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Reducing copper leaching from treated wood by sol-gel derived TiO_2 and SiO_2 depositions

Abstract: The antileaching efficacy of sol-gel-derived TiO_2 - and SiO_2 -based precursors has been evaluated through laboratory leaching trials with pine sapwood in two different ways. In a one-step process, wood was vacuum impregnated by the precursor solutions containing CuCl_2 . The copper (Cu) emission rates of the sol-gel-based impregnated woods were up to 70% lower than that of wood treated with pure CuCl_2 solution at the same level of concentration. More improvement (80%) could be achieved in a two-step process, in which sol-gel precursors were introduced into an already CuCl_2 -treated wood. The refinement was attributed to several effects. In the one-step approach, Cu was embedded in the TiO_2 / SiO_2 gels formed in the wood texture. During a two-step impregnation, gel layers that were formed in the wooden interior acted as an effective diffusion barrier. The sol-gel impregnations made wood more hydrophobic; therefore, the low amount of water that penetrated the cell wall was less efficient to leach out Cu.

Keywords: copper leachability, SiO_2 -based gel, sol-gel treatment of wood, TiO_2 -based gel, wood impregnation, wood protection

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Introduction

The efforts to reduce the leaching of the active components of wood preservatives have a long history. In chromated copper arsenate (CCA), chromium (Cr) is a fixating agent for copper (Cu) and arsenic, which impedes Cu elution to some extent (Cooper et al. 1994; Lebow et al. 1999). However, the situation is more critical for the Cu-based wood

preservatives free of Cr, where relatively higher amounts of the active ingredients are liberated from the treated wood (Humar et al. 2005; Temiz et al. 2006; Pankras et al. 2012). This fact is problematic from the viewpoint of environmental protection, healthcare, and protective performance and the service life of protected wood (Yu et al. 2009).

The reducing leachability of Cu-containing wood preservatives is still a challenge. The chemical and physical methods were tested in this context. Lowering water uptake by treatment of wood surfaces by water repellants, polymers, and nanoparticles was one of the approaches (Häger 1980; Cooper et al. 1997; Cui and Walcheski 2000; Lebow et al. 2003; Mourant et al. 2009; Salma et al. 2010; Sun et al. 2010; Treu et al. 2011; Pankras et al. 2012). Thicker coatings and paints were also applied for this purpose (Stilwell 1998; Lebow et al. 2004). In general, coating materials reduced Cu leaching efficiently. Semitransparent stains, which are common for exterior finishing, were also tested in the context with CCA (Veenin and Veenin 2001; U.S. Environmental Protection Agency 2005), alkaline Cu quaternary, and Cu azole (Nejad and Cooper 2010). Some studies found microwave and hot air postimpregnation processes for Cu fixation successful to a certain extent (Yu et al. 2009, 2010).

The sol-gel-derived precursor materials as wood modifier were extensively investigated (Saka et al. 1992, 2001; Saka and Ueno 1997). Only a few reports are available concerning the leaching resistance of active components embedded into a sol-gel nanomatrix (Böttcher et al. 2000; Mahltig et al. 2008). However, the effectiveness of these materials with details of emission rates and cumulative emissions was not demonstrated by standard leaching tests.

The present article is an attempt to bridge this gap and the main focus was on determining the influence of TiO_2 and SiO_2 depositions on Cu leaching when these depositions were formed by the sol-gel processing of titanium (Ti) and silicon (Si) alkoxides applied to wood in one-step or two-step impregnations along with CuCl_2 treatment. The role of TiO_2 and SiO_2 barriers was evaluated in laboratory-scale leaching tests (Figure 1). In a one-step impregnation, the sol-gel is made of Ti and Si alkoxides, which also contain CuCl_2 as an active

Figure 1 Sample preparation by a one-step and a two-step process.

component. The expectation is that a mixture of Cu and Si or Ti ions is prepared at an atomic level and that a Cu silicate or titanate is possibly formed. This chemical interaction of Cu with precursors may provide a better fixation and may reduce leaching. Similar leaching trials will also be performed with CuCl₂-treated wood that is impregnated by sol-gel precursors in the second step of the two-step impregnation. Supposedly, Cu will be enveloped in the latter treatment by a formed silica or titania layer on CuCl₂ and what may hinder its leaching.

Materials and methods

Wood specimens

Wood specimens [50 mm (length)×25 mm×15 mm (transverse)] were prepared from Scots pine sapwood (*Pinus sylvestris* L.) according to the Organisation for Economic Co-operation and Development and DIN EN respective standards (DIN EN 113 1996; OECD Guideline 313 2007). All the samples were free of defects and fungal infections. For calculating the weight percentage gains (WPG), the samples were weighed also in the oven-dried (18 h, 103°C) state.

Impregnation solutions and wood treatments

The titania- and silica-based precursor solutions were prepared by mixing basic reagents such as titanium(IV) isopropoxide (TIP; 97%; Alfa Aesar, Karlsruhe, Germany) and tetraethoxysilane (TEOS; >99%; Fluka, Munich, Germany) in 2-propanol (99.5%; Sigma-Aldrich, Munich, Germany) and ethanol (99.8%; AppliChem GmbH, Darmstadt, Germany), respectively, in the presence of acid catalysts. Ti alkoxide precursor solution (S1) was prepared by dropping 1 M TIP into 10 M 2-propanol under vigorous stirring. A catalyst (HNO₃; 65%; AppliChem GmbH, Darmstadt, Germany) was added for pH adjustment to 2. The precursor S1 contained an equivalent amount of TiO₂ of approximately 9% (by mass). The synthesis of Si alkoxide solution (S2), with SiO₂ solid content of approximately 11% (by mass), was carried out by heating the mixture of 1 M TEOS, 7 M ethanol, and 1 M water (acidified with HCl; 37%; AppliChem GmbH, Darmstadt, Germany) to 50–70°C for 1–7 h. The mixed precursor solution (S3) was derived from S1 and S2 solutions by mixing in the ratio of 1:1 (by mass).

CuCl₂ (>98%; Merck, Darmstadt, Germany) was added to all the prepared precursor solutions (S1–S3) in an amount of 1.2% as well as to 2-propanol to prepare a model Cu-based wood impregnation solution (Table 1). The solutions were stored at 17°C in a storage tank immediately after the preparation for the whole period of impregnation. Before impregnation, the oven-dried wood specimens (five per treatment) were evacuated at 100–300 Pa for 1 h. Wood was treated in one-step or two-step impregnation. The preparation steps of all the wood samples for the following leaching experiments are presented in Figure 1.

The one-step vacuum impregnation was carried out initially at 100–200 Pa with pure CuCl₂ and also titania- and silica-based CuCl₂-containing precursor solutions S1–S3. Then, specimens were further soaked at 5–10 kPa for 2 h at 20–23°C. The impregnated specimens were dried and cured to ensure a more complete hydrolysis and condensation (via sol-gel route) of the precursors as well as to allow the fixation of the impregnating liquids into the treated wood. For all the samples impregnated in one step and in two steps, the drying and curing procedures included the storage of 1–7 days under a moist atmosphere (relative humidity of 95% achieved by a supersaturated solution of KNO₃) at 20–23°C, ambient air drying for 7–10 days, and a final curing at 103°C for 18 h.

In the two-step impregnation procedure, the specimens were first treated with CuCl₂ solution similar to the one-step procedure and cured under ambient conditions for 4–7 days and dried for 18 h at 103°C followed by another impregnation with precursor solutions S1–S3 under the same conditions. After the second impregnation, the wood specimens were dried following similar postimpregnation curing procedures adopted for drying one-step impregnated samples as described above.

Methods

Liquid uptakes and respective retentions (*R*) as a measure for the content of inserted substances in the tested specimens per impregnation cycle were calculated by the following equation (Temiz et al. 2006; Yildiz 2007):

$$R \text{ (kg/m}^3\text{)} = [(m_2 - m_1) \times C \times 10] / V \quad (1)$$

where *m*₁ and *m*₂ are the masses of test specimens before and after impregnation, (*m*₂−*m*₁) is the amount of solution absorbed during

Solutions, mixtures, processes	Wood code	Solid amount (mass%)	Liquid uptake (mass%)	Retention (kg m ⁻³)	Total retention (kg m ⁻³)	WPG (mass%)
One-step impregnation						
CuCl ₂ propanol solution	CuW	1.2	48.2 (3.4)	3.5 (0.3)	3.5 (0.3)	2.5 (0.2)
CuCl ₂ +S1 (TIP)	CuT1	10.2	55.9 (3.1)	35 (2.0)	35 (2.0)	10.6 (1.1)
CuCl ₂ +S2 (TEOS)	CuS1	12.2	57.6 (4.9)	43 (3.6)	43 (3.6)	12.4 (1.3)
CuCl ₂ +S3 (TEOS+TIP)	CuM1	11.2	47.3 (2.7)	32 (2.1)	32 (2.1)	11.3 (1.2)
Two-step impregnation						
First: CuCl ₂ propanol solution	CuT2	1.2	47.4 (1.7)	3.5 (0.1)	34.5 (1.8)	2.4 (0.2)
Second: S1 (TIP)		9	55.5 (3.0)	31 (1.7)		9.53 (1.0)
First: CuCl ₂ propanol solution	CuS2	1.2	49.0 (3.0)	3.6 (0.2)	38.4 (1.4)	2.4 (0.2)
Second: S2 (TEOS)		11	51.5 (1.7)	34.8 (1.2)		11.6 (1.2)
First: CuCl ₂ propanol solution	CuM2	1.2	49.8 (2.2)	3.7 (0.2)	33.2 (1.8)	2.5 (0.2)
Second: S3 (TEOS+TIP)		10	48.1 (2.6)	29.5 (1.6)		9.6 (1.1)

Table 1 Details of chemicals and treatments in the one-step and two-step impregnation. Numbers in parentheses are standard deviations.

impregnation expressed in grams, C is the solid content (%) of impregnating solution, and V is the volume of the treated sample (cm³).

The WPG of each treated sample was calculated from the difference of the sample mass before and after treatment divided by the initial mass of the impregnated sample (Donath et al. 2004).

A continuous submersion test was employed according to the leaching guideline (OECD Guideline 313 2007) to assess the Cu leachability of the treated wood. Each immersion vessel was filled with 500 ml deionized water along with five test specimens as per treatment. The test assemblies were covered with parafilm to avoid evaporation. Water was replaced following strictly a defined timetable (0.25, 1, 2, 4, 8, 15, 22, and 29 days) given in the standard. The specimens were weighed at each water exchange to calculate the water uptake during the respective interval. The leachates were collected into glass bottles immediately after each leaching period and stored in a storage tank at 4°C until analysis. The Cu contents of the leachates were determined by atomic absorption spectrophotometry (AAS; UNICAM 969 AA spectrometer). The analytical results of leachates (expressed as Cu concentrations in mg L⁻¹) were converted to Cu emission rates (mg m² per day) by following the guideline (OECD Guideline 313 2007). An additional test for the determination of the total leachable Cu was performed. Five grams of an impregnated and dried wood sample were crushed to chips (<1 mm in diameter) and eluted two to three times by H₂SO₄ (10%) for approximately 12 h followed by an AAS Cu analysis.

The surface morphology was studied by an environmental scanning electron microscope (ESEM; XL-30; Philips, Hamburg, Germany). The selected test specimens (leached and unleached) with cross-sectional cuts in 5 mm thickness were prepared and sputtered with carbon before record ESEM images.

Results and discussion

Treated wood and its microstructure

The characteristic details of treated woods are summarized in Table 1 and the examples of ESEM images are displayed

in Figure 2. The liquid uptakes of solutions S1 and S2 in one-step impregnated wood (CuT1 and CuS1) were higher than the wood treated with CuCl₂ solution (CuW) because of the higher densities of the precursor liquids. However, the mixed precursor S3 with 1.2% CuCl₂ was absorbed slightly less (CuM1wood) than the wood treated with the pure CuCl₂ solution (Table 1). Probably, this is due to the less penetration of the mixed precursor S3 because of its higher particle size. As precursor S2 contained more water, its mixing in S1 results in a prompt hydrolysis of Ti alkoxide and the partial formation of titania gel particulates causing larger particle sizes in the mixed precursor (S3). A similar absorption trend was observed during the two-step process. The retention levels for CuT1, CuS1, and CuM1 were higher compared with wood treated with a pure CuCl₂ solution because of the larger concentrations as well as the higher liquid uptakes of sol-gel-derived precursor solutions.

For the double impregnated wood series, CuT2, CuS2, and CuM2, the total retentions were comparatively lower than their single impregnated counterparts. This decrease was attributed to the lower liquid absorption during the second impregnation cycle, which is caused by blocking cell wall microvoids by solid CuCl₂ as a consequence of the first impregnation step. WPGs after the final curing are higher for both single and double impregnated wood series. However, WPGs were slightly lower for the latter case (CuT2, CuS2, and CuM2) than those for the former (CuT1, CuS1, and CuM1) as the solution uptake was lower during the second impregnation cycle of the treatment as described above.

The amount of Cu is expected to be the same in all treated wood samples because the same defined amount of 1.2 mass% CuCl₂ was added to the sol-gel precursors

Figure 2 ESEM images of wood samples.

(a) CuW treated with 1.2% CuCl_2 solution, (b) CuM1 (unleached) treated with mixed precursor solution S3 containing 1.2% CuCl_2 , and (c) CuM1 after leaching.

(S1–S3) and to the pure CuCl_2 propanol solution, and the liquid uptake was also similar. The analysis of the initial Cu content in the wood samples determined by AAS gives the following values in the following order: 45 mg Cu for the CuCl_2 -treated sample (CuW), 40 mg Cu for the CuT1 sample, and 56 mg Cu for the CuS1 sample.

The ESEM images (Figure 2a and b) indicate that the impregnating liquids were taken up evenly into the whole wood matrix, and after the final oven drying, the substances were deposited in the form of thin layers. The deposition in the lumen was not observed in CuW wood treated with CuCl_2 solution because of the low solid amount (Figure 2a). However, a considerable amount of loosely packed substances was found in the lumen of the sol-gel-treated wood (Figure 2b for CuM1). The investigation of element distribution did not detect an image contrast for Cu in TiO_2 or SiO_2 depositions. The assumption is, however, that CuCl_2 is embedded randomly in the sol-gel-based material (TiO_2 and SiO_2) and uniformly deposited in the wood texture of one-step treated CuM1 samples (Figure 2b). The ESEM image recorded from leached CuM1 samples (Figure 2c) shows that a considerable amount of the material deposited on the cell walls has been washed out during the leaching trial. Nevertheless, still a considerable amount of solid gels is present in the lumen. This

observation supports the subsequent result of lower Cu disposal from CuM1 wood compared with CuCl_2 -treated wood (CuW).

Assessment of Cu leaching

Cu leachability in terms of its concentration, leaching rates, and cumulative leaching was determined by analyzing the leachates collected from the single impregnated wood (CuT1, CuS1, and CuM1) along with only CuCl_2 -treated wood (CuW) during 29 days of leaching (Figure 3).

The maximum amount of Cu was released from wood treated only with CuCl_2 solution. Here, a higher Cu loss is visible in the early phase (first 2 days) followed by a slower Cu release over time (Figure 3a). The Cu from the rapid leaching phase is probably coming from the surfaces and the slow phase from the inner parts of the specimens. After 2 days of leaching, the higher Cu contents were released again until the end of leaching test due to the nonuniform leaching of CuCl_2 from the CuCl_2 -treated wood (CuW). Temiz et al. (2006) observed similar nonuniform leaching patterns for CCA and other Cu-based preservatives. CuT1, CuS1, and CuM1 showed similar nonuniform leaching behavior as that of CuW, but the Cu leaching was

Figure 3 Assessing the degree of Cu leaching from wood treated by a one-step impregnation with TiO_2 - and SiO_2 -based solutions (S1–S3), whereas each mix contained 1.2% CuCl_2 .

considerably lower during the whole experiment due to the retardant effect of the sol-gel depositions. The sample CuM1 released twice as small Cu than the sample CuW (Figure 3a).

The highest leaching rates were consequently detected for specimens impregnated solely with CuCl_2 (CuW) followed by CuS1, CuT1, and CuM1 (Figure 3b). The cumulative emission results (Figure 3c) also demonstrate the retarding effects of TiO_2 , SiO_2 , and their combined sol-gel depositions in the case of one-step impregnation with CuCl_2 . Approximately 30% (CuS1), 40% (CuT1), and 70% (CuM1) less Cu was leached from specimens compared with CuCl_2 -treated wood (CuW). Böttcher et al. (2000) demonstrated the leaching behavior of boron-based systems, which could be reduced by infiltrating SiO_2 sols as boron was embedded into the nanoscaled SiO_2 gel matrix. It is believed that, in the precursor mixtures,

the Cu ions were chemically attached with Si and Ti ions in the form of their respective silicate and titanate and fixated thus Cu in the wood structure more efficiently.

The diminished water uptake (Figure 3b) can also be contributed to the reduced leaching rates. Water uptake for CuM1 and CuT1 (except CuS1) was lower than CuCl_2 -treated wood (CuW). This seems reasonable because previous studies (Donath et al. 2006; Weigenand et al. 2007; Hübert et al. 2010; Unger et al. 2012) revealed that wood treated with silica, silicons, or titania partially filled the lumen of treated wood. This inhibited the passage of water into the wooden structures and resulted in less water uptake. However, CuS1 was not successful in this regard. The specimen CuM1 released the less Cu, which also took up the least water. In contrast, CuW absorbed the most water and Cu leaching was also most extensive. Cu leaching and water uptake were correlated also in CuT1.

Figure 4 Assessing the degree of Cu leaching from wood treated by a two-step impregnation. In the first step: 1.2% CuCl_2 alcoholic solution; in the second step: TiO_2 - and SiO_2 -based precursors (S1–S3).

Obviously, less water uptake entails less leachability of Cu from the test specimens because of the lack of water for leaching.

The leaching results of Cu for double-step impregnated wood specimens (CuT2, CuS2, and CuM2) along with only CuCl₂-treated wood (CuW) are presented in Figure 4. After the first short immersion period, the Cu concentrations of leachates collected from CuS2 and CuM2 were not very different from that of CuW. An exception is CuT2 that initially released very much less Cu. After 2 days of leaching, the Cu concentrations were decreased markedly in all leachates of double-treated specimens compared with experiments with CuW (Figure 4a). After this early phase, the same non-uniform leaching trend was prevailing as already observed for the single-step impregnations. Figure 4b shows that the least amount of Cu was liberated from CuT2. For the specimens CuS2 and CuM2, moderate leaching rates can be observed. The cumulative emission of Cu compiled for the whole leaching period reveals that sol-gel-treated wood released 50–80% less Cu than CuW. The correlation between Cu leaching and water uptake for CuT2, CuS2, and CuM2 is similar to that of specimens treated in a single step.

Accordingly, the postimpregnation of CuCl₂-treated wood with sol-gel precursor solutions provides an extra fixation to CuCl₂ as sol-gel deposition films act as barriers to water absorption.

Conclusions

The application of CuCl₂ mixed Ti and Si alkoxide precursors to wood reduces the Cu leaching rates remarkably in comparison with CuCl₂-treated wood. This is probably due to the embedding action of TiO₂ and SiO₂ depositions formed by sol-gel processing. The antileaching efficiency of these materials was further improved in a second impregnation step to already impregnated wood with CuCl₂. In this case, the gels have a barrier function impeding leaching. There is a correlation between water uptakes and Cu leaching rates in both one-step and two-step impregnated specimens. These preliminary findings are encouraging for the continuation of the efforts to limit the leachability of Cu- and boron-based preservatives, which are free of Cr, by means of sol-gel impregnation.

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