of this paper was to optimize the preservative solution retention into pine wood samples (*Pinus sylvestris* L.). Sodium dichromate was used as the active substance in the preservative. Retention of 2-4 kg/m^3 were assumed. Additional, conventional retention (without practical application) of 1 kg/m^3 was applied. Chromium adsorption degree in the pine wood structure was measured with the XRF spectrometer. Optimal preservative penetration is achieved using 2 kg/m^3 retention. Raising of the retention to 3 kg/m^3 does not cause significant change in absorption degree. Retention of 4 kg/m^3 causes the highest absorption degree and is assigned for wood used in extreme conditions. The lowest concentration of chromium is visible in the central part of each sample.

Keywords: chromium, preservative treatment, adsorption, pine, XRF spectrometry.

INTRODUCTION

Toxicity of chromium compounds for insects and fungus is quite small. That is why the addition of another salts (e.g. copper salts) is necessary to improve preservative characteristic. Preservatives containing chromium are mainly CCA (chromium, copper and arsenic compounds) and CCB (chromium, copper and boron compounds). Above mentioned preservatives contains chromium most often in dichromates and chromium oxide (CrO_3), copper in copper (II) sulfate ($CuSO_4*5H_2O$) or copper (II) oxide, arsenic in arsenic oxide ($As_2O_5*2H_2O$), boron in boric acid. CCA preservative contains circa 20% CuO, 35-60% CrO_3 and 15-45% As_2O_5 (Shiau et al. 2000).

Chromium in CCA and CCB preservatives is the consolidating substance and biological corosion inhibitor. It is considered that chromates generate the hydrophobic effect in wood. That is why chromium based preservatives may be used in the III and IV hazard class, what means contact with ground and sea water (Krajewski & Witomski 2005). Chromium reacts with lignin and carbohydrates after introducing into wood structure. Slightly soluble (and hard to wash out) compounds are formed as a result of chromium reduction from +VI to +III oxidationnumber. Phenolic groups included in lignin may be (among others) the reducing factor. Many papers have showed that efficiency of the penetration and consolidation of preservatives components in wood may depend on its hardness, lignin and extractives content (Pizzi 1990).

Nowadays the dispute goes on in EU countries which have been lasted since 1998, when the Biocydes Directive was created. It controls the application of biocydes in biocidal preparations. Chromium compounds were acknowledged as active substances and there should be withdraw from the circulation (basing on the Directive). Some of producers objected this rule. It caused a lot of studies on chromium based preparations. New decree was introduced which states that these preparations may be used only after proving that chromium is not the active substance in given preservative.

One of the significant matter is the possibility of chromium absorption degree estimation. Modern instrumental techniques are used for this purpose, including XRF spectrometry (Makinen et al. 2005; Jacobi et al. 2007). The aim of this paper is to examine the penetration and migration of chromium in the structure of pine wood samples (*Pinus sylvestris* L.) and to specify the optimal retention of labour-liquid based on sodium

dichromate.

MATERIALS AND METHODS

Samples were collected from one board of scots pine (*Pinus sylvestris* L.) without visible defects. Initial samples dimensions were 50x25x15 mm. Mean samples humidity was 6,93 % and mean density – 579 kg/m^3.

Sodium dichromate was the active substance in the preservative. According to the standard, 2 kg/m^3 is the minium retention of the active substance. Retentions of 3 and 4 kg/m^3 are also used. Conventional retention of 1 kg/m^3 was added for studies usage. Three samples were chosen for each retention (1, 2, 3 and 4 kg/m^3), for each of them the model low pressure preservation was performed. Samples were the half cut along fibres.

X-ray spectrometry (Spectro Midex M) was used to analyse the chromium concentration gradient. Samples surfaces uncovered after half-cutting were measured with mapping method. Results are presented in chromium „impulse counts".

RESULTS AND DISCUSSION

Results obtained by mapping of samples surfaces with XRF spectrometer are presented on diagrams which show chromium concentration gradient (impulse counts) from the 4th to 47th mm of samples (distance from the sample front in the direction along fibres). Additional figures showing chromium concentration gradient on the first three milimeters from both sample fronts are presented for the first sample. It is because the penetration of the preservative into this sample area is the most effective. To compare the penetration for different retentions, the internal sample part should be taken into consideration.

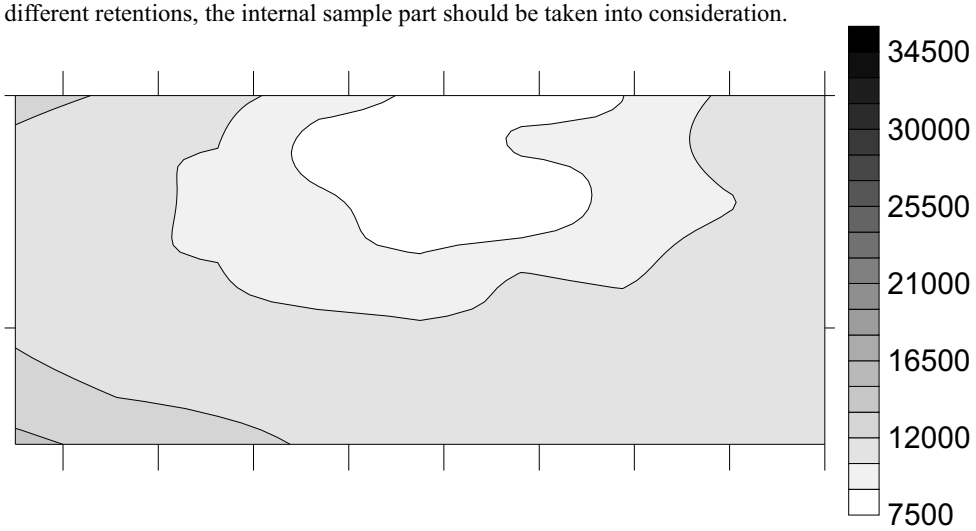

Fig. 1 Chromium concentration gradient (impulse counts) in the pine wood sample for the assumed retention of 1 kg/m^3 between 4th and 47th milimeter from the left sample front

Fig. 1 presents chromium concentration gradient on the sample surface between 4th and 47th milimeter from the left sample front. Majority of sample area on this diagram is occupied by the colour corresponding to the impulse counts range of 10500-12000. Colours corresponding to the lowest range of impulse counts (7500-10500) take place in the sample

center.

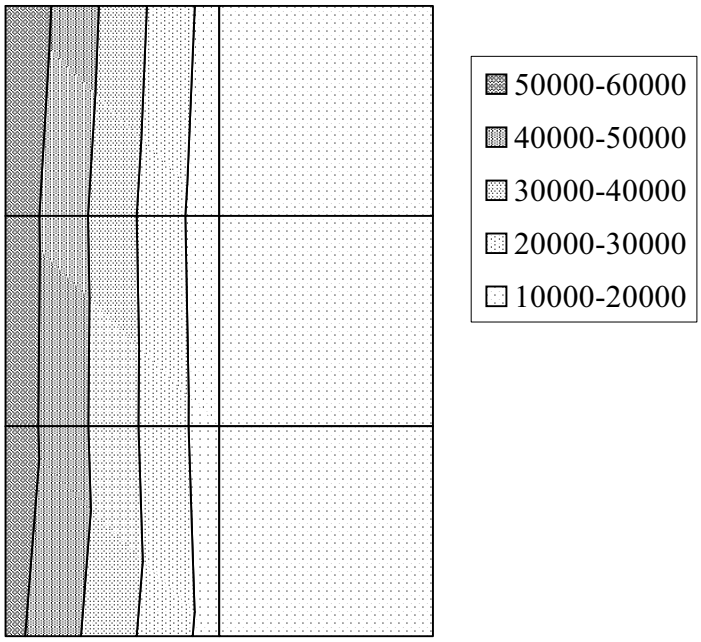

Fig. 1a Chromium concentration gradient in the pine wood sample for the assumed retention of
1 kg/m^3 3 mm from the left sample front

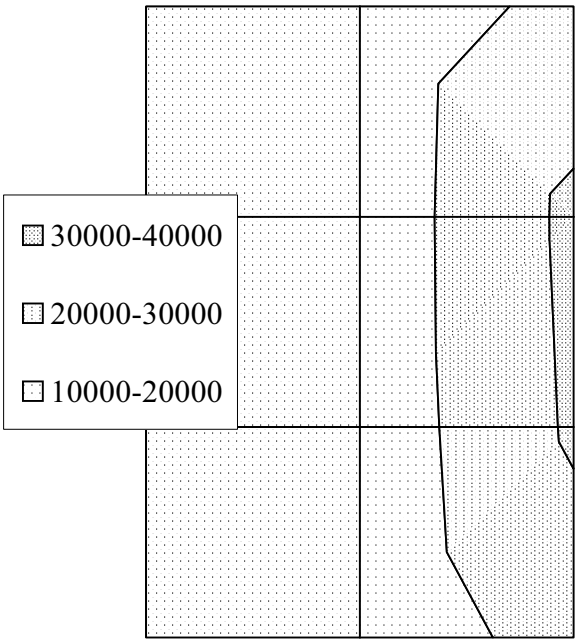

Fig. 1b Chromium concentration gradient in the pine wood sample for the assumed retention of
1 kg/m^3 3 mm from the right sample front

Figures 1a and 1b shows that there are much higher values of chromium impulse counts near sample fronts. Values are higher near the left front (20000-60000) in relation to the right front (20000-40000).

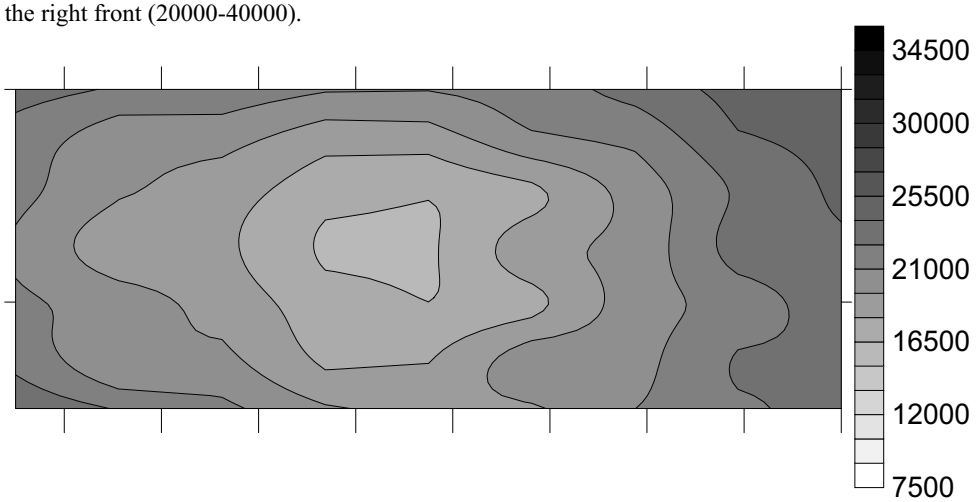

Fig. 2 Chromium concentration gradient (impulse counts) in the pine wood sample for the assumed retention of 2 kg/m^3 between 4th and 47th milimeter from the left sample front

Fig. 2 shows very regular gradient in the sample which was treated with the solution corresponding to the assumed retention of 2 kg/m^3 Chromium concentration icreases in the direction from the sample center to the front. Values of chromium impulse counts vary from 15000 to 24000.

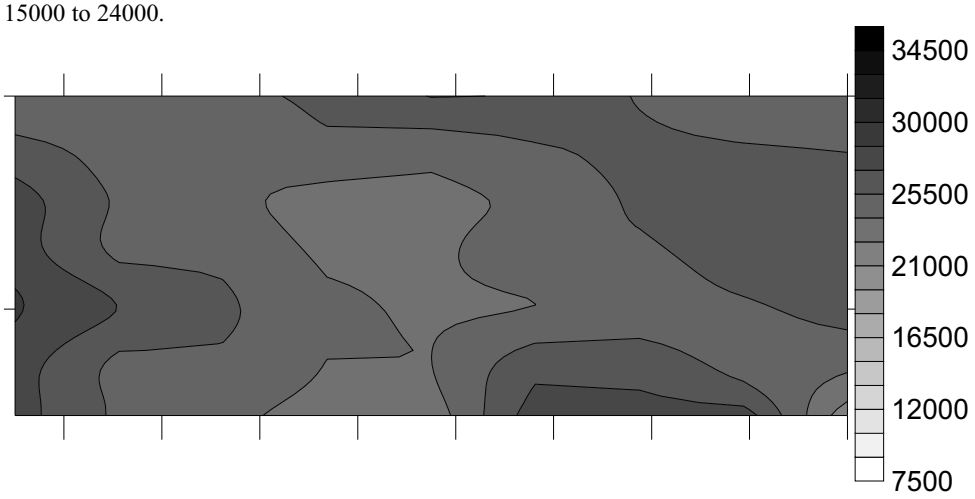

Fig. 3 Chromium concentration gradient (impulse counts) in the pine wood sample for the assumed retention of 3 kg/m^3 between 4th and 47th milimeter from the left sample front

Diagram for the assumed retention of 3 kg/m^3 is presented in the fig. 3. Values of chromium impulse counts vary from 22500 to 28500. Gradient is much less regular in relation to previous sample but the decrease of impulse counts with the distance from sample fronts (and sides) remains observable.

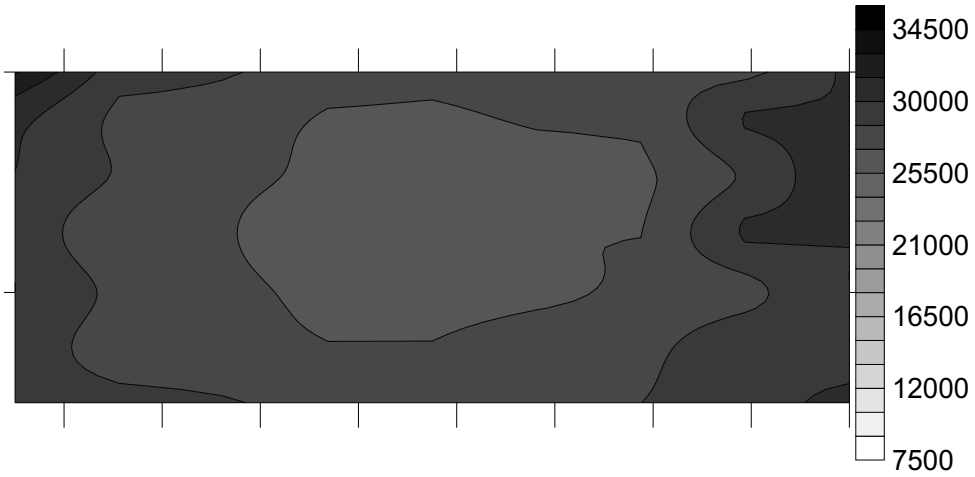

Fig. 4 Chromium concentration gradient (impulse counts) in the pine wood sample for the assumed retention of 4 kg/m^3 between 4th and 47th milimeter from the left sample front

Chromium concentration gradient presented in the fig. 4 (assumed retention of 4 kg/m^3) is quite regular. Chromium impulse counts decrease with the disance from the sample fronts and sides. Values vary from 22500 in the sample center to circa 33000 in external layers.

Tab. 1 presents mean values of chromium impulse counts for all examined samples.

Tab. 1 Mean values of chromium impulse counts in studied samples (whole sample surface)

Retention	1 kg/m^3	2 kg/m^3	3 kg/m^3	4 kg/m^3
Mean chromium impulse counts	14560	29149	32138	42866

Retention of 1 kg/m^3, without practical application, diverges significantly from the others with its efficiency. Mean value of impulse counts for this retention is about twice lower in relation to the following retention of 2 kg/m^3. Differences between higher retentions are much smaller. Value for the retention of 3 kg/m^3 is circa 10 % higher than for the retention of 2 kg/m^3, while the value for the highest retention is about 32 % higher. Retention of 2 kg/m^3 seems to be optimal because the raising of active substance concetration does not result in adequate increase of the chromium content in the sample.

CONCLUSION

XRF technique is very usefull for studying sodium dichromate absorption degree in the scots pine saples (*Pinus sylvestris* L.). It allows for exact measuring chromium concentration gradient in any sample area and estimate the preservation quality. X-ray spectrometry may be also use to determine chromium desorption from the wood structure after assumed exploitation time.

Increasing of active substance concentration from 2 to 3 kg/m^3 does not cause adequate raise of its absorption degree, so optimal wood preservation is achieved for the assumed retention of 2 kg/m^3. The highest retention (4 kg/m^3) is assigned for wood used in extreme conditions and in fact causes the highest absorption degree. Comparing 2 and 3 kg/m^3 retentions, using retention of 3 kg/m^3 is rather unjustified, basing of our results. The lowest concentration of chromium is observable always in the sample center.

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Streszczenie: *Migracja związków chromu w próbkach drewna sosny zwyczajnej (Pinus sylvestris L.).* Badania miały na celu zoptymalizowanie retencji roztworu impregnującego w próbkach drewna sosny zwyczajnej (*Pinus sylvestris* L.). Jako substancję czynną w impregnacie użyto dwuchromianu sodu. Zastosowane retencje impregnatu wynosiły od 2 do 4 kg/m^3. Na potrzeby badań zastosowano także umowną retencję 1 kg/m^3. Stopień adsorpcji chromu w drewnie mierzony był przy użyciu spektrometru XRF. Optymalna impregnacja drewna została osiągnięta przy zastosowaniu retencji 2 kg/m^3. Podwyższanie stężenia do 3 kg/m^3 nie powoduje znaczącego polepszenia stopnia impregnacji. Cechą wspólną zjawisk dyfuzji zachodzących w drewnie jest to, że najmniejsze stężenie chromu obserwuje się w części centralnej analizowanych próbek.

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