

# Effect of Amine Functionalization and Ageing on Copper and Boron Leaching from Wood Preservatives Grafted to Siloxane Networks

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The study evaluated copper, boron, and silicon release from wood samples treated with sol-gel formulations based on tetraethoxysilane (TEOS) and 3-aminopropyltriethoxysilane (APTES) functionalized with copper (II) chloride and boric acid, respectively. The adopted leaching procedure was Japanese protocol JIS K 1571 (2004). Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Electron Spray Ionization Mass Spectrometry (ESI-MS) were employed for analyzing the leached solutions. The obtained results highlighted the important role of the amine function that was derived from the APTES precursor, in anchoring both copper and boron through coordinative and ionic interactions, respectively. In fact, copper formulations with TEOS alone (without APTES) showed higher copper leaching. In contrast, the silicon leaching was decreased due to better siloxane reticulation performed by TEOS alone. In addition, ageing (two months) of the samples treated with APTES containing formulation TEOS/APTES/Cu 10:1:0.2 resulted in a reduction of copper leaching (from 27% in the fresh samples to 7% in the aged ones), which was attributable to increased efficiency of inorganic sol-gel polymerization. The TEOS/APTES/B 1:1:0.2 formulation gave a leaching value of 20%, which was lower in comparison with the values reported in previous literature.

**Keywords:** 3-Aminopropyltriethoxysilane; Boric acid; Copper; Tetraethoxysilane

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## INTRODUCTION

Copper(II) salts and boric acid have been utilized for wood preservatives against fungi and insects for almost two centuries. The use of boron salts has been prominent in structural timber in protected and aboveground conditions (Lloyd *et al.* 1990; Lloyd and Manning 1995; Peylo and Willeitner 1999; Humphrey *et al.* 2002; Grace *et al.* 2006) due to their low resistance to leaching when in contact with water (Drysdale 1994; Hughes 2006; Tsunoda *et al.* 2006; Dhyani and Kandem 2012).

The leaching of copper and boron from treated wood might cause environmental risk, as reported in data regarding the bioaccumulation and toxicity of leachates from preservative-treated wood (Schultz *et al.* 2008).

In the past, chromated copper arsenates (CCA) and chromated-copper-borates (CCB) represented diffused solutions to limit copper or boron releasing (Hingston *et al.* 2001; Kartal *et al.* 2007a; Obanda *et al.* 2008; Lesar *et al.* 2009, 2012). However, their utilization was reduced in the wood preservation markets when arsenic compounds and

later chromium compounds were restricted in the European Union due to EU Regulation 528 (2012). More recent proposals for the reduction of copper leaching have involved copper complexes, *i.e.* carboxylic acids (octanoic, 2-ethylhexanoic, decanoic) (Humar *et al.* 2004) or with ethanolamine (Humar and Lesar 2008). The copper salts without chromium and arsenic, utilized recently for in-ground wood preservation released higher copper amounts than CCA-treated wood (Temiz *et al.* 2006).

The research on boron has been directed towards partial fixation systems to reduce boron leaching (Pizzi and Baecker 1996) but allow for sufficient mobility to maintain the borates preservative action (Thévenon *et al.* 1999).

Obanda *et al.* (2008) summarizes the strategies employed for reducing the boron leaching in wood preservatives. The methods tested include: surface coating of boron-treated wood with layers of varnish, resin or hydrophobic wax (Peylo and Willeitner 2009), or impregnation with an aqueous liquid dispersion or emulsion that contains borates and rosin/resin derivatives simultaneously; employment of organic-boron compounds (OBC), especially aromatic acids, such as phenyl boric acid (PBA), whose leaching resistance is supposed to be due to their possibility to interact with the aromatic subunits of lignin and to restricting the access of water to the boron (Liu *et al.* 1994); physical wood treatments *via* heating and steaming for compression, to induce the conversion of boron in wood in the formation of trimeric hydroxyborate ions and/or metaboric esters with the water molecules (Yalinkilic *et al.* 1999); and the chemical complexation of a borate compound with an agent capable of forming a water-insoluble complex in wood upon dehydration (Baysal and Yalinkilic 2005) mainly in combination with inorganic metals such as zinc borate, copper borate complexes (Furuno *et al.* 2003, 2006; Manning 2008). Furthermore, stabilized boron esters and other complexes with ammonium were also employed, *i.e.* ammoniacal and ammonium borates (Walker 1997; Kartal and Imamura 2004; Lyon *et al.* 2007) and borate-amine oxide formulations (Tseng *et al.* 2003). Some studies also attest that some ammonium complexes did not lead to the loss of activity of boron (Humphrey *et al.* 2002) because they progressively hydrolyze to release boric acid.

Additionally, Yamaguchi (2003) proposed the addition of boron compounds to silicon emulsions. This addition creates silicic acid/boric acid complexes well-fixed into wood with good efficacy against termites, and whose solubility may also be reduced by treating wood in a second step with a soluble metal salt that reacts *in situ* to form water insoluble metallic silicates (Kazunobu 1995).

The silica modification of wood (Donath *et al.* 2004; Mai and Militz 2004; Unger *et al.* 2013) represents one of the most promising alternatives employed to reduce boron or metal leaching (Saka and Ueno 1997; Kartal and Imamura 2004; Kartal *et al.* 2007a; Terziev *et al.* 2009), thus increasing biological resistance against wood degrading fungi and insects (Kartal *et al.* 2007b). Tetraethoxysilane and methyltriethoxysilane as modifying silicon-based compounds were described for their potential to limit both boron (Kartal *et al.* 2009) and copper release (Townsend *et al.* 2005). The modification of wood with siloxane materials bearing amino groups was also performed (Palanti *et al.* 2011): tetraethoxysilane (TEOS) and triethoxysilanes functionalized with amino groups, such as 3-aminopropyltriethoxysilane (APTES), were used as precursors; their hydrolysis and co-condensation (the sol-gel process) was allowed to take place *in situ*. This process generates hybrid inorganic-organic silica xerogel particles penetrating the wood cell walls.

The addition of copper salts or boric acid to these formulations improved the wood resistance against biological attack (Feci *et al.* 2009) already partially conferred by the siloxane modification (Mai and Militz 2004; Cookson *et al.* 2007), and by the amino groups themselves (Donath *et al.* 2006; Ghosh *et al.* 2009).

The formulation with copper was already characterized by means of spectroscopic (solid state NMR, ESR, FTIR) and microscopic (SEM) investigations and the wood resulted in being successfully interpenetrated with the xerogel, and the copper (II) effectively diffused inside the wood by coordination linkages with the amine functions (Vignali *et al.* 2011).

Preliminary leaching tests to evaluate copper fixation to wood modified with NH<sub>2</sub>-R functionalized silica xerogel gave good results (Palanti *et al.* 2011). The combination of TEOS, APTES, and boric acid proved to have good efficacy against *C. puteana*, *P. placenta*, and *T. versicolor*, even after a leaching EN 84 procedure, and this formulation was shown to be effective also against *H. bajulus* (Palanti *et al.* 2012a). Previous literature provides a variety of employed regulatory leaching procedures: the EN 1250 (Humar *et al.* 2004, 2005, 2007), the ECS 1994 (Humar *et al.* 2004), the EN 84 procedure (Humar *et al.* 2004; Palanti *et al.* 2012a,b), the Japanese Industrial Standard (JIS) K 1571 (2004) (Kartal *et al.* 2007b), and the OECD Guidelines (Temiz *et al.* 2006). Among these, the JIS K1571 was chosen in this work, providing the release trend during a ten-day testing period. This study evaluates copper, boron, and silicon release from wood samples treated with TEOS-APTES-CuCl<sub>2</sub> (TACu) and TEOS-APTES-H<sub>3</sub>BO<sub>3</sub> (TAB) formulations through the leaching procedure JIS K 1571 (2004). Additionally, this study aims to confirm that the presence of APTES in the sol-gel siloxanes formulations reinforces copper and boron anchoring through coordinative and ionic interactions, respectively.

## EXPERIMENTAL

### Materials

Wood blocks of Scots pine (*Pinus sylvestris* L.), sapwood, 30 x 10 x 5 mm<sup>3</sup> (mini-blocks) were conditioned to a constant mass at 20 °C and 65% relative humidity before being subjected to the impregnation process with the formulations reported in Table 1.

**Table 1.** Formulations and Reagents

Formulations	Molar Ratio	TEOS (T) (mmol)	APTES (A) (mmol)	H <sub>3</sub> BO <sub>3</sub> (B) (mmol)	CuCl <sub>2</sub> (Cu) (mmol)	ETOH Solvent (mL)
1. TACu	10:1: 0.2	44.8	4.28	-	0.86	11
2. TCu	10:1	49.28	-	-	4.93	11
3. TCu	25:1	49.28	-	-	1.96	11
4. TCu	50:1	49.28	-	-	0.98	11
5. TAB	1:1:0.4	44.8	42.8	17.12	-	20
6. TAB	1:1:0.2	44.8	42.8	8.54	-	20

Stock ethanol solutions (Sigma Aldrich, Milan, Italy) were prepared for utilization for the samples treatment, containing TEOS (99%, Sigma Aldrich, Milan, Italy) and APTES (99%, Sigma Aldrich, Milan, Italy) in different ratios, with the addition of copper (II) chloride (99%, Sigma Aldrich, Milan, Italy) or boric acid (99,5%, Sigma Aldrich, Milan, Italy). Formulations with TEOS and copper (II) chloride without APTES were also prepared to compare the effect of the TEOS concentration and APTES presence/absence on the Cu release.

All of the formulations were maintained under a dry atmosphere until their use as sol-gel precursors. Then, the wood samples were treated with a vacuum-atmospheric pressure cycle (6 replicates for each formulation were used). After a vacuum exposure (5.5 kPa) of 45 min, the wood blocks were dipped in the sol-gel solutions and maintained under vacuum for 15 min. Subsequently the mixture was gently stirred for 30 min under a dry nitrogen atmosphere (1 atm). After impregnation, the wood samples were removed from the treatment solutions, lightly wiped to remove the trace of solution from the surface, weighed to determine the solution retention, and dried at room temperature and atmospheric pressure.

After the removal of the samples, the solutions were allowed to undergo the sol-gel process at room temperature (approximately 1 h). The performance of impregnation was evaluated by calculating the weight percentage gain ( $WPG_1$ ). The  $WPG_1$  was calculated according to Eq. 1,

$$WPG_1 = [(M_t - M_0) / M_0] \times 100 \quad (1)$$

where  $M_0$  and  $M_t$  are the oven-dried ( $103 \pm 5^\circ\text{C}$ , 24 h) mass (g) of the untreated and sol-gel-treated wood, respectively.

## Methods

The leaching test, conducted according to JIS K 1571 (2004), was performed by the immersion of the sol-gel treated wood blocks in deionized water stirred with a magnetic stirrer (400 rpm to 450 rpm) at  $27^\circ\text{C}$  for 8 h followed by drying at  $60^\circ\text{C}$  for 16 h. This cycle was repeated 10 times. After each leaching cycle, the water was renewed with fresh deionized water in a ratio of 10:1 (volumes of water to a volume of wood). After the impregnation of the different formulations (Table 1), the samples were oven-dried, left in air at room temperature (R.T.), and lastly were exposed to the leaching procedure after one day (freshly prepared samples) or after two months (aged samples) in duplicate for each test. The solutions that corresponded to each leaching day were diluted to 100 mL in a volumetric flask and analysed with an inductively coupled plasma atomic emission (ICP-AES) spectrometer (Horiba Jobin Yvon, Edison, NJ, USA) to determine the copper ( $\lambda = 324.800 \text{ nm}$ ), boron ( $\lambda = 249.773 \text{ nm}$ ), and silicon ( $\lambda = 251.611 \text{ nm}$ ) amounts.

A Jobin Yvon Ultima 2 was employed for the ICP-AES; the operating conditions were: power generator (normal condition 1000 W, plasma gas flow rate 12 L/min, nebulization pressure 300 kPa, nebulization flow rate 0.50 L/min, and pump speed of 20 rpm).

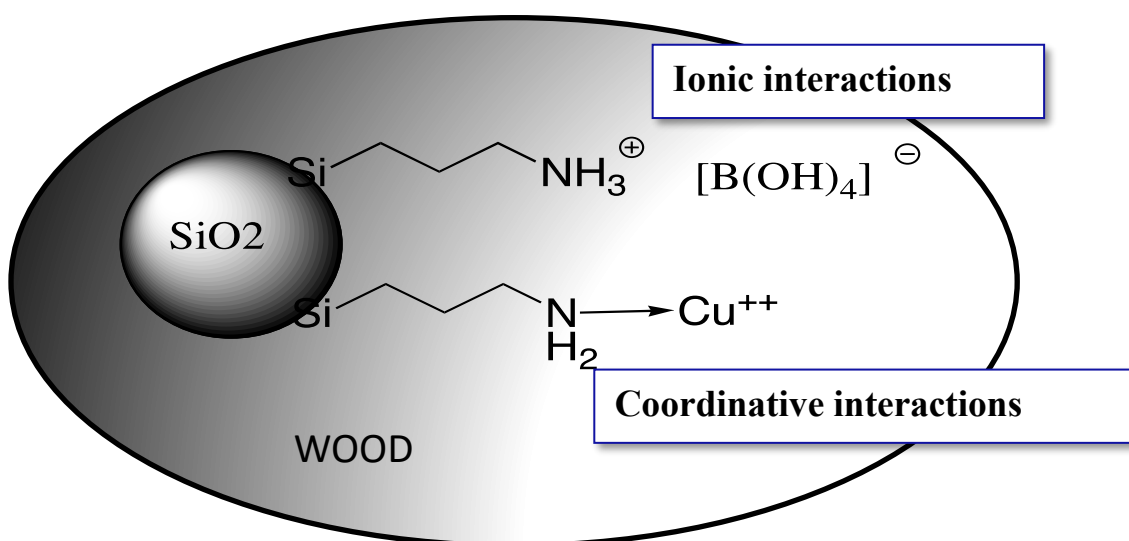
The total amounts of leached Cu, B, and Si from the samples were calculated by the sum of the relevant amounts determined in the water leaching, and the obtained data were compared to Cu, B, and Si total content. For this purpose, two wood samples treated with each of the six formulations 1-6 (Table 1) were ground and mineralized with 70%

HNO<sub>3</sub> and 40% HF acid in a microwave oven for 45 min at 180 °C before the ICP-AES measurements.

Finally, an LTQ XL FT Orbitrap Mass spectrometer with a Ion Trap technology of new generation (Linear Trap) coupled with HPLC Dionex Ultimate 3000 accessorized with Electrospray (ES) source was used for qualitative analyses of silica fragments released from treated samples in water solutions. For this purpose, two wood samples, treated with formulation TACu 10:1:0.2 were dipped in a 10% H<sub>2</sub>SO<sub>4</sub> bath for 24 h at R.T., under stirring. The extracted solutions were subjected to ESI-MS analysis.

## RESULTS AND DISCUSSION

As discussed in the introduction, the presence of APTES should have favoured the copper and boron grafting through coordinative and ionic interactions, as sketched in Fig. 1.



**Fig. 1.** Modes of grafting of copper cations and tetrahydroxoborate anions (derived from boric acid and water in alkaline environment) to amine-functionalized silica particle.

However, APTES, bringing only three hydrolyzable alkoxy groups, was less effective than TEOS (exhibiting four alkoxy groups) in producing inorganic siloxane reticulation through hydrolysis and condensation reactions (the sol-gel process). Indeed, in the case of APTES-containing formulations, a soluble oligomeric species (such as POSS, *vide infra*) might have been formed.

The WPG<sub>1</sub> values obtained with the six formulations reported in Table 1 are shown in Table 2. They showed high values of the standard deviations. It was interesting to note that the copper amount appeared to influence the WPG<sub>1</sub> values exhibited by samples 2 through 4 (TEOS/Cu). Actually, with increased copper amounts, the WPG<sub>1</sub> values decreased, which suggested that the Cu<sup>2+</sup> cation could have played a role in the formation of oligomeric siloxanes that were less able to penetrate the wooden structure.

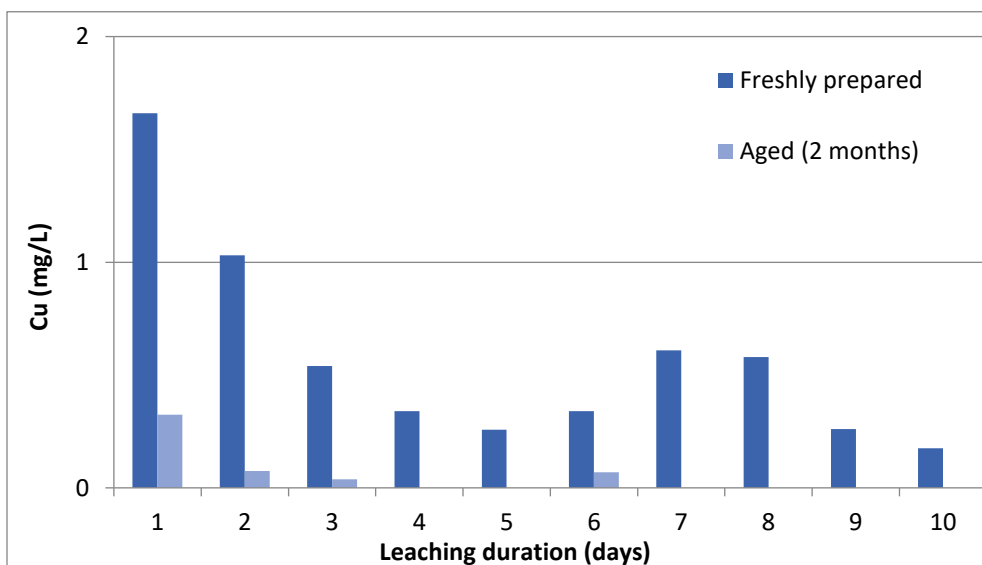
Figure 2 shows the trend of copper leaching during the 10 days required by the JIS protocol from two samples impregnated with formulation 1, but with differing ageing times: 0.1 and 2.0 months. For both, the higher amount of released copper was recorded

during the first day of leaching, as expected. Then it decreased, but a further increase was observed after the sixth day, and reached a maximum in the seventh day. In the freshly prepared samples, leaching was much higher than in the aged samples and the Cu loss was also easily observed as a discoloration of the sample during the leaching procedure.

**Table 2.** WPG<sub>1</sub> and Standard Deviation of the Wood Mini-blocks for the Different Formulations

Formulation (N = 6)	Molar Ratio	Ageing (months)	WPG <sub>1</sub> (%)
1. TACu,	10:1: 0.2	0.1 and 2	19.2 ± 8.3
2. TCu	10:1	0.1	21.4 ± 6.7
3. TCu	25:1	0.1	27.2 ± 3.6
4. TCu	50:1	0.1	31.1 ± 4.6
5. TAB	1:1:0.4	4	22.6 ± 9.1
6. TAB	1:1:0.2	4	25.0 ± 7.5

\*N: Replicates



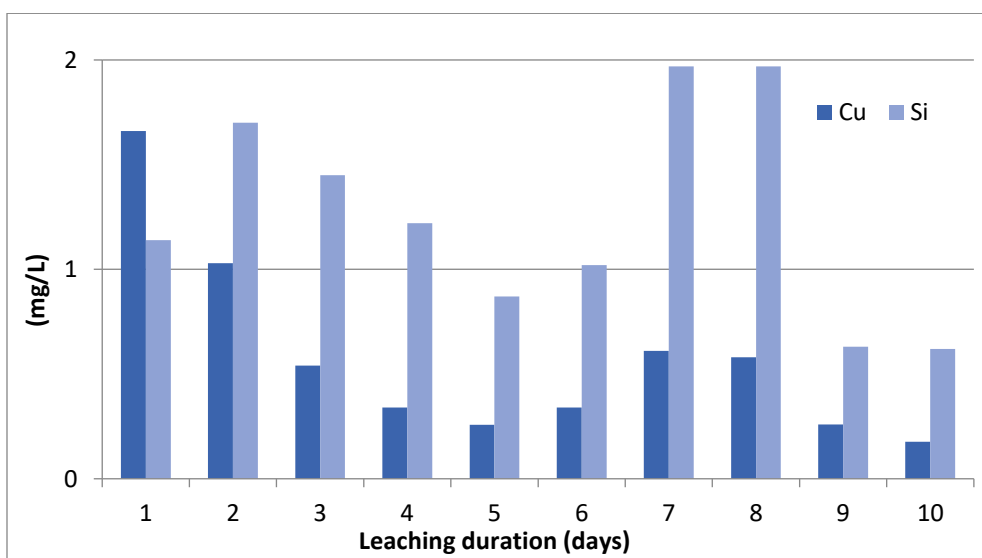
**Fig. 2.** Comparison between copper leaching (mg/L) from fresh and two-months aged samples treated with formulation 1 (TACu 10:1:0.2)

With the freshly treated sample, the final amount of released Cu was  $0.346 \text{ kg/m}^3 \pm 0.008 \text{ kg/m}^3$ , which represented approximately 27% of the Cu content ( $1.264 \text{ kg/m}^3 \pm 0.013 \text{ kg/m}^3$ ) that was in the non-leached samples. In contrast, the final amount of copper released from the aged specimens during the leaching procedure was  $0.083 \text{ kg/m}^3 \pm 0.006 \text{ kg/m}^3$ , which was approximately 7% of the total Cu content. This was a satisfactory result, considering that Cu water-soluble salts, such as copper sulphate, have been reported to have at least 50% of the Cu leached out (Humar *et al.* 2005). These results demonstrated that ageing of the xerogel was an important factor in determining copper retention. In fact, it produced further inorganic reticulation, through sol-gel condensation

reactions, with a consequent reduction of the soluble siloxane oligomers previously mentioned.

Therefore, with the TACu treatments, the copper release in the first leaching days was attributable both to weakly interacting copper and to copper coordinated to amine functions that belonged to soluble siloxane oligomers. In contrast, the copper leaching observed around the seventh day was reasonably attributable to the hydrolysis processes that involved part of the silica network. This resulted in the release of siloxane oligomers dragging copper cations coordinated to amine functions and bonded to silanolate groups.

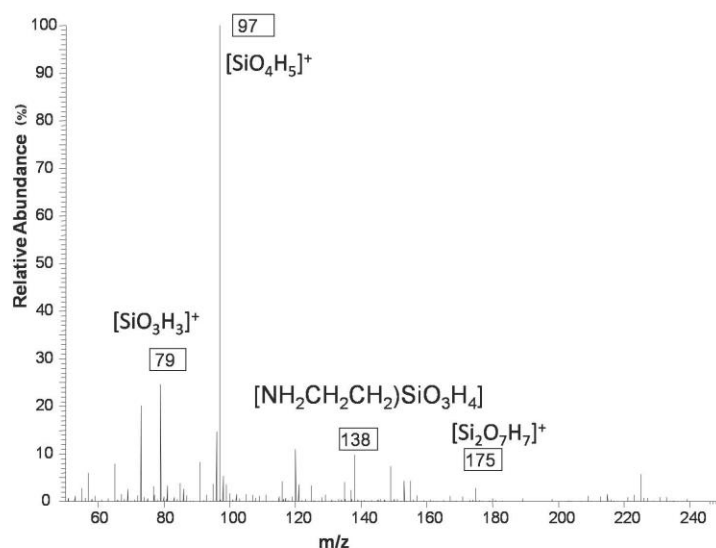
This hypothesis was supported by the analogue trend in the silicon release, which attested that the seventh day Cu release was effectively induced by the hydrolysis of the silica network (Fig. 3). Figure 3 showed the silicon and copper leaching results for the shortly aged samples treated with formulation 1.



**Fig. 3.** Comparison between leaching (mg/L) of silicon (Si) and copper (Cu) from the fresh samples treated with formulation 1 (TACu 10:1:0.2)

In this regard, to gain any insight into the silicon species released by hydrolysis, the ESI mass spectrum of the solution extracted from the TACu-treated samples *via* rapid acidic hydrolysis (Fig. 4), showed the presence of numerous silicon containing species. This included fragments that contained the amine function like that at  $m/z$  138, which corresponded to  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiO}_3\text{H}_4^+$ , as expected.

Leaching treatments were also performed on the samples impregnated with TCu formulations (without APTES) to evaluate separately the silica network and the amino-groups contribution in the retention of copper. Different copper concentrations (TCu 50:1, TCu 25:1, and TCu 10:1, see Table 1) were tested and compared. In the absence of amino-groups, copper was supposed eventually to interact with the xerogel only *via* covalent Si-O-Cu linkages (copper-silanolate interactions). As for the previous tests, all the samples were oven-dried after the impregnation procedure to determine the dry mass. However, in these cases browning of the wood samples was observed, possibly due to the formation of CuO, as copper is no longer protected by the amino functions. The darkening increased with increasing amounts of starting copper, probably because a major metal amount was weakly bonded to the polymer.



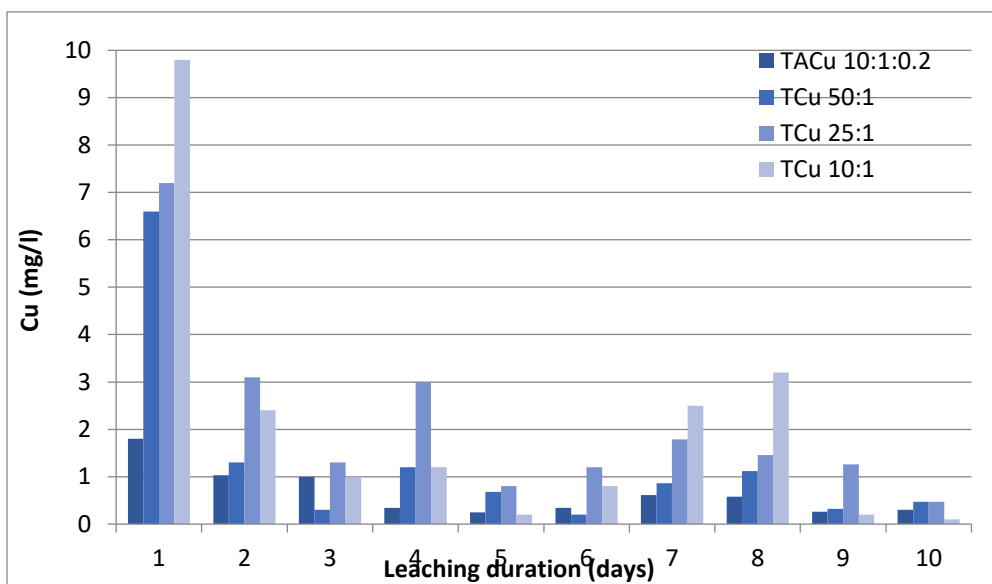
**Fig. 4.** Mass spectrum of the leaching waters obtained from fresh formulation 1-treated sample; Relative abundance (%) of the silica fragments with low molecular weight relieved are reported in the spectrum

The WPG<sub>1</sub> values that resulted for the three treatments decreased with the increase of the Cu amount (Table 2). These results suggested that the presence of copper could perhaps influence the sol fluidity and reticulation, *e.g.* promoting the formation of oligomers that penetrated more difficultly into the wooden structure.

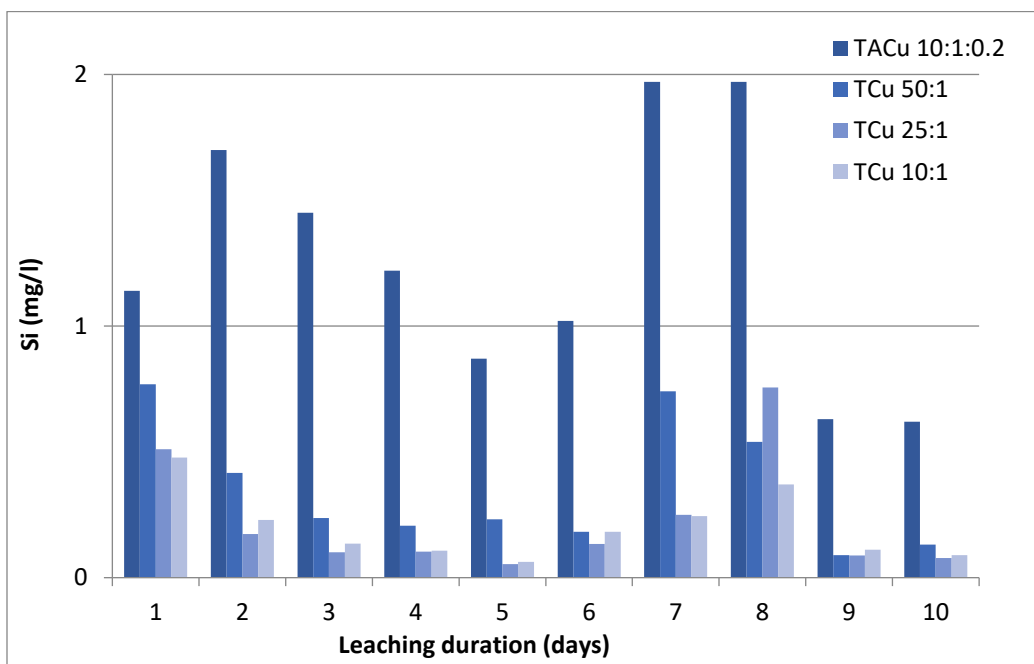
The trend of copper and silicon release during leaching of the three TCu formulations showed an increase after eight to nine days. This increase could have been due to the partial hydrolytic breakdown of the silica network. The copper released in 10 days from the sample treated with the TCu 50:1 formulation was  $1.531 \text{ kg/m}^3 \pm 0.023 \text{ kg/m}^3$ , which was 90% of the total amount ( $1.696 \text{ kg/m}^3 \pm 0.006 \text{ kg/m}^3$ ). Analogous results were obtained for TCu 25:1 ( $3.285 \text{ kg/m}^3 \pm 0.009 \text{ kg/m}^3$  total Cu amount and  $2.858 \text{ kg/m}^3 \pm 0.041 \text{ kg/m}^3$  Cu release in 10 days *i.e.* 86% of leaching) and TCu 10:1 ( $3.242 \text{ kg/m}^3 \pm 0.018 \text{ kg/m}^3$  total Cu amount;  $2.819 \text{ kg/m}^3 \pm 0.263 \text{ kg/m}^3$  Cu release in 10 days *i.e.* 87 % of leaching). Compared to the formulation containing APTES, it appeared that the TCu treatments allowed wood to reach higher copper absorption values; nevertheless the samples exhibited a low resistance to leaching because of the weak Cu interaction with the polymer. It was worthy to note that copper leaching for the TCu formulations occurred mainly in the first day, which confirmed the weak copper-siloxane interactions. The Cu leaching comparison among the four treatments 1 through 4 is reported in Fig. 5.

Conversely, the silicon release, shown in Fig. 6, decreased with increased copper amount, which suggested that the presence of copper influenced the silica texture. The percentages of silicon released during the complete leaching cycles were: 0.28% (TCu 50:1), 0.26 % (TCu 25:1), and 0.16 % (TCu 10:1). The daily silicon releases appeared lower than those observed for the sample treated with the TEOS-APTES formulation (Fig. 6), due to the trend of APTES forming oligomers, such as  $(\text{CH}_2)_3\text{NH}_2)_8\text{Si}_8\text{O}_{12}$ , called polyhedral oligomeric silsesquioxanes (POSS), that were more easily leached out from the wooden structure (Li *et al.* 2001).





**Fig. 5.** Comparison of Cu leaching from fresh samples treated with formulations 1 (with APTES), and 2, 3, and 4 (without APTES)



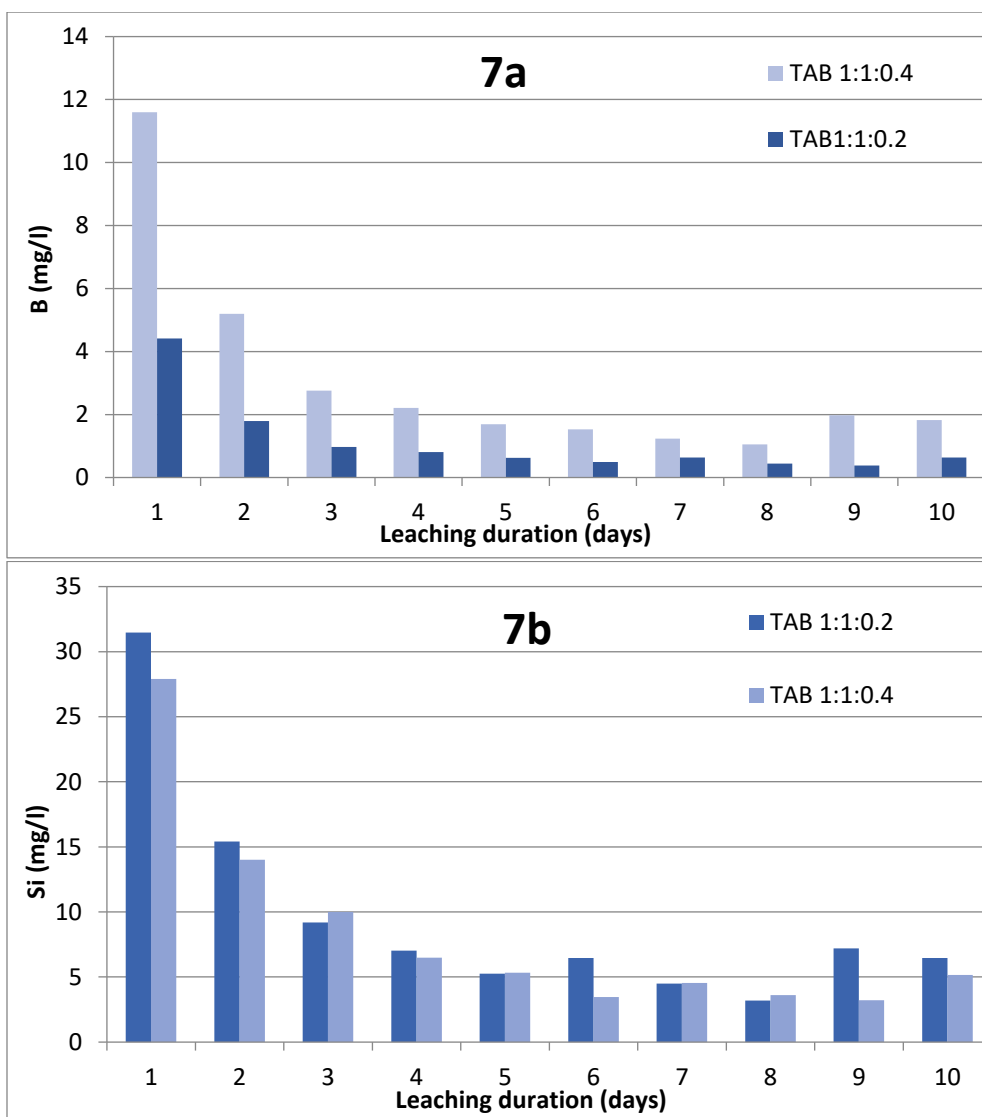
**Fig. 6.** Silicon release (mg/l) from fresh samples treated with formulations 1, 2, 3, and 4

The samples treated with formulations 5 and 6 contained boron and were subjected to the leaching procedure after 4 months of ageing, they showed the higher amount of released boron during the first day (Fig. 7a). Then, the boron leaching decreased. For the samples treated with copper, a further increase was observed in correspondence of the ninth and tenth leaching days, possibly due to hydrolysis, which involved the partial release of covalently bonded boron of the borosilicate chains.

The two release steps (first leaching day; ninth and tenth leaching days) suggested that boron interacted with the wood-silica system in two ways: (i) by formation of

tetrahydroxoborates *via* interacting with the protonated amino groups (Fig. 1), whose retention and activity efficiency were already demonstrated by Furuno *et al.* (2003) and Lyon *et al.* (2007); (ii) the formation of borosilicates by condensation with silanol groups, which gave rise to Si-O-B linkages (Yamaguchi 2003).

Boron's earliest release was possibly due to intact  $\text{H}_3\text{BO}_3$  and  $[\text{B}(\text{OH})_4]^-$  species anchored to protonated amine functions of the siloxane network, whereas the release during the last days of the leaching test could have been due to the hydrolysis of borosilicates.



**Fig. 7.** (a) Boron release (mg/l) and (b) Silicon release from aged samples treated with formulation 5 and 6

The total amount of released boron was much higher in the TAB 1:1:0.4 formulation compared to the TAB 1:1:0.2 (Figs. 7a and b). The boron that leached out from the sample treated with the TAB 1:1:0.4 formulation was  $1.470 \text{ kg/m}^3 \pm 0.028 \text{ kg/m}^3$ , *i.e.* approximately 56% of the total boron amount ( $2.611 \text{ kg/m}^3 \pm 0.033 \text{ kg/m}^3$ ). Furthermore, only  $0.494 \text{ kg/m}^3 \pm 0.008 \text{ kg/m}^3$  of boron was released from the 4-month

aged sample treated with the TAB 1:1:0.2 formulation, which corresponded to only approximately 20% of the total boron amount ( $2.386 \text{ kg/m}^3 \pm 0.031 \text{ kg/m}^3$ ).

The amount of boron in TAB 1:1:0.4 seemed to exceed the fixation “capacity” of the silica network, whereas a lower boron amount found more easily adequate fixation. The presence of APTES contributed to boron fixation into the wood. As reported above, the value of boron release, when the APTES is in the formulation, was between 20% and 56% lower if compared to values reported in the literature for boric acid coupled with silicon compounds; without APTES, the boron leaching was around 60% (Kartal *et al.* 2009).

The same samples, with different starting boron concentrations and substantially different amounts of leached boron, show no relevant difference among the silicon release during the 10-day test. This suggested that the amount of boron engaged in strong interactions with the siloxane network cannot exceed a threshold value and, unlike copper-treated samples, the silicon release seemed to be narrowly influenced by the boron amount (Fig. 7b).

## CONCLUSIONS

This paper investigated the influence of amine functions and ageing procedures on leaching of copper, boron, and silicon from wood treated with copper and boron anchored to siloxane sol-gel networks. The main objectives have been attained by confirming two important effects:

1. It has been demonstrated that the presence of grafted amine functions, provided by the APTES precursor, lowered the copper leaching compared to the silica xerogels formulations without APTES.
2. The ageing of wood samples, interpenetrated with copper or boron containing siloxane xerogels, resulted in a decrease in copper and boron leaching compared to the corresponding fresh samples. This was due to the completion of the hydrolysis and condensation reaction of the sol-gel process. This effect is expected to be generally applicable to the sol-gel siloxane networks.

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