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EXAFS study of chromated copper arsenate timber preservative in wood

Abstract Copper and arsenic K-edge X-ray absorption fine structure spectroscopy (EXAFS) of pine wood (*Pinus radiata*) treated with chromated copper arsenate (CCA) timber preservative have been measured. Refinement of the data is consistent with arsenate anions bound to chromium and copper ions isolated from other heavy elements, regardless of depth into the wood. This constitutes the first substantive analysis of CCA's fixation products and has a number of implications for models of fixation.

Key words EXAFS · XAFS · Chromated copper arsenate · CCA · Timber preservative · Fixation

Introduction

Chromated copper arsenate (CCA) timber preservative has been used extensively worldwide for more than 40 years. It greatly increases the service life of timber exposed to weather, in ground contact, or immersed in water. With ordinary conditions the preservative is strongly "fixed" in wood and therefore resistant to leaching.[1] However, the chemistry of fixation is largely a matter for conjecture because of the difficulty of in situ analysis. The heterogeneous wood matrix hinders the use of most spectroscopic meth-

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ods, particularly as the migration of extractives can seriously affect surface techniques.[2] The treated wood matrix is an amorphous natural polymer containing metal ions and, as such, should be of interest to inorganic and organometallic chemists. The technique used here to probe the role of metal ions in treated timber could be extended to other systems involving metal ion interactions with complex matrices (e.g., investigation of environmental heavy metal speciation in humic substances).

The extended X-ray absorption fine structure spectroscopy technique (EXAFS) was considered to be best suited to the exploration of chemical structure in situ because it uses penetrating X-radiation yet does not require long-range order in the sample. Illman and Dowd[3] have used the related technique, X-ray absorption near edge spectroscopy (XANES), on CCA-treated wood with some success.

The fixation process is driven by the reaction of chromium (VI) with wood constituents.[4]

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
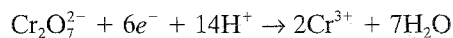
The consumption of H^+ causes substantial changes in pH, which are thought to precipitate inorganic material on the wood cell walls and promote interaction between Cu^{2+} or Cr^{3+} and binding groups in the wood such as carboxylates.[5] Chromotropic acid spot tests, XPS results,[6] and ESR have all shown that Cr^{VI} is definitely not present in fully fixed timber, although trace amounts of Cr^V intermediates have been observed to persist for up to 6 months.[5,7] Therefore, the Cr is present as Cr^{III}, which can confidently be expected to have six oxygen donors in an octahedral geometry under these conditions. Insoluble polymeric $CrAsO_4 \cdot nH_2O$ rapidly precipitates at pH 2.3 or more.[8] Because modern "type I" CCA has a Cr/As ratio of 2:1, no more than half the Cr could fix in this way. Additional compounds might include hydroxides, carbonates, and wood complexes. With multiple sites expected, it is unlikely that the system has sufficient short-range order to obtain useful information by EXAFS. On the other hand, it seems likely that most of the As fixes as $CrAsO_4 \cdot nH_2O$, and that most of the copper fixes as Cu^{II}–wood carboxylate complexes. EXAFS analysis should be able to confirm or reject this hypothesis.

Experimental

EXAFS was used to examine treated pine wood stakes cut from the outer surface (sapwood) of a CCA-treated fence post to the heartwood at the centre. The impregnation process generally gives rise to a small amount of "sludging" in bulk preservative solution. Because this precipitation has been considered analogous to fixation outside the wood,[4] a selected timber treatment plant sludge was also analysed with the treated wood samples. It has previously been characterised in detail[8] and shown to be an impure chromium (III) arsenate hydrate, containing 45% (w/w) O, 25.5% As, 16.0% Cr, 3.2% Cu, 2.96% H, 2.37% C, 0.9% Na, 0.5% S, 0.2% Sb, and 0.20% Fe.

Samples

The samples are shown in Table 1. Chromated copper arsenate oxide-treated wood was supplied by Cantapine Ltd. (Christchurch, New Zealand), a subsidiary of Goldpine Ltd. The timber used was high-density *Pinus radiata* roundwood from Nelson, New Zealand, nominal diameter 150 mm, treated with Koppers-Hickson's GoldTan oxide to a calculated preservative retention of about 12 kg m^{-3} or 16 kg m^{-3} ("H4" and "H5" industry standard loadings, respectively). It should be noted that the timber treatment industry states retentions on an "oxide basis" (i.e., the preservative loading assuming fixation as Cr_2O_3, CuO, and As_2O_5). Although this convention is not chemically accurate, it simplifies calculations and the comparisons between salt and oxide formulations. The former contain spectator ions, normally SO_4^{2-} and either Na^+ or K^+, whereas the latter do not. Salt-treated *P. radiata* roundwood, nominal diameter 100 mm, was supplied by Mike Cairns Ltd. (Christchurch, New Zealand). The wood came from a similar source and was treated to about 12 kg m^{-3} according to the same standards. New Zealand Standard MP 3640 specifies pressure treatment with a "type I" CCA concentrate containing 43%–47% Cr, 23%–25% Cu, and 30%–32% As (whether salt or oxide). Treated timber must be held for a minimum of 48 h at ambient temperature, after which the preservative is considered completely "fixed" and the timber is drip-free. These samples were not ground up until several weeks after treatment.

An unblemished board of about 25 mm width, including the core, was cut from each log. The board was then cut up along the grain to yield three stakes of equal dimensions, each covering one-third of the distance between surface and core. These stakes were milled to sawdust using a table-mounted circular saw with carbide-tipped blade, which ground finely without perceptible heating. The sawdust was collected in plastic bags covering the hopper underneath the blade and from the tabletop, the apparatus being vacuumed clean between stakes. It was then air-dried with some mild heating, sieved through a 60 mesh filter, and the resulting dust stored in tightly sealed 14-ml sample vials with Teflon-lined caps. Unfortunately, time constraints prevented examination of the middle and inner thirds of the oxide-treated wood.

XAFS measurements

Room-temperature X-ray absorption measurements were made on bending-magnet beamline 20B at the Australian National Beamline Facility in the Photon Factory, Tsukuba, Japan, using the standard arrangement. The monochromator was a Si (III) channel-cut crystal detuned such that the intensity incident on the sample was approximately one-half of that measured when the crystal faces were in perfect alignment. This was necessary to reject higher-order harmonics.

Absorption data were collected for the K-edges of both copper and arsenic. Foils of the appropriate metal were used for energy calibration. For CCA sludge, it was necessary to study arsenic in transmission mode using an ion chamber detector. A suitable concentration of absorber was obtained by dilution to 60% (by weight) with boron nitride. All other experiments were conducted in fluorescence mode, without dilution, using a Canberra GL 0110S 10-element Ge array detector. The samples were held in a 1-mm aluminum spacer with KAPTON tape windows. There was no visible degradation of the samples during analysis.

Data analysis

XAS and XAFS data were processed and analysed with the XFIT software suite,[9] and model XAFS data were calculated with the curved-wave multiple scattering program[10,11] FEFF6.01 using scattering paths of up to four legs. XFIT employs Levenberg-Marquardt iterative nonlinear least-squares fitting to optimise selected model parameters such that χ^2, the sum of the squares of the differences between the calculated and observed XAFS, is minimised.

Because the fluorescence detector had 10 elements, and each treated wood sample was run twice, there were 20 XAS data sets for each fluorescence experiment, except the sludge Cu, which had only 10. No systematic differences between channels or runs were observed, so all the data for a particular sample were averaged into a single data set. After normalisation, the XAFS oscillations were extracted from the XAS through a cubic spline fitting procedure. At the same time, the data were transformed into photoelectron momenta k in units of kg Å s^{-1}, and weighted by a factor of k^3 to compensate for the amplitude attenuation at increasing distances from the absorption edge. While the

Table 1. Samples

Medium	Formulation	Retention (kg m^{-3})	Section
Sludge	N/A	N/A	N/A
Treated wood	Salt	12	Outer
			Middle
			Inner
	Oxide	12	Outer
		16	Outer

Fig. 1. Arsenic EXAFS spectra

Legend:
- Outer H4 salt
- Middle H4 salt
- Inner H4 salt
- Outer H4 oxide
- Outer H5 oxide
- Sludge

y-axis: Normalized absorption k^3 weighted

x-axis: Photoelectron momentum (k) / 10^{-10} kg m s^{-1}
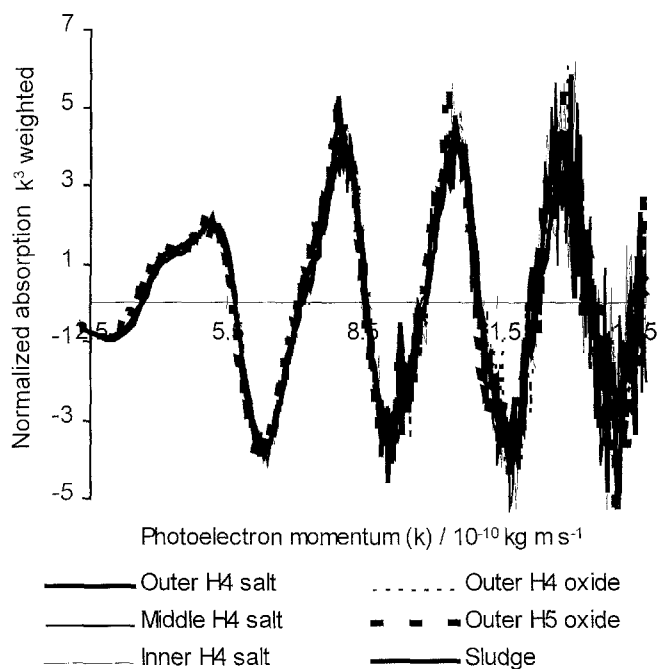
spectra become quite noisy at high values of k, XAFS was observable up to $k \approx 13$ for copper and $k \approx 14$ for arsenic (Fig. 1). Accordingly, the windows for both calculated and observed EXAFS were $[3k, 13k]$ or $[3k, 14k]$, with edges smoothed by cosine functions extending a further $0.5\,\text{Å}$.

A variety of simple model structures were proposed for each sample, and the theoretical XAFS of these models were constructed ab initio. The model parameters were then refined until the statistical difference between calculated and observed XAFS was minimised. Parameter restraints were not generally necessary for the best-fit models. If any parameters repeatedly refined to zero, excessively large values, or chemically implausible values such as bond lengths $<1\,\text{Å}$, the model was discarded. The goodness-of-fit was determined by the parameter

$$R = \frac{\int_{k=0}^{\infty} \left[\chi_{calc}(k) - \chi_{obs}(k)\right]^2 \partial k}{\int_{k=0}^{\infty} \chi_{obs}(k)^2 \partial k}$$

where $\chi_{calc}(k)$ and $\chi_{obs}(k)$ are the calculated and observed filtered EXAFS curves. Standard deviations for most fitted parameters were also obtained, using the Monte Carlo analysis included in XFIT.

Results

The results of the fitting procedure are shown in Tables 2 and 3. The arsenic EXAFS of sludge was originally modelled with a simple As–O_m–Cr_n structure. A bond length of

Table 2. Best fit EXAFS parameters for As-O-Cr model

Model[a]	Sludge, value	$R = 14.76$ e.s.d.	Wood, value	$R = 14.26$ e.s.d.
O shell				
E_0	−11.64		−11.78	
S_0^2	1.086	0.002	0.8004	
N_1	3.830	0.007	4.870	0.016
x_1	1.680	0.000	1.686	0.000
σ_1^2	0.002499		0.001803	
Cr shell				
N_2	5.132	0.067	5.740	0.061
x_2	2.975	0.003	2.961	0.001
y_2	−1.353	0.008	−1.392	0.001
σ_2^2	0.01093		0.01058	
|Cr-O|	1.873		1.894	

[a] E_0 is the threshold energy correction in electron volts; S_0^2 is the many-body amplitude reduction factor; N is the number of atoms in the shell; x, y are the Cartesian coordinates of the scatterer in anstroms (Å); and σ^2 is the Debye-Waller thermal parameter

Table 3. Best-fit EXAFS parameters for Cu-O model

O shell	Sludge, value	$R = 30.62$ e.s.d.	Wood, value	$R = 20.06$ e.s.d.
E_0	−15.25		−15.97	
S_0^2	0.7208	0.009	0.6322	0.002
N_1	3.604	0.046	4.783	0.016
x_1	1.950	0.002	1.944	0.001
σ_1^2	0.003149		0.004292	

See Table 2 caption for symbol definitions

$1.68\,\text{Å}$ was returned for As–O, consistent with the crystallographic values[1] of $1.61 < |\text{As–O}| < 1.73$ in euchroite $Cu_2(OH)AsO_4 \cdot 3H_2O$, and similar values in other simple arsenates. The best-fit bond length for $|\text{Cr–O}|$ was a reasonable $1.88\,\text{Å}$, and the oxygen shell occupancy was appropriately 4. The overall fit was good, although the scale factor S_0^2 was high. More detailed geometries (e.g., with each oxygen atom of the arsenate tetrahedron considered separately) failed to improve the fit. A Cu_p–O_q–As–O_m–Cr_n structure produced an equally good result but was considered unwarranted because the number of copper atoms remained substantially less than one during refinement.

There were, however, serious problems in modelling the copper EXAFS of sludge, as indicated by the poor R value (Table 3). The immediate environment of the Cu atoms was simulated by three oxygen shells placed at varying distances along the x, y, and z axes. Regardless of the positions and occupancies of the shells, the only convergent fits were for four O atoms and all Cu–O bond lengths equal to $1.95\,\text{Å}$. This is a good match for the $1.92 < |\text{Cu–O}| < 2.08$ spacings for the four O atoms close to Cu in euchroite,[12] though surprising in that Cu^{II} would be expected to have a distorted octahedral geometry with two more oxygen atoms farther away. In euchroite, they are found at a distance of 2.42–$2.72\,\text{Å}$. In this case, the addition of another O shell does not result in a better fit, nor was the fit improved by a second shell of As, Cr, or Cu. Clearly the copper exists in a variety
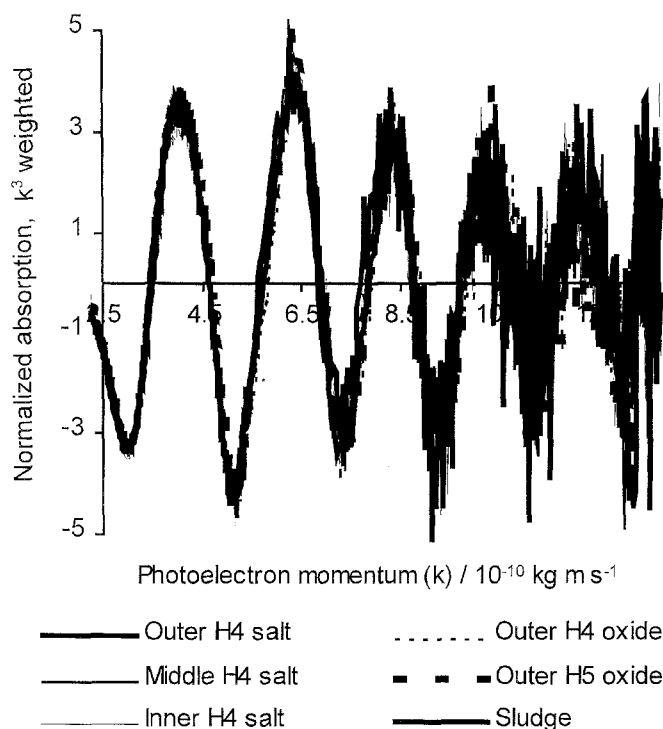
Fig. 2. Copper EXAFS spectra

Fig. 3. Fourier transforms of the copper EXAFS for the H4 salt outer layer sample and the calculated EXAFS for the Cu_p-O_q model

the fitting process. It is not clear whether this is due to disorder in the system or simply to the difficulty of distinguishing between random noise and the effect of a small scatterer such as carbon.

of environments, not unexpected for a minor constituent of an impure material.

The EXAFS spectra of all five treated wood samples were indistinguishable (Figs. 1, 2), and initial analyses showed that the same model gave the best fit in each case. Comparing fits, the largest standard deviation for any single parameter was 7.5% for the occupancy of the O shell in the Cu model. Thus, there is no evidence that the chemical mechanisms of fixation vary between heartwood and sapwood, between salt and oxide formulations, or between preservative loadings of 12 and 16 kg m^{-3}. The As XAFS also matched the sludge spectrum, consistent with the expectation that As fixes as $CrAsO_4 \cdot nH_2O$.

The tabulated models were obtained by refining to all five data sets simultaneously. The fit to the As–O_m–Cr_n model is even better than in sludge and yields essentially identical parameters (Table 2). Replacing Cr with Cu gives a substantially poorer fit; furthermore, the M–O bond length is clearly shorter than would be expected for Cu–O.

Unlike sludge, the copper XAFS of treated wood can be adequately modelled. Again, the best fit was close to four O atoms, consistent with the usual square planar or elongated octahedral geometry (Table 3). There was no improvement on adding a second shell of Cr, Cu, or As; nor is there any sign of a large next nearest neighbour in the Fourier transform (Fig. 3). This is consistent with the hypothesis that copper ions are complexed to wood rather than to inorganic species. Unfortunately, it was not possible to obtain a stable fit when a carbon atom was added to the model; the occupancy and position of the shell varied substantially during
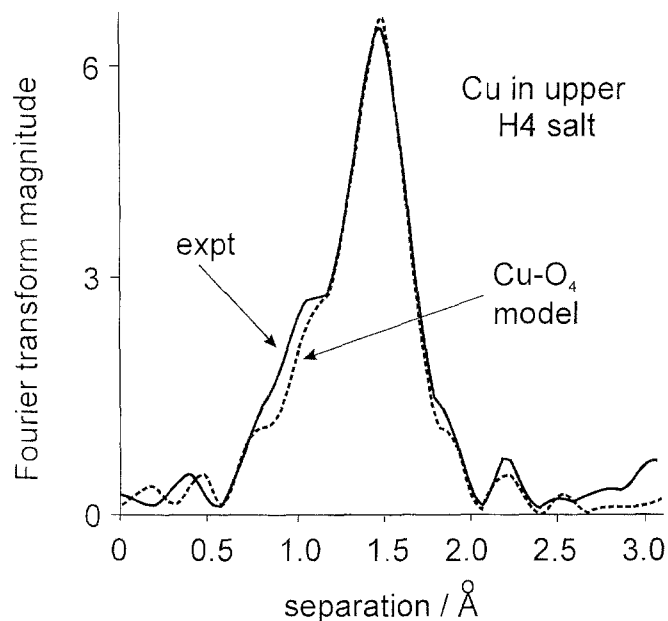
Conclusions

The results of this novel EXAFS study of CCA-treated wood are consistent with the hypothesis that arsenic is fixed as $CrAsO_4 \cdot nH_2O$, and Cu is complexed to binding sites in the wood. This is particularly interesting, as it disagrees with the theoretical models of Dahlgren and Hartford[13–16] and of Pizzi et al.[17,18] in which the final fixation products contain large proportions of copper (II) arsenates. The construction of an alternative fixation scheme will be considered in a separate article.

We have shown that the EXAFS technique can be applied as a probe of the interactions between heavy metal ions and a heterogeneous, spectroscopically challenging material such as the wood matrix. In addition to the application to CCA and related preservatives, it may offer an insight into fixation of the new copper-based alternatives that are under development by a number of groups worldwide.

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