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# PREDICTION OF LONG TERM LEACHING POTENTIAL OF INORGANIC WOOD PRESERVATIVES BY DIFFUSION MODELING

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## Abstract

A novel approach is presented for describing the leaching of inorganic wood preservatives, including fixed chromated copper arsenate (CCA-C), amine copper quaternary (ACQ-C), copper azole (CA-B), and disodium octaborate tetrahydrate (DOT). The approach is based on a physical model where some portion of the preservative dissociates into absorbed water, then diffuses to the sample surface according to Fick's second law of diffusion. Transverse and longitudinal diffusion coefficients are determined for each of these preservatives in southern yellow pine, and the corresponding leaching curves are found to fit well with laboratory leaching data. Although further refining and validation of the model is required, this approach should allow the estimation of potential risk from leaching over a wide range of specified conditions, and insight into reasons for the differences in leaching performance between different preservatives or different applications of the same preservative.

# 1 Introduction

For environmental and health risk assessment of new and currently used wood preservatives, there is a need for quantified predictions of leachate flux in service. Currently there is a lack of understanding of the factors affecting leaching and lack of agreement on appropriate test methods to predict in-service leaching (Hingston, Collins, Murphy & Lester 2001). Attempts to understand wood preservative leaching are confronted with an array of contributing, often inter-related factors, including

- free water distribution and movement,
- kinetics and equilibrium state of preservative dissociation,
- sample dimensions,
- duration of leaching,
- temperature,
- wood permeability and other physiological factors which vary between species and within species,
- preservative type, formulation, and differences in treatment techniques,
- depletion of preservatives within the wood, and
- checking and splitting.

Additionally, leaching experiments have not been performed or presented in a consistent manner. The AWPA leaching standard for CCA requires only that after treatment samples be allowed to "dry naturally," which does not ensure proper fixation. Soil tests taken near treated wood in service may contain sawdust or other treated wood bits, which could drastically exaggerate leaching estimates. Leaching results are sometimes presented as a flux (*i.e.*, $mg/cm^2/day$) and other times as a percentage of the amount present in the wood.

Thus it is not surprising that field and lab tests with several of these factors uncontrolled by the experimenter may produce contradictory and inconclusive results. This paper presents a physical model for the leaching of water-based wood preservatives which provides a framework for individually assessing the contributions of most of these factors, and for developing a consistent and relevant approach to assessing the leaching potential of wood preservatives.

The leaching mechanism of the model is based on diffusion of dissolved preservatives through free water in the cell lumens from the interior to exposed surfaces of the wood, in a three-stage process as suggested by Cooper (1994):

1. absorption and adsorption of water. This occurs slowly through rainfall or immersion in service, or rapidly by vacuum treatment in some lab tests.
2. dissolving of preservative components from precipitates or weak bonds in the wood matrix, and finally
3. diffusion and advection (following the movement of water) to the surface of the wood.

Stage 1 is yet to be addressed quantitatively and is an important area of future research. This paper deals with items 2 and 3, avoiding water movement by dealing only with samples vacuum-treated with water then leached by continuous immersion.

Such a model has a number of potential applications:

- improving our qualitative understanding of how water-based preservatives are leached from wood,
- explaining the vast differences in leaching performance observed in different leaching protocols,
- relating performance in laboratory leaching tests to performance in service,
- providing guidance into simple, relevant laboratory methods for assessing leaching potential and comparing different preservatives and treatments, and
- providing new insight into ways of improving leaching performance.

# 2 Methods

## 2.1 Leaching Model

The movement of preservatives to the sample surface is described as pure Fickian diffusion, following Fick's second law of diffusion:

$$\frac{\partial C}{\partial t} = \left( D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \right) \tag{1}$$

This equation can be solved exactly for simple boundary conditions and sample dimensions, or numerically for arbitrarily difficult problems. For the purpose of modeling the effect of diffusion and measuring the diffusion coefficients in a lab setting, this paper uses the exact analytical solution for one-dimensional and three-dimensional diffusion in a rectangular parallelpiped.

The 1-D solution for diffusion in a plane sheet bounded by $-a < x < a$ with constant diffusion coefficient, uniform initial concentration $C_o$, and constant boundary concentration $C_1$ is given by Crank (1975, eq. 4.17) but with an erroneous factor of 2. The correct solution, derived by the author, is

$$\frac{C - C_o}{C_1 - C_o} = 1 - \frac{2}{\pi} \sum_{l=0}^{\infty} \frac{(-1)^l}{2l+1} e^{-D(2l+1)^2 \pi^2 t / 4a^2} \cos \frac{(2l+1)\pi x}{2a}. \tag{2}$$

The total mass $M(t)$ of substance leached as a fraction of what can be leached after infinite time $M_\infty$ is

$$\frac{M(t)}{M_\infty} = 1 - \sum_{l=0}^{\infty} \frac{8}{(2l+1)^2 \pi^2} e^{\frac{-D(2l+1)^2 \pi^2 t}{4a^2}}. \tag{3}$$

For three-dimensional diffusion from a rectangular block,

$$\frac{M(t)}{M_\infty} = 1 - \left( \frac{8}{\pi^2} \right)^3 \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{e^{-\alpha t}}{(2l+1)^2 (2m+1)^2 (2n+1)^2}, \tag{4}$$

where

$$\alpha = \frac{\pi^2}{4} \left[ D_1 \left( \frac{2l+1}{a} \right)^2 + D_2 \left( \frac{2m+1}{b} \right)^2 + D_3 \left( \frac{2n+1}{c} \right)^2 \right],$$

a, b, c = sample dimensions, and

$D_a, D_b, D_c$ = corresponding diffusion coefficients.

For times greater than an hour, only the first ten terms of the infinite sum are needed for more than adequate accuracy, *i.e.*, relative accuracy better than $10^{-6}$. These solutions are useful for modeling continuous leaching, after the preservative is first allowed to dissociate to a uniform equilibrium concentration where no additional dissociation occurs. More complex solutions to the diffusion equation are possible, generally requiring numerical methods rather than the exact analytical solutions presented here.

## 2.2 Dissociation Experiments

Experiments were performed to isolate the dissociation stage of leaching in CCA. One set of 25mm cubic blocks of red pine sapwood were cut from an airdry industrially treated pole. A second set was cut from an untreated red pine pole, treated by a full-cell process with 0.9% CCA-C and fixed under accelerated conditions at 80C and high humidity. These samples were then oven dried and equilibrated to airdry condition. To begin the experiment, all samples were vacuum treated with water. Each block was then expressed with a hydraulic press at times between 0 and 7 days after saturation, with two replicates per time and $t = 0$ taken as the moment of releasing the vacuum. The expressed solutions were analysed by Inductively Coupled Plasma Spectroscopy (ICP) for concentration of dissolved Cr, Cu, and As.

## 2.3 Leaching Experiments

### One-dimensional leaching

25mm samples were cut from 38 x 140mm southern yellow pine boards commercially treated with chromated copper arsenate (CCA-C), amine copper quaternary (ACQ-C), copper azole (CA-B) and disodium octaborate tetrahydrate (DOT). Leaching was restricted to one direction by coating four sides with silicone sealant, leaving only two opposing faces exposed.

To experimentally isolate the effect of diffusion, the airdry treated samples were vacuum treated with water, allowed to sit for five days to allow dissociated preservatives to reach a uniform, near equilibrium concentration, then immersed in water for continuous leaching without moisture movement. Leachate samples were taken at regular intervals and analysed by ICP for analyte concentration. $M_\infty$ was determined by expressing samples five days after vacuum treatment and multiplying the concentration of dissociated preservatives by the volume of water taken up during vacuum treatment. The mass leached as a function of time was then modeled by equation 3, using an optimisation algorithm to determine the best fit value of the diffusion coefficient $D$ for the experimental dataset, as described by Waldron & Cooper (2001).

### Three-dimensional leaching

The three-dimensional model was tested against an AWPA standard leaching test on industrially produced CCA treated blocks, performed by Taylor (2001). Since no dissociation information is available for this data, $M_\infty$ was considered a free variable for the optimisation algorithm in addition to $D$. Rather than attempting to fit to three diffusion coefficients, one in each direction, the transverse diffusion coefficients were assumed to be one-tenth the longitudinal diffusion coefficient.

As per the AWPA standard these blocks were vacuum treated and leached immediately, unlike the one-dimensional leaching tests. However, due to the relatively rapid initial dissociation of preservative components as seen in section 3.1, this is not as significant for continuous leaching as it would be for intermittent leaching and drying. Samples which were continuously leached immediately after vacuum treatment appear to follow a pure diffusion model very closely.

# 3 Results and Discussion

## 3.1 Dissociation

Figure 1 shows the increase in concentration of Cr, Cu, and As in the cell lumens of industrially produced CCA-treated wood after the samples were saturated with water at $t = 0$. It shows rapid initial dissociation, followed by a levelling off and apparent equilibrium around [Cr]=20ppm, [Cu]=40ppm, and [As]=120ppm. Subsequent tests have shown that additional preservative, particularly arsenic, continues to dissolve over following weeks. These very slowly dissolving components will not contribute significantly to leaching, however, except in very severe leaching tests involving prolonged continuous leaching.

Similar tests on samples cut to size then CCA-treated in the lab, shown in figure 2, showed very different dissociation characteristics including lower dissociation concentrations and greater variability. These two sample preparations had very similar mass balances of Cr/Cu/As and similar CCA retention, so the source of the difference is not clear. However, as seen later, the dissociation properties have a direct effect on leaching potential, and offer a fast, convenient way of comparing the leachability of wood treated by different methods.

## 3.2 Leaching

### One-dimensional leaching

Results of the laboratory tests and modeled curves for longitudinal boron leaching from DOT-treated samples, longitudinal copper leaching from CA-treated samples, and longitudinal and transverse arsenic leaching from CCA are shown in figures 3 through 6. The close fits show that the model describes experimental leaching well at least empirically, although its predictive ability must still be proven.

The computed diffusion coefficients, measured dissociation limits in solid wood, and leachable amount of preservative from finely ground wood are shown in table 1. The quantity of preservative which dissociates in solid wood, used in the leaching model, is comparable to the amount leached from finely ground wood for DOT-boron and ACQ-Cu, but is significantly less in solid wood for CCA and CA. Assuming the quantity leached from finely ground wood is ultimately available to leach from solid wood but the quantity which dissociates in solid wood is all that is available before leaching begins, then the model in its present form cannot accurately describe severe leaching of CCA and CA. To account for this "reservoir" effect during severe leaching tests will require a numerical solution to the diffusion equation, rather than the analytical solution described in this paper. However most real-world, non-submerged treated wood applications are unlikely to cause severe enough leaching to tap significantly into this reservoir.

The diffusion coefficients are about a factor of 10 greater in the longitudinal direction than the transverse direction. Large differences are also observed in the dissociated concentrations and diffusion coefficients of the different preservatives. The high dissociation and high $D$ of DOT boron both contribute to it having the highest leachability of the preservatives tested. At the other end of the spectrum, the low $D$ and dissociated quantity of Cr in CCA contribute to Cr being the most leach resistant of the preservative components. Leachability of the other preservatives fall between these extremes. Copper in CA and ACQ leaches significantly faster than copper in CCA, due to higher dissociated amounts and $D$ values.

| Preservative | Retention ($kg/m^3$) | Total leached from sawdust (%) | Total Dissociated (%) | $D_L$ ($cm^2/s$) | $D_T$ ($cm^2/s$) |
|---|---|---|---|---|---|
| ACQ | 1.82 CuO | 34.9 | 28.1 | $1.9 \times 10^{-6}$ | $0.15 \times 10^{-6}$ |
| CuA | 1.21 CuO | 26.2 | 9.3 | $1.4 \times 10^{-6}$ | * |
| DOT | 2.28 $B_2O_3$ | 100 | 91.0 | $8.6 \times 10^{-6}$ | $0.58 \times 10^{-6}$ |
| CCA-As | 1.44 $As_2O_5$ | 39.5 | 5.5 | $0.60 \times 10^{-6}$ | $0.05 \times 10^{-6}$ |
| CCA-Cu | 0.86 CuO | 20.4 | 4.3 | $0.43 \times 10^{-6}$ | * |
| CCA-Cr | 2.01 $CrO_3$ | 7.4 | 2.1 | $0.21 \times 10^{-6}$ | $0.08 \times 10^{-6}$ |

*coating failed

Table 1: Measured percentage of preservative leached from finely ground wood and dissociated in solid wood, and computed diffusion coefficients.

### AWPA standard test of three-dimensional CCA leaching

The three-dimensional leaching data and model show even closer agreement than in one dimension, likely due to imperfections in the silicon coating used to restrict diffusion to one dimension. The three-dimensional leaching experiments by Taylor (2001) should not be compared too closely to the one-dimensional experiments since the treatment and leaching methods are different, however Taylor's samples do appear to have significantly higher Cu and Cr leaching and diffusion coefficients, as given in table 2. This suggests a possibility of affecting leaching modifying the diffusion coefficients, as will be discussed further in the Recommendations.

## 4 Model application

The values of $M_\infty$ and $D$ shown in table 1 can be used to predict leachate quantities for a wide variety of sample dimensions and leaching scenarios. To demonstrate, they were used to predict leaching from the top surface only of 38mm southern yellow pine deck boards treated with DOT, CCA, and ACQ

| element | $D_L (cm^2/s)$ | $M_\infty$ (% of retention) |
|---|---|---|
| As | $0.51 \times 10^{-6}$ | 11.0 |
| Cu | $1.1 \times 10^{-6}$ | 6.4 |
| Cr | $1.3 \times 10^{-6}$ | 1.1 |

Table 2: Computed longitudinal diffusion coefficients and percentage of preservative component available for leaching after infinite time, as computed by the three-dimensional diffusion model.

exposed to one year of *continuous* leaching. The model predicts the loss of almost all the DOT, and 2/3 of the dissociated copper from CCA and ACQ, as shown in figure 8.

Although this leaching scenario is hypothetical and requires validation, it demonstrates the utility of the model for predicting comparative performance of different preservatives based on dissociated preservative quantities and diffusion coefficient. Further refinement of the model is needed to make predictions under more sophisticated leaching scenarios. Also, current predictions for severe leaching of CCA-treated wood may be underestimated until a better understanding of the reservoir affect in CCA in incorporated into the model.

## Some special implications and limitations of this approach

1. Leaching predictions based on this model are dependent on the duration of leaching, but not the intensity of rainfall or other exposure. This is consistent with studies that show that more leaching occurs per unit rainfall by slow steady rainfall than by intense downpour (Taylor 2001), and that the amount of leaching occuring over a fixed leaching time is independent of inteny of rainfall (Klipp, Willeitner, Brandt & Muller-Grimm 1991).

2. The simplified model presented in this paper assumes the wood is fully saturated with water and that dissociation is complete before the start of continuous contact with water. Further refinements are needed to model intermittent leaching and dissociation of preservative after the start of leaching.

3. Intermittent wetting and drying is a complex problem, involving the

simultaneous movement of water with dissolving and diffusion of the preservative. This problem is solvable using numerical methods, but first requires a quantitative study of water movement during such conditions and modeling of the water movement.

4. The leaching of iodine, methanol, and pentachlorophenol from wood have also been successfully modeled by a diffusion process (Haloui & Vergnaud 1997, Haloui, Bouzon & Vergnaud 1995, Rabai & Vergnaud 1997, Haloui, Kouali, Bouzon & Vergnaud 1994, Fakhouri & Vergnaud 1994). These models do not include bleeding or volatilization, although it is possible to include volatilization in a diffusion model.

5. The normal range of atmospheric temperatures may have a significant effect on dissociation rate and equilibrium, but is not expected theoretically to have much effect on diffusion coefficients, which are proportional to the absolute temperature in kelvin. Experiments are still needed to confirm this.

# 5 Recommendations

Clearly, low equilibrium dissociated concentration and low $D$ are desirable for the best leaching performance. In intermittent leaching scenarios, the rate of dissociation would also play an important role. This should be kept in mind for any attempts to improve leaching performance of existing or new wood preservatives. Diffusion coefficient is affected by the size of diffusing molecules (larger molecules diffuse more slowly), and by the presence different molecules which can interfere with each other's diffusion. For example, a large ion may slow the diffusion of another small ion through coulomb interactions. Dissociated concentration decreases with improved bonding between the wood and preservative, and is also affected by the lattice structure of precipitated low-solubility analytes, as discussed for example by Hammes (1978). Lattice structure of precipitates can be sensitive to the conditions under which they are formed, and this may be a cause of some of the unexplained differences in leaching performance of similarly produced samples of treated wood. Study of the lattice structure of inorganic wood preservative precipitates in the cell lumens seems like a promising approach to improving preservative leaching performance.

# 6 Conclusions

The advantages of this approach based on the physical leaching process over a purely empirical or statistical approach are worth emphasizing. An accurate physical model is extensible to many different situations which may never have been tested in the laboratory, which empirical or statistical descriptions of data are not. For example, once the diffusion coefficients and dissociation characteristics of a particular preservative-wood system have been measured, they can be used to compute leaching values for arbitrary lumber dimensions and intermittent leaching.

Physical modeling also provides a description of the mechanisms behind the leaching process, which statistical modeling does not. This improved understanding can help identify the relative significance and complex interrelations of the factors affecting leaching, and may provide insight into improving the wood preservative leaching performance.

The modeling presented here explains the rapid leaching of boron in terms of its high diffusion coeffient and high initial dissociated concentration. It predicts that ACQ-C will have higher initial copper leaching rates than CCA and CA-B due to greater dissociation, but the latter will leach for a much longer time due to lower diffusion coefficients and a reservoir of preservative which does not dissociate initially.

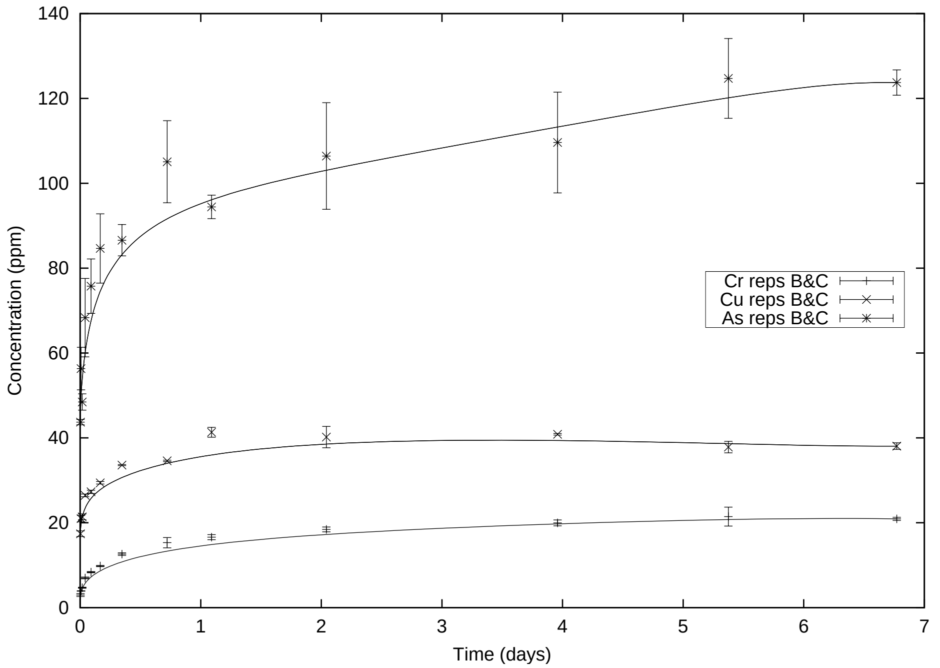

Figure 1: Dissolved Cr, Cu and As concentration for 2 replicates from the interior of an industrially treated pole.

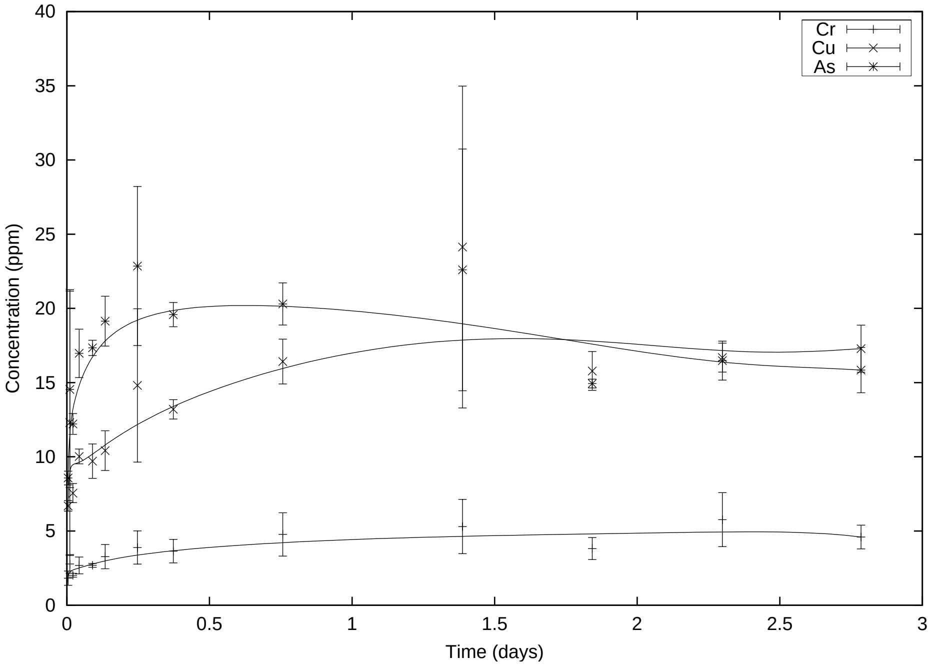

Figure 2: Dissolved Cr, Cu and As concentration for 3 replicates of lab treated samples.

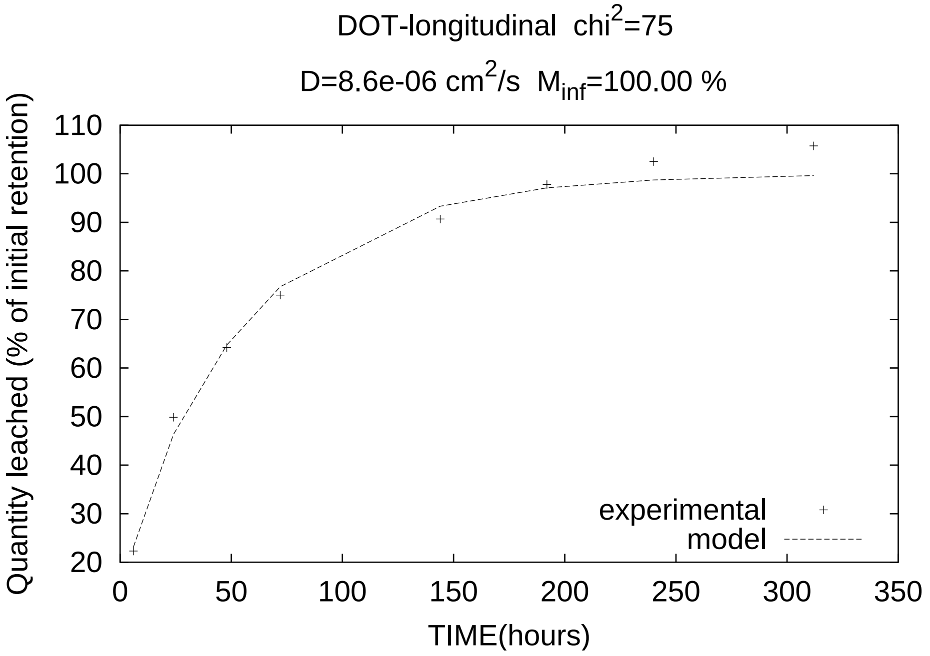

Figure 3: Longitudinal leaching of boron from DOT-treated sample with best fit analytical solution

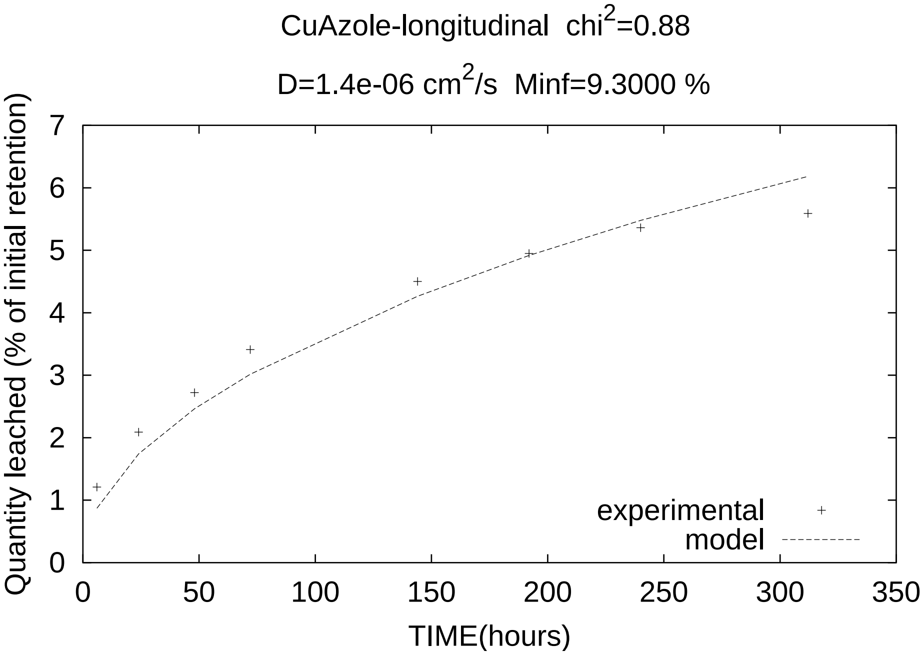

Figure 4: Longitudinal leaching of copper from CA-treated sample with best fit analytical solution

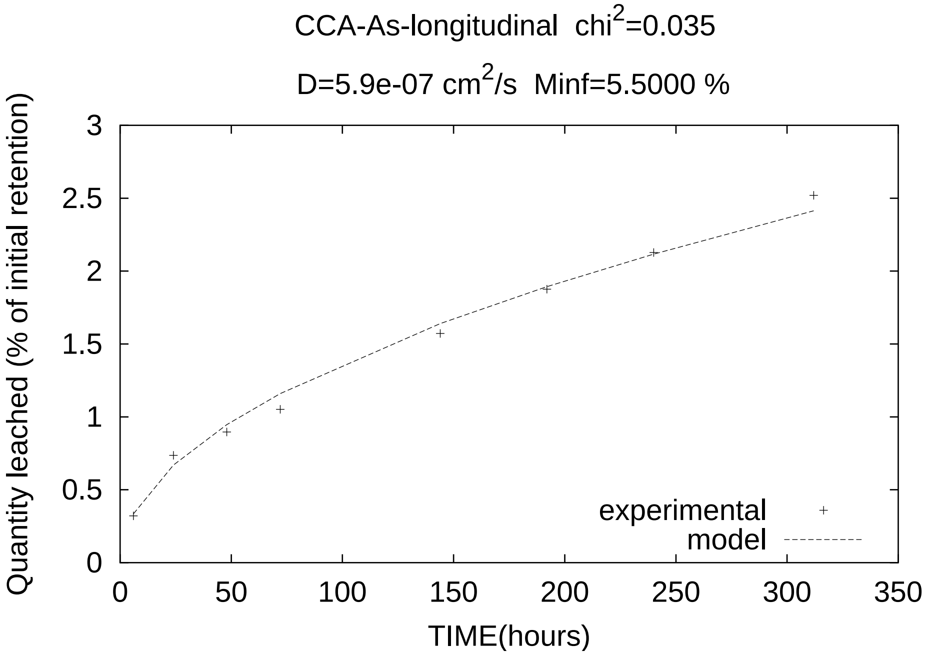

Figure 5: Longitudinal leaching of arsenic from CCA-treated sample with best fit analytical solution

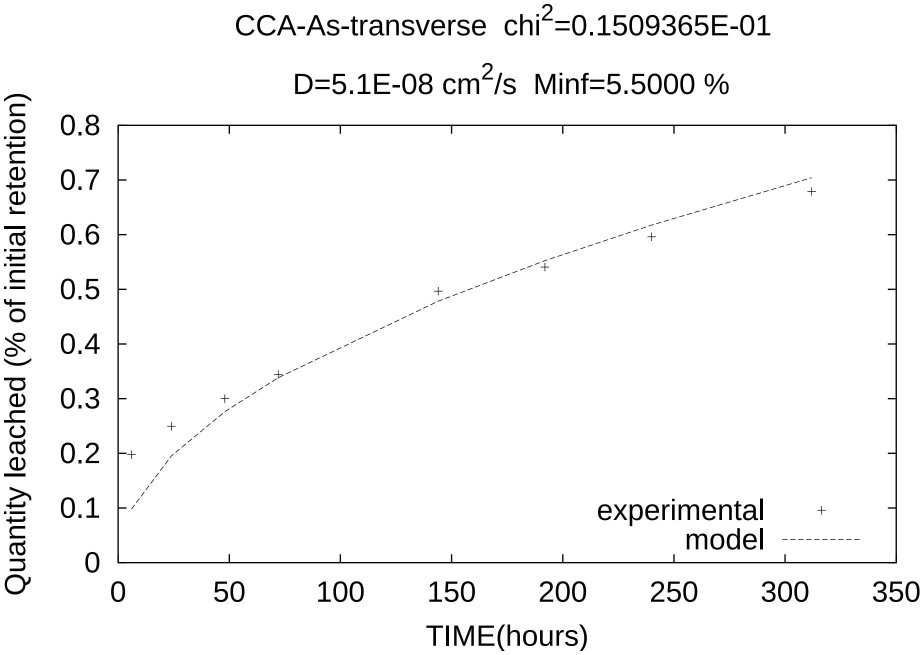

Figure 6: Transverse leaching of arsenic from CCA-treated sample with best fit analytical solution

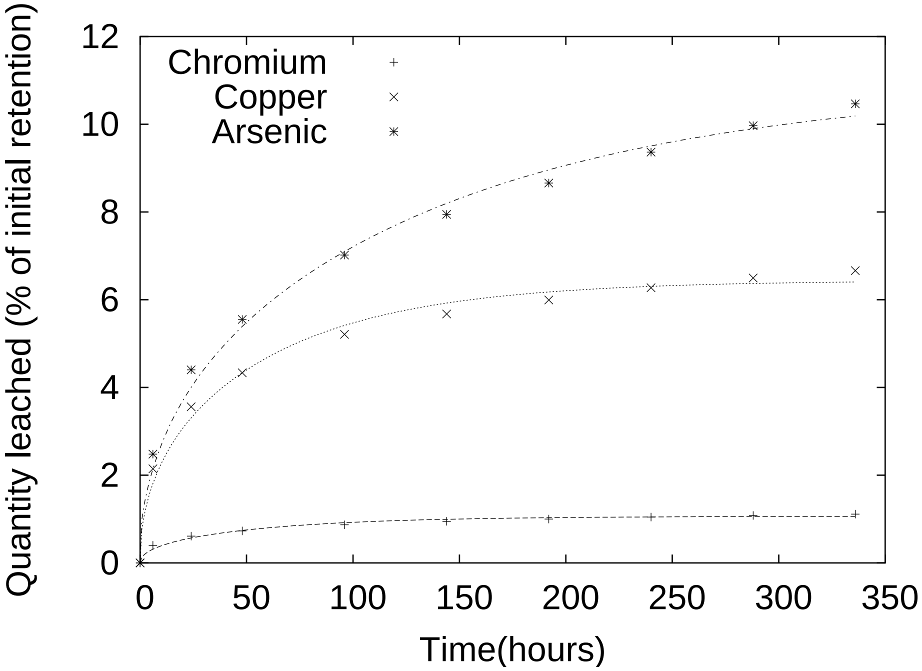

Figure 7: AWPA standard leaching test

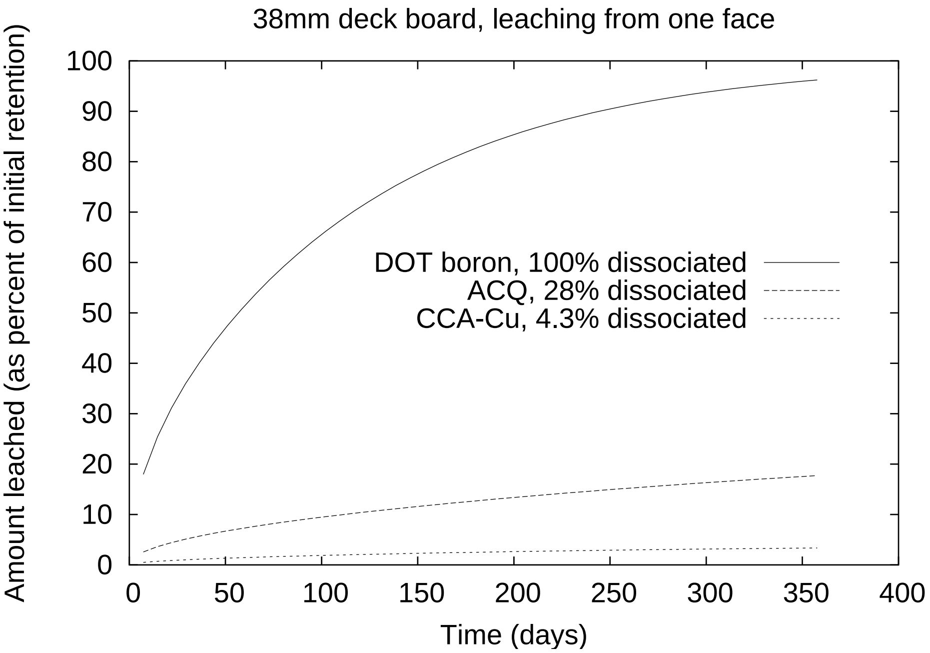

Figure 8: Predicted leaching of DOT (boron), ACQ (copper) and CCA (copper) from one transverse surface of a 38mm southern pine deck board during one year of *continuous* leaching

# 7. Literature

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