



Modelling inorganic biocide emission from treated wood in water

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ARTICLE INFO

Article history:

Received 27 February 2011

Received in revised form 23 June 2011

Accepted 24 June 2011

Available online 7 July 2011

Keywords:

Wood

Biocide

Leaching test

Modelling

ABSTRACT

The objective of this work is to develop a chemical model for explaining the leaching behaviour of inorganic biocides from treated wood. The standard leaching test XP CEN/TS14429 was applied to a commercial construction material made of treated *Pinus sylvestris* (Copper Boron Azole preservative). The experimental results were used for developing a chemical model under PHREEQC[®] (a geochemical software, with LLNL, MINTEQA2 data bases) by considering the released species detected in the eluates: main biocides Cu and B, other trace biocides (Cr and Zn), other elements like Ca, K, Cl, SO₄²⁻, dissolved organic matter (DOC). The model is based on chemical phenomena at liquid/solid interfaces (complexation, ion exchange and hydrolysis) and is satisfactory for the leaching behaviour representation. The simulation results confronted with the experiments confirmed the hypotheses of: (1) biocide fixation by surface complexation reactions with wood specific sites (carboxyl and phenol for Cu, Zn, Cr(III), aliphatic hydroxyl for B, ion exchange to a lesser extent) and (2) biocide mobilisation by extractives (DOC) coming from the wood. The maximum of Cu, Cr(III) and Zn fixation occurred at neutral pH (including the natural pH of wood), while B fixation was favoured at alkaline pH.

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1. Introduction

Leaching of biocides from construction materials in contact with water could be a threat for the environment and is currently a research subject receiving attention from the European regulation authorities (CEN/TC351 Construction Products – Assessment of Release of Dangerous Substances). Implementation of an experimental leaching test for construction materials is still in progress at European level and modelling tools will be necessary in a second step to interpret data and then to assess leaching behaviour and its environmental impact.

Different classes of biocides were used in wood treatment according to the legislative constraints imposing increasingly strict conditions. Thus, in the Sixties, the aldrin and the creosotes were usually employed (now prohibited). Then products known under the name of “CCA—copper, chromium, arsenic” were extensively used for wood treatment. Nowadays, the CCA treatment is prohibited for residential constructions. The alternatives to these biocides are the so called “new generation biocides”, based for example on

boron, copper and various organic substances of synthesis such as the propiconazole and the tebuconazole.

The product studied in this research is a commercial construction product made of *Pinus sylvestris* treated with Copper Boron Azole preservative. Target elements are inorganic biocides, the major elements present in eluates and dissolved organic matter. Numerous authors (literature review in [1–4]) have studied the fixation and/or leaching of biocides in different leaching conditions and emitted hypotheses and qualitative explanations concerning the immobilisation of biocides in wood: different inorganic salts, oxides, and even organo-metal complexes seem to co-exist. No quantitative modelling of leaching processes from wooden materials has been reported.

Tentative modelling of metal release from treated wood in standard leaching tests was presented in [5]. In their model, the authors used fulvic acid as a surrogate for dissolved organic matter and the NICA-Donnan model to explain the leaching behaviour. Wood properties (acid/base behaviour, complexation and hydrolysis of wood fibres) and biocide fixation were not considered and no information was given about the model principles or the values used for the parameters. Diffusion and generic 1st order reaction kinetics were considered in [6] in order to explain the time dependence of biocide release, without a description of the chemical properties and reactions. To date, no mechanistic modelling has been published that is able to explain biocide leaching behaviour

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in terms of chemical reactions and in coherence with the wood properties.

In our opinion, a reliable modelling approach for biocide release needs to bring together the experimental leaching results and fundamental knowledge about wood/biocide chemistry. This study aims to develop a mechanistic model to explain the release of inorganic biocides from treated wood. The chemical model developed here is the first step of a complex modelling approach coupling chemistry and transport phenomena for the environmental assessment of pollutant release from wooden materials. An experimental leaching study (equilibrium leaching test) was performed on treated wood and the experimental results were used for model development and calibration.

Because biocides simultaneously interact with wood solid matrix and with the soluble species in the liquid phase, we point out that it is necessary to consider two compartments: (1) a wood compartment with its solid components, mainly cellulose, hemicellulose, lignin and inorganic compounds in small quantities; and (2) an aqueous compartment in contact with the wood, containing: (i) DOC coming out of the wood (molecules containing carboxyl, phenol, alcohol, and ketone groups) and (ii) inorganic species endogenous to wood.

An accurate representation of metal biocides requires a description of the main chemical processes in each compartment. So, in order to support the model development and to justify its hypotheses, a brief presentation of the current state of knowledge on specific wood/biocide chemical properties is given below.

2. Wood/biocide properties

Wood is composed of cellulose, hemicellulose and lignin, minor polysaccharides and a small fraction of compounds extractable in water or solvents. Numerous studies report the acid/base properties of lignin, cellulose and hemicellulose materials, e.g. [7–10]. Cellulose is a rather neutral polymer, while hemicellulose and lignin contain dissociating groups. Carboxyl groups are attached mainly to hemicelluloses and pectins and have pK_a values between 3 and 5. Lignin contains phenolic groups ($pK_a = 7.5–10.5$) and small quantities of carboxyl as a result of oxidation processes. The solubility and acid/base properties of wood extractives in water have been very little investigated. Balaban and Uçar [11] found that their acidity is due mainly to carboxyl groups and that solubility rises with temperature and alkali content.

Complexation and ion exchange are the two main mechanisms of interaction of metal ions with wood components. Most authors studying transition metal complexation by wood materials agree that: (i) the functional groups involved in surface specific complexation are phenol and carboxyl, (ii) the phenolic sites have significantly higher affinity for transition metals (Cu, Pb, Zn, Ni, Fe, Cd) than the carboxylic sites, (iii) the extent of metal sorption depends on pH and ionic strength [8–10,12], and (iv) cellulose has a very low sorption capacity for heavy metals [13] and forms rather unstable complexes with copper [14].

Several complexation modelling attempts for metal/wood systems are reported in the literature. We can distinguish models based on Langmuir adsorption theory and surface complexation models. The first model category (e.g. [15,16]) allows the material adsorption capacity and conditional adsorption constants to be determined, but is less relevant for explaining the pH and ionic strength dependence of the sorption process. The second model category is based on stoichiometric reactions between ligand site and metal ion. The non-electrostatic surface complexation model used by [10] belongs to this model category. In this work, a correct representation of the experimental data required monodentate

complexes to be considered in the model for every metal studied (Pb, Cu, Cd, Zn, Ni) but also bidentate complexes for several of them, like Cu. Other authors [8,12] have shown that a surface complexation model based on the electrostatic double-layer theory could be used successfully to describe proton and metal (Cu, Cd, Ni, Pb, Zn) binding to the lignocellulosic substrate over a wide range of conditions. These authors determined the intrinsic complexation constants for the cited metals, with a stoichiometry of 1:1. Discussing different modelling approaches used for metal/natural organic matter sorption, they argue that the NICA-Donnan model and Model VI use 11 and 10 parameters respectively to fit a single-metal binding. This is a strong limitation for accurate determination of the model parameters and also for their ease of use. The advantages of the electrostatic double-layer model are its simplicity and its capability to describe the ionic strength-dependent electrostatic interactions that influence the adsorption of ions onto electrically charged surfaces.

A review of Cr adsorption theories is given in [17]. Cr behaves as Cr(III) and Cr(VI) in aqueous phase. In contact with biomaterials like wood, Cr(VI) transforms into Cr(III) by an adsorption-coupled reduction mechanism [18,19] involving adsorption steps of both Cr species and reduction of Cr(VI) such that Cr(III) becomes dominant in the system. The study reported in [18] shows that Cr(III) is retained by inner-sphere complexation with carboxyl groups formed after lignin oxidation while adsorption on cellulose is insignificant. According to [20], Cr(III) adsorption on biomaterials cannot be explained solely by an ion exchange mechanism; carboxyl and phenolic groups would be involved in Cr fixation. A reaction path is proposed leading to mono and polydentate complexes and involving free and hydroxylated Cr^{-3} ions. Despite the abundance of literature on the subject [17], no intrinsic complexation (or ion exchange) constants have been determined.

Boron leachability in treated wood is recognised to be high but its chemistry in wood is far from well understood. B (introduced as boric acid) can form organic complexes in which B is linked to wood by O bridges [21]. A reaction path has been proposed [22] between the negatively charged hydroxocomplex $B(OH)_4^-$ and hydroxyl groups on polysaccharides with formation of a bidentate complex. This reaction requires the presence of two -OH in favourable position. No complexation constants are available in the literature.

Alkaline and alkaline earth metals are expected to be especially involved in ion exchange reactions with carboxyl and, to a lesser extent, phenol groups. No information was retrieved in the current literature about other groups reacting with these metals. According to [23,24], Ca is exchanged by carboxylic groups present in different wood components (hemicellulose, pectins or lignin). Other authors have concluded that the majority of Ca (and also Na, K, Mg) tends to be bound by carboxyl sites [12] or non-specific sites [9], thus explaining the lack of competition between Ca and Cu.

Hundreds of extractives have been identified in water and organic solvents; they belong to many chemical classes: fats, fatty acids, fatty alcohols, phenols, terpenes, polyphenols, tannins, lignans, steroids, resin acids, rosin, waxes. Acetic and formic acids are the main volatile acids in wood and, like other extractives, originate from the decomposition of wood polymers due to the reaction with hydroxyl ion ([25–28]). Complexation properties of wood extractives with respect to metals have not been studied to date. Several complexation constants exist for some specific organic compounds, in particular for volatile organic acids.

The mineral part of wood is mainly composed of several major elements Ca, Mg, K, Si, Na, Cl (up to 80% of the ash). In addition to carboxyl groups on polymers, these metals are probably bound, on oxalate, carbonate, sulphate, and silicates.

3. Experiment

The construction product studied was a wood duckboard in *Pinus sylvestris*, industrially treated for outdoor use (class IV—wood in contact with the ground, wood placed horizontally outside, wood in contact with fresh water, etc.). In order to assure the complete neutrality and the public availability of the results, the studied product was bought on the ordinary market. Identification of the preservative used for the treatment was realised afterwards in an independent laboratory. The product was treated with a so-called new generation preservative, based on Copper Boron Azole. The elements monitored during experiments were chosen after a screening analysis:

- inorganic biocides from preservative treatment, i.e. Cu and B,
- other inorganic biocides identified in eluates, i.e. Cr and Zn,
- the major elements present in eluates, i.e. Ca, K, Cl, SO₄²⁻, and
- DOC.

The experimental study (details reported in [29,30]) consisted in the determination of the acid/base properties of a wood sample and of the pH influence on the release of elements and organic compounds, following the leaching procedure of European standard XP CEN/TS 14429 [31]. This test consisted of a series of extractions on crushed material (size <1 mm) at a liquid to solid ratio of 10 L/kg. The leachants contained pre-selected amounts of acid (HNO₃) or base (NaOH) in order to obtain 8 final pH values covering a large pH range. After a contact time of 48 h, at the end of which equilibrium conditions were reached (stationary pH values observed), the eluates were filtered through 0.45 μm pore size membranes. Eluate compositions were determined by using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) for metals, Dionex Ionic Chromatograph 25 for anions, and a TOC analyser (5000A Shimadzu) for DOC.

Additionally, wood moisture and total elemental content were determined. Total content was determined by aqua regia extraction and solution analysis by ICP-Optical Emission Spectrophotometry. The experiments were done in duplicate and the concentration relative error was 5 to 10%.

4. Model development

A chemical model was developed in PHREEQC geochemical software, combining the following major processes:

- (1) At the wood/liquid interface: (i) Cu, Cr and Zn surface complexation with phenol and carboxyl groups; (ii) ion exchange by carboxyl groups involving Ca, Zn; (iii) B weak complexation by cellulose; (iv) DOC solubilisation.
- (2) In the aqueous phase: (i) equilibrium reactions of mineral species, (ii) metal complexation and acid/base reactions of dissolved organic matter.
- (3) Dissolution/precipitation of inorganic solids like oxides, carbonates, and silicates.

Data from the literature were used as much as possible for parameter values and, if no data were available, missing values were determined by model adjustment on experimental leaching results. For the literature data, sensitivity analysis was performed in order to check the relevance and adequacy of the values.

Most of the equilibrium constants were taken from data bases commonly used with PHREEQC (MINTEQ and LLNL). Only mechanisms and reaction parameters studied in this work and not included in such data bases or literature are presented below.

For the *Pinus sylvestris* wood used in this study, the mean composition indicated by [32,33] was considered, i.e. 27% lignin, 28% hemicellulose and 40% cellulose, the rest being extractives (about 4%) and minerals.

In agreement with the literature cited in Section 2, we considered that phenol and carboxyl groups of lignin were responsible for metal complexation on wood. In Table 1, Lig.acO⁻ and Lig.phO⁻ correspond respectively to carboxyl and phenolic groups in wood linked by a generic lignin Lig. Dzombak and Morel diffuse double-layer model with the Donnan diffuse layer model was used (implemented in PHREEQC, with default thickness). This model requires the following input parameters: intrinsic complexation constants, site density and specific surface area of the material. These data are very scarce in the literature. Acid/base and intrinsic complexation constants for Cu and Zn were taken from [12], constants determined on a lignin isolated from wheat bran. An H⁺/metal⁺² stoichiometry of 1/1 was considered, as in most of the relevant literature. Concerning Cr sorption, it was considered that all Cr occurred as trivalent species and gave inner-sphere complexes with carboxyl and phenolic groups on lignin. Due to lack of data, only the monodentate complex species formed by CrOH⁺² ion was considered, based on the experimental observation that major adsorption occurred for acid-to-neutral pH. Both constants were estimated by fitting the model to experimental Cr concentration (Table 1).

For the specific surface area of wood fibres, Ravat et al. [12] reported 185 m²/g. For lignin isolated from black liquor, Guo et al. [10] found a value of 21.7 m²/g, which was estimated to be too small. Due to data scarcity, a sensitivity analysis was performed and a mean value of 100 m²/g of wood was chosen. The site densities determined by the same authors were 0.08 mmol/g and 0.28 mmol/g of lignin material for carboxyl and phenolic groups respectively. After adaptation for our wood composition (27% lignin), these values were used in the model and gave good simulation results. The sensitivity analysis showed that slightly lower values fitted the model better and this result seems logical for the following reasons: (i) a given theoretical lignin composition was considered, the real content being unknown; (ii) it can be assumed that not all lignin sites were accessible for leaching.

For modelling of B release, we considered boric acid and its bidentate complex with cellulose substrate, Cel.alOH (see reaction in Table 1, according to [22]). It was considered that only 2/3 of cellulose hydroxyl groups were in proximity and favourable for reaction (site density calculated from cellulose molecular formula is given in Table 1). The complexation constant was fitted for B behaviour representation.

Ion exchange reaction with low affinity sites was considered to explain Ca behaviour. Carboxyl groups of hemicellulose were considered as exchange sites. The ion exchange model implemented with PHREEQC requires exchange constants and the site concentration in the system. There are no constant data for this process. Concerning site density, we adapted the results of [24] who found 0.08 mmol/g of cotton wood, these groups being attached to hemicellulose. This value was too high to fit the experimental neutralisation curve and was therefore adjusted (Table 1). The exchange constant was also estimated by fitting the model for Ca experimental concentration. The same acidity constant was considered for all carboxyl sites.

The other mineral constituents were also considered in the model. All reactions in the liquid phase were considered with constants taken from the LLNL and MINTEQ data bases. Calculation of saturation indexes for all elements including Cu, Cr, B, Zn, Ca, did not show any saturation, thus demonstrating that the release behaviour from wood, in our experimental test conditions (high

Table 1
Parameters used in the model.

Reaction	log K	Reference
H ⁺ + Lig.acO ⁻ = Lig.acOH	3.37	[12]
H ⁺ + Lig.phO ⁻ = Lig.phOH	8.34	
Lig.acO ⁻ + Zn ⁺² = Lig.acOZn ⁺	2.62	
Lig.phO ⁻ + Zn ⁺² = Lig.phOZn ⁺	5.7	
Lig.acO ⁻ + Cu ⁺² = Lig.acOCu ⁺	3.58	
Lig.phO ⁻ + Cu ⁺² = Lig.phOCu ⁺	7.56	
Lig.acO ⁻ + CrOH ⁺² = Lig.acOCrOH ⁺	4.3	This study
Lig.phO ⁻ + CrOH ⁺² = Lig.phOCrOH ⁺	3.8	
2Cel.alOH + BO ₂ ⁻ = (Cel.alOH) ₂ BO ₂ ⁻	0.7	
H ⁺ + X ⁻ = HX	3.37	[12]
Ca ⁺² + 2X ⁻ = CaX ₂	2.5	This study
Zn ⁺² + 2X ⁻ = ZnX ₂	2.5	
DOCs ^{-0.13} + 0.13 H ⁺ = H _{0.13} DOCs	3	
DOCs ^{-0.13} + 0.13 Zn ⁺² = Zn _{0.13} DOCs ^{+0.13}	-0.6	
DOCs ^{-0.13} + 0.13 Cu ⁺² = Cu _{0.13} DOCs ^{+0.13}	1	
Site density carboxyl (hemicellulose)	0.04 mol/kg wood	Adapted from [24]
Carboxyl (lignin)	0.01 mol/kg wood	Adapted from [12]
Phenol (lignin)	0.06 mol/kg wood	
Hydroxyl (cellulose)	0.50 mol/kg wood	This work
Specific surface	100 m ² /g	Mean of literature data
Kinetic constant k	0.027 (mol/L) ^{1.13}	This study

liquid/solid ratio), was not governed by precipitation/dissolution reactions of mineral compounds.

The dissolved organic carbon (DOC) in eluates is composed of the so-called extractives of the wood and participates in the acid/base reactions and metal complexation. Fig. 1 shows that the concentration of DOC (expressed as mol carbon/L) rose significantly with the pH, which is in agreement with the literature information. Two groups of extractives were considered in the model: (i) acetic and formic acids, and (ii) weak acid compounds.

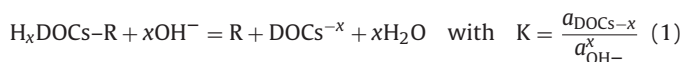
Carboxylic compounds (in free molecules and linked on wood) determined the pH of the wood in water and thus their quantities were determined by calculation/simulation of the neutralisation curve. The quantities found (Table 2) were of the same order of magnitude as those reported by [25].

The extractives fraction having weaker acid properties (in terms of Broensted acidity) could be expected to possess complexation properties, for example through the intermediary of phenol, carboxyl and ketone groups or other Lewis acid groups. This organic matter, noted DOCs in the model, has a pH dependent solubility, as observed experimentally. The complexation capacity with respect to transition metals like Cu and Zn was expected to be significant, a hypothesis verified in this work.

Table 2
Initial composition of the system, for 100 g of wood in 1 L pure water.

Solid species	mol/L
Boric acid (B(OH) ₃)	0.00086
Cu(OH) ₂	0.002
SiO ₂ (am)	Possible to precipitate
Wollastonite (CaSiO ₃)	0.0024
Soluble species	mol/L
Cl ⁻	0.0002
K ⁺	0.001
SO ₄ ⁻²	0.00023
Zn ⁺²	3.2e-5
CrO ₄ ⁻²	8.7e-7
Na ⁺	8.4e-5
HCO ₃ ⁻	1.4e-5
Acetate (CH ₃ COO ⁻)	0.001
Formate (HCOO ⁻)	0.002

In order to represent the behaviour of DOCs, an irreversible reaction of solid organic matrix with OH⁻ was considered:



where R is a solid organic polymer containing a labile fraction (noted DOCs) able to be released in the alkaline solution. The soluble fraction is represented by a surrogate compound containing x moles of labile H⁺ per mole of carbon. The formula of this compound is then H_xDOCs and its concentration in the eluates is expressed as mol carbon/L solution. As these molecules have very weak acid/base properties, the protonation reaction must be rapid and right shifted.



Reaction (1) had to be irreversible in the test conditions. There was no information about its kinetics and equilibrium constant. For these reasons, the reaction was considered to have a certain degree of advancement for the test duration, depending on pH conditions. The kinetics must depend only on OH⁻ if the solid surface does not evolve significantly during the reaction:

$$\frac{dC_{\text{DOCs}^{-x}}}{dt} = k_r (a_{\text{OH}^-})^x$$

As DOCs^{-x} transforms rapidly into the protonated form, H_xDOCs forms with the same kinetic rate. Moreover, the global DOCs concentration could be approximated by C_{H_xDOCs}.

$$C_{\text{DOCs}^{-x}} + C_{\text{H}_x\text{DOCs}} = C_{\text{DOCs}} \approx C_{\text{H}_x\text{DOCs}}$$

$$\frac{dC_{\text{DOCs}^{-x}}}{dt} = \frac{dC_{\text{H}_x\text{DOCs}}}{dt} \approx \frac{dC_{\text{DOCs}}}{dt}$$

As OH⁻ concentration is imposed by the chemical composition of the eluate and is constant in time, the concentration of dissolved organic compounds DOCs at a given time t is given by the combination of equations above:

$$C_{\text{DOCs}}(t) = k_r t (a_{\text{OH}^-})^x$$

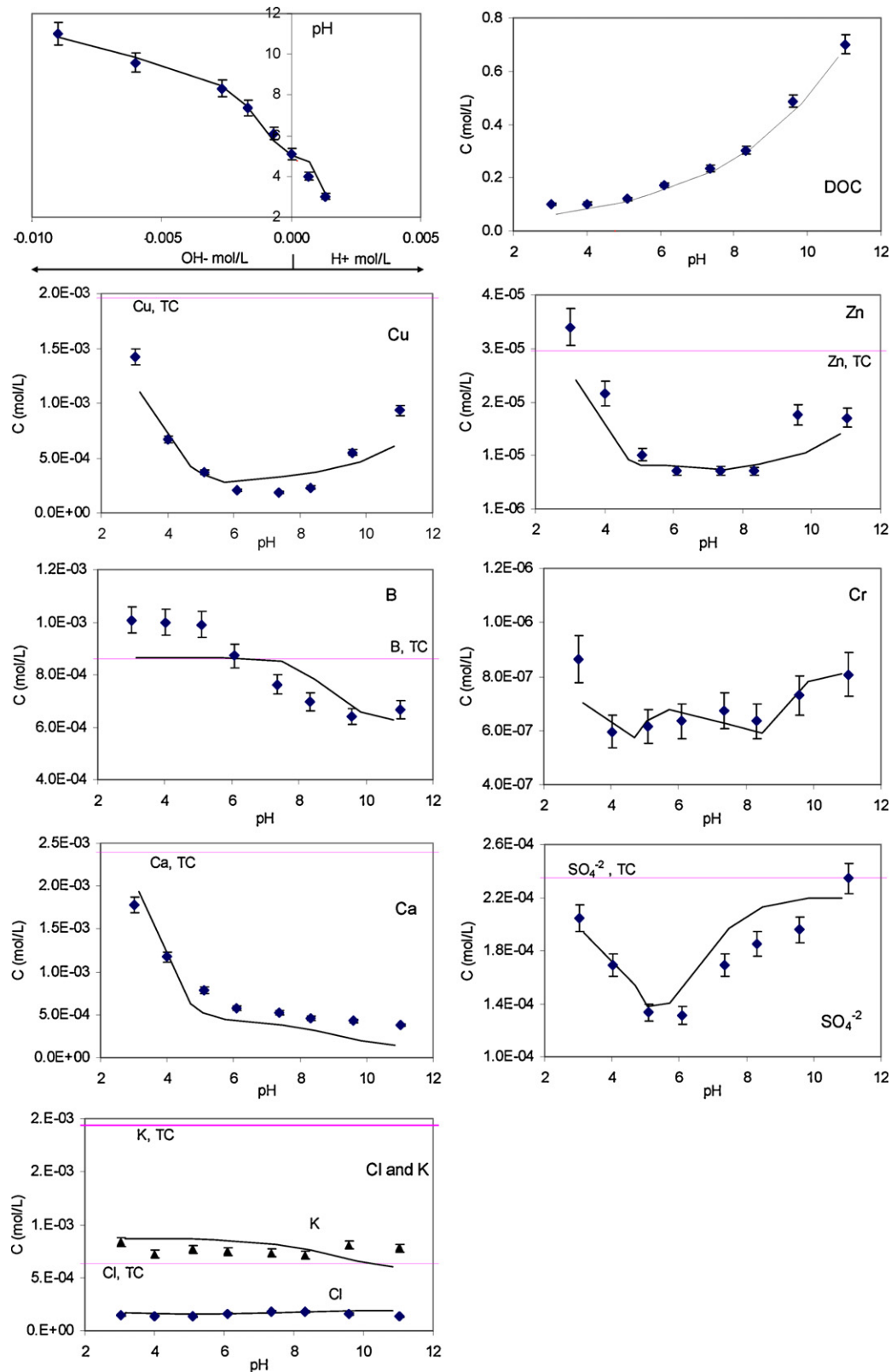


Fig. 1. Acid/base neutralisation curve, DOC and element release in function of pH. Experimental data: dots; simulation results: curves.

For a given time interval, e.g. test duration, the above equation may be written in the more useful form:

$$C_{\text{DOCs}}(t) = k(a_{\text{H}^+})^{-x} \quad (2)$$

We observe that the experimental data for dissolved organic carbon vs H^+ (Fig. 1) obey a power function of the

same form as Eq. (2), thus validating the kinetic model. The constants k and x were determined from these experimental data by statistical regression. In this way, the hypothetical organic compound dissolved in alkaline conditions was found to contain $x=0.13$ atoms of acid H per mole of C (formula $\text{H}_{0.13}\text{DOCs}$).

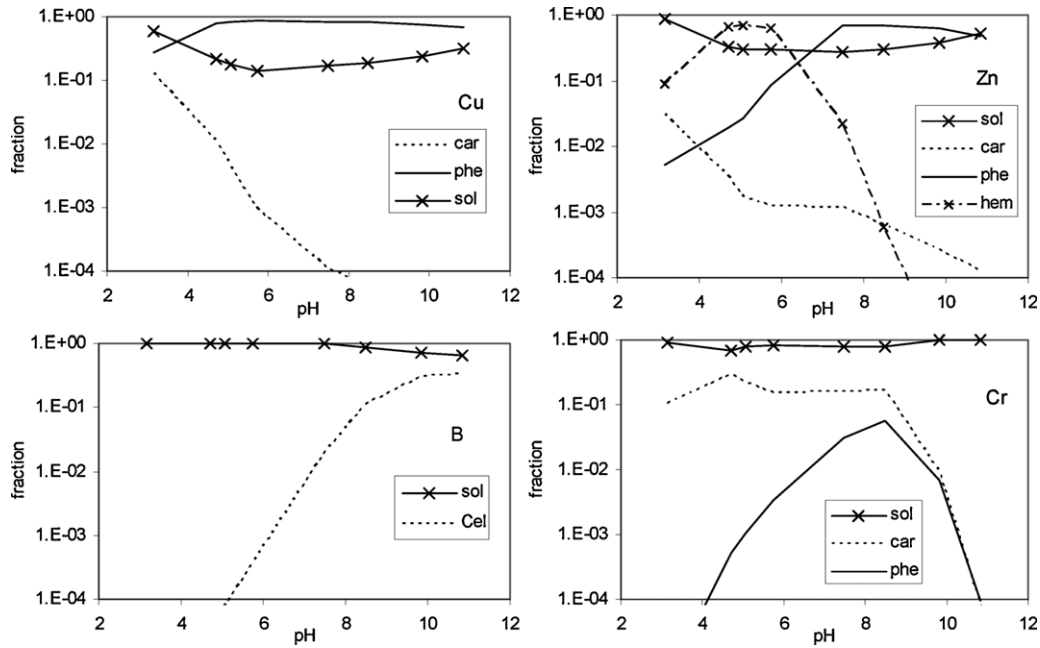


Fig. 2. Fraction of elements distributed between solution (sol) and wood compartments, fixed on different site types: car: carboxyl (lignin); phe: phenolic (lignin); cel: cellulose; hem: hemicellulose.

The acidity constant was determined by fitting the model on the neutralisation curve. In fact, DOCs acidity did not modify the global acid–base properties of the eluates (weaker acidity in comparison with small fatty acids). The sensitivity study showed that a value of $K_a = 3 \pm 1$ satisfied this condition.

Metal complexation with wood extractives has never been studied so far. Therefore, the release of well identified organic compounds by woods in contact with water, in different conditions, has not been studied at all. We based our model hypothesis on generic knowledge about metal complexation with natural organic matter [34], and also on the knowledge of particular metal/ligand behaviour for some identified extractives like acetic and formic acids.

As wood solution is a mixture of various unidentified compounds, we used the generic compound $H_{0.13}DOCs$ to express the complexation reaction. The model considers that the metal competes with H^+ for the binding sites and that $metal^{+2}:H^+$ stoichiometry is 1:1 since extractives are relatively small organic compounds tending to contain only one binding site. Consequently $Cu_{0.13}DOCs^{+0.13}$ and $Zn_{0.13}DOCs^{+0.13}$ were considered as generic complexes in this study. Their complexation constants were fitted to give the best concentration simulation and the values obtained are listed in Table 1.

The initial composition of wood is proposed in Table 2 supposing that the elements behave as solid phases, fixed on fibres and dissolved in the interstitial solution. To this composition were added the different active surfaces with their respective site densities listed in Table 1. By adding, in simulations, the quantity of acid or base used in the test experiments, it was possible to simulate the neutralisation curve, DOC and concentration vs pH curves.

5. Model application and discussion

The leaching test results and total target element contents are presented in graph form in Fig. 1: acid/base neutralisation curve (pH vs added H^+ or OH^-), DOC vs pH and element concentration vs pH. The pH of the wood sample in pure water was 5.1 and no particular plateau or inflexion was observed on the neutralisation curve, proving that many acid/base couples existed in the system. DOC showed a significant increase with pH. The most concentrated elements were Cu, Ca and K. For all elements except B, the release remained lower than their total content except for extreme pH conditions. Cu and Zn behaviour were similar, i.e. a variation of one order of magnitude over the pH range with a minimum at neutral pH. B concentration was maximum in acidic conditions and dropped at neutral to basic. The

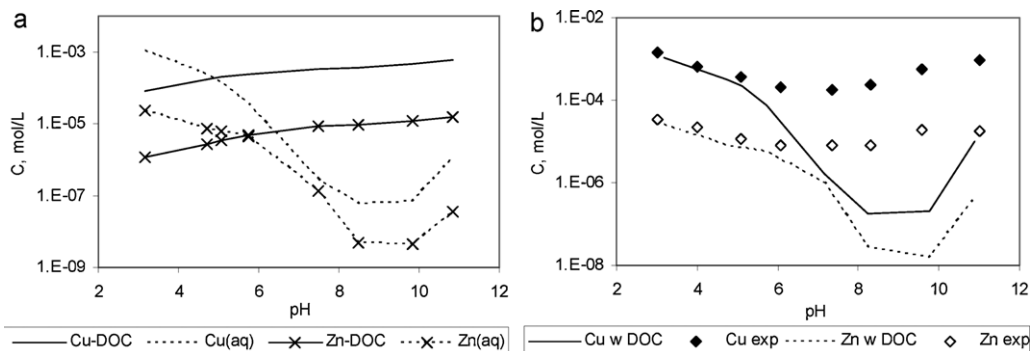


Fig. 3. Role of DOC in metal release. (a) Concentration of Cu and Zn linked on DOC (-DOC) and as mineral aqueous species (aq). (b) Cu and Zn experimental concentration (exp) and simulation without DOC complexation (wDOC).

inconsistency between total content and eluate concentration at acid pH could be explained by the inhomogeneity of wood samples. Cl and K have constant concentrations in the pH range. SO_4^{-2} and Cr are trace species probably present in the preservative treatment of the wood as impurities; their concentration shows a minimum in the neutral range but the variation is smaller than for Cu and Zn. Ca concentration decreased most from the acid to the neutral domain and less for basic pH. Biocides, DOC and pH behaviours observed in this study were very similar to the experimental data reported in [35] for many treated wood products subjected to the same leaching test.

The modelling efforts were focused on representing biocide behaviour. Competing processes were considered with particular attention being paid to describing Cu, Zn, Cr, B, DOC and Ca behaviour. For the other elements, only inorganic species and reactions were considered.

Fig. 1 presents the simulation results compared with experimental data for the leaching test and shows good agreement, with a mean error over all simulated/experimental points of 16%.

The speciation and quantitative distribution of species in wood material is not necessarily at equilibrium and is obviously unknown. Nevertheless, the equilibrium state of wood in contact with water at a given liquid/solid ratio could be calculated by equilibrating the different compartments with their initial composition. In this way, it is possible to estimate the distribution of biocides among different compartments and according to the pH.

At the natural pH of wood (pH 5.1) the majority of Cu and Zn is observed to be linked to wood on different sites (Fig. 2). When pH is lower, this fraction decreases due to site protonation.

In the neutral region, surface complexation of Cu, Zn and Cr is maximum and diminishes with pH increase. The availability of phenolic sites increase as does the deprotonation of DOC. Despite the high complexation capacity of phenolic sites, the activity of DOC becomes more and more important for metal extraction into the liquid phase. Nevertheless, the linked fraction of metal remains dominant.

The particular behaviour of Cr depends on the abundance of the complexing species, which is assumed to be the hydroxylated cation—the major species at pH 4.5. It is at this pH point that Cr release is minimum in experimental tests and also according to simulations. It is possible that Cr(III) could also be complexed by DOCs. However, the very low concentration and the weak variation of its concentration vs pH suggest a less significant process, and therefore it was not considered in the model. Boron mobility is slightly reduced at basic pH by linking on hydroxyl sites. At acid and neutral pH no significant B fixation occurs, confirming the experimental results reported in the literature.

The model considers all major elements present in wood, like Ca, K, Cl. Their presence is important for ionic strength and pH calculations. Some of the accompanying ions are captured in the Donnan phase, this process being highlighted by SO_4^{-2} behaviour (Fig. 1), for which no particular reaction was considered in the model. The curve shape is due only to the evolution of the Donnan phase surrounding the different complexation sites, with a maximum level at neutral pH.

The role of DOC in metal mobilisation could be better decrypted by identifying the speciation at different pH values (Fig. 3a). At acid pH (including natural pH of wood), the proportion of metals linked to DOC is relatively low because of DOC protonation and low DOC solubility. At natural pH, there are sensibly equivalent quantities of soluble Cu complexed with DOC and as mineral species, mainly free Cu^{+2} . The same speciation trends are observed for Zn. Fig. 3b demonstrates the role of DOC for metal mobilisation by comparing the experimental data with a simulation case without DOC/metal complexation. Without DOC, a very low metal concentration would be observed but for pH values higher than the wood natural pH. This

means that, in natural conditions, the fixation mechanism plays the major role. This result demonstrates that considering only the role of dissolved organic matter (as reported in the literature) and not taking the wood fixation mechanisms into account could lead to erroneous evaluation of the leaching process, especially in dynamic conditions in open systems and over long time periods.

6. Conclusion

The chemical model developed aims to represent leaching behaviour for several inorganic biocides in wood and to help in the interpretation of equilibrium leaching tests such as the European standard XP CEN/TS14429.

The model uses chemical properties and reactions that are well recognised for wood material and also hypotheses based on recent literature. The state of the art on fixation/leaching mechanisms showed that: (i) the complexation properties of lignin and the behaviour of Cu and Zn have already been thoroughly studied; (ii) mechanisms of Ca and Cr fixation are not settled in the literature and therefore no data exist for the reaction constants; (iii) concerning B, in the literature it is mostly considered that no reaction occurs; (iv) no studies exist on biocide/extractives interactions.

Starting from the current knowledge, the modelling of treated wood leaching behaviour is a complex task still requiring more specific investigations. Hence, the developed model considers the following main processes: complexation of Cu, Cr(III) and Zn by phenol and carboxyl groups, ion exchange of Ca and Zn by carboxyl, weak complexation of B by cellulose, pH dependent solubilization of organic extractives, complexation of Cu and Zn by the soluble extractives. The lack of data was circumvented by several sustained hypotheses especially for B, Cr fixation and DOC activity, and by adjustment of several parameters on experimental leaching test data.

The simulation results obtained shown that the model is adapted to the objective of equilibrium leaching behaviour description. Validation on different treated wood materials could improve the model and the level of knowledge, and is therefore planned. The chemical model is currently coupled with appropriate transport models for the simulation and representation of dynamic release of biocides in different conditions (laboratory dynamic tests and field pilots), with the final aim of environmental assessment of wooden construction materials.

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