

A SIMULTANEOUS DIFFUSION AND REACTION MODEL FOR THE LEACHING OF Cr^{6+} FROM UNFIXED CCA-TREATED WOOD

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Summary

A physical model for the simultaneous diffusion and reaction of any substance which undergoes a first order reaction in wood is presented. Using this model and a laboratory leaching experiment with small wood samples immersed in water, the radial and tangential diffusion coefficients and the reaction rate constant of Cr^{6+} in unfixed CCA-treated red pine were measured. The reaction rate constant at room temperature in red pine from one pole was measured to be between 0.20 to 0.29 days⁻¹, in close agreement with previous standard fixation rate experiments. The first measurements of the diffusion coefficients of Cr^{6+} in wood are presented. The radial diffusion coefficient was measured to be between $D_R = 0.5$ and 3.5 mm²/day; the tangential diffusion coefficient was significantly less, between $D_T = 0.13$ and 0.64 mm²/day. The model was also used to calculate final chromium retention throughout the samples after losses due to leaching. This model represents a starting point for a more generalized model which could be used to determine reaction rate and diffusion coefficients for all the components of unfixed CCA and to predict quantities leached and retained in commercial treated wood products under a broad range of atmospheric conditions.

1. Introduction

Chromated copper arsenate (CCA) is the most widely used wood preservative in North America. It is used in residential applications such as decks and fences, as well as industrial applications such as utility poles and marine pilings. One of the major advantages of CCA over traditional organic preservatives is that after treatment, CCA undergoes a chemical fixation reaction which binds it to the wood matrix. Before fixation is complete, however, CCA is readily leachable, toxic, and mobile in the environment. Thus it is important from the points of view of human health, environmental damage, and preservative efficacy that CCA-treated wood undergoes sufficient fixation before leaving the treatment plant.

This work incorporates the simultaneous fixation and diffusion of Cr^{6+} , one component of unfixed CCA, into a leaching model capable of predicting leaching after any degree of incomplete fixation and under periodic leaching conditions. It can also be used to predict the retention of fixed chromium throughout the sample after experiencing these leaching conditions.

The model should be considered to be in its preliminary stages, as it has only been applied to laboratory leaching tests of small samples at room temperature. However,

it is expected to be equally applicable to larger samples under a broad range of atmospheric conditions. The results to date show great promise for application of this model to industrial products.

1.1 Why is CCA fixation important?

CCA treatment solution contains several highly toxic ingredients: divalent copper, hexavalent chromium, and pentavalent arsenic. Copper is toxic to aquatic life even in trace quantities; the Canadian water quality objectives for aquatic environments place an upper limit of 1 part per billion on copper contamination in water. Cr^{6+} can easily cross biological membranes, and can cause significant health problems including respiratory problems, cancer, skin ulceration and dermatitis. As^{5+} is less acutely toxic than Cr^{6+} , but is also a concern. Limits on acceptable contamination by these elements in soil and groundwater have been set by the governments of Ontario (Ont Jan. 1989) and Quebec (Sta 1988).

These components of freshly treated CCA products are water soluble and highly susceptible to transport by contact with rain or skin. However, CCA undergoes a fixation reaction which both binds it directly to the wood substance and converts it to a less toxic form. This results in a safe and effective preservative treatment as long as the fixation reaction is allowed to sufficiently complete in a secure treatment area. A secure treatment area must protect treated products from rain, recover dripped preservative solution on drip pads, and prevent human contact with unfixed products. Insufficient fixation facilities have in some cases resulted in severe contamination of the treatment site, requiring expensive remediation.

A thorough understanding of the fixation and leaching of unfixed CCA solution is highly desirable for setting standards of good treatment practice and predicting the consequences of poor practices. CCA fixation rate is reasonably well understood, and is discussed in section 1.3. The proposed research will incorporate this information into a diffusion model of Cr^{6+} to provide a more complete picture of the movement of unfixed CCA.

1.2 Why follow Cr^{6+} ?

The CCA fixation reaction is characterized by changes in the valency states of chromium copper, and arsenic. The change in chromium from its hexavalent state Cr^{6+} to its trivalent state Cr^{3+} has been most commonly chosen to measure the progress or the fixation reaction, for several reasons (Cooper, Ung, Kaldas & Taylor 1995):

- The change in valency state of chromium occurs more slowly than for copper or arsenic, so measuring Cr^{6+} is a conservative approach to monitoring fixation,
- Cr^{6+} is very reactive and is easy to detect and quantify,
- and Cr^{6+} is perhaps the most hazardous of the CCA solution components. It has both acute and chronic toxic effects and, unlike arsenic, is very mobile in soil and can be significantly absorbed through human skin.

1.3 Existing model for the conversion of $\text{Cr}^{6+} \rightarrow \text{Cr}^{3+}$ during fixation

When a red pine is treated with CCA at room temperature (22°C), 53% of the Cr^{6+} reacts within about 3 hours at room temperature through a rapid initial reaction. This reaction would normally always be complete before the treated product is exposed to leaching conditions. The other half reacts through a much slower secondary reaction, at an exponential rate. The progress of the slower exponential reaction at near saturated moisture conditions has been quantified by Cooper & Chen (n.d.):

$$[\text{Cr}^{6+}(t)] = [\text{Cr}_0^{6+}] e^{-4.0 \times 10^{10} e^{-69811/(8.314 \cdot T)} t} \quad (1)$$

where $[\text{Cr}^{6+}(t)]$ is the concentration of Cr^{6+} at fixation time t ,

$[\text{Cr}_0^{6+}]$ is the initial concentration of Cr^{6+} ,

t is the time in seconds, and

T is the temperature in Kelvin.

This model uses the exponential form of the secondary reaction but measures the reaction rate independently.

2. Methodology

2.1 Sample preparation

The samples used for the experiment were 19mm cubes of red pine sapwood, from two poles of different density. Samples from the lighter pole had an average density of $408 \pm 10 \text{ kg/m}^3$; those from the heavier pole had an average density of $534 \pm 3 \text{ kg/m}^3$.

The leaching experiment was performed on 5 different sample groups, with 5 replicates in each group. The samples were cut with two faces parallel to the annual rings so that by coating four faces diffusion could be restricted the radial, tangential, or longitudinal direction. Groups A, B, C, and D were prepared from the low density pole, and group E from the high density pole. Groups A, B, and C were placed on a shaker operating at 60rpm, while the samples in group D were kept off the shaker. Group B was coated to allow tangential diffusion, while the others were coated to allow radial diffusion. Group C was the same as group A except that the leachwater was changed only twice over the duration of the experiment, rather than after each of the 15 Cr^{6+} concentration measurements. The experimental conditions for the four groups are summarized in table 1.

The samples were treated in a pressure retort for 20 minutes under vacuum then 30 minutes under 100psi, in a 1.77% CCA-C solution. The CCA concentration was measured by x-ray fluorescence spectroscopy with an Oxford Lab-X 3000. Weight gain from the pressure treatment, averaged over all samples, was $206 \pm 6\%$ of air dry weight, corresponding to a CCA retention of $14.9 \pm 0.6 \text{ kg}$ per cubic meter of air dry wood. The samples were then removed from the retort and clamped between two boards to protect

two opposing faces while permitting the other 4 faces to be coated. An initial coating of polyurethane was applied and allowed to cure for 12 hours, followed by a coating of marine epoxy which was allowed to cure for 24 hours. During this time the samples were enclosed in a plastic bag with wet rags to keep the humidity high and reduce evaporation. The coatings were then visually inspected and touched up with 5-minute epoxy where needed before immersing in water. Each sample wiped off with a paper towel then immersed in a separate jar with a lid containing 400mL of distilled water at room temperature, approximately 22°C. The samples were immersed approximately 54 hours after the CCA pressure treatment. Several extra samples were prepared and expressed at the same time the others were immersed, for a direct measurement of initial Cr⁶⁺ concentration. Unfortunately these extra samples were all from the high density pole which showed a much faster than expected reaction rate, so no reliable estimate of the initial Cr⁶⁺ concentration in the low density pole was obtained.

2.2 Leaching experiment

At varying time intervals, the leachwater for each sample was tested for Cr⁶⁺ concentration using the diphenylcarbazide method (Cooper & Ung 1993). Between 1g and 40g of leachwater, depending on the Cr⁶⁺ concentration, was weighed into a 50mL flask. 0.5mL of diphenylcarbazide was added then the flask was topped up to 50g of total liquid with 0.5N sulfuric acid. In an acidic solution, Cr⁶⁺ undergoes a colour reaction with diphenylcarbazide to produce a purple solution which absorbs visible light in direct proportion to the Cr⁶⁺ concentration. The colour solutions were analyzed in a spectrophotometer at 540nm, with at least three standard solutions of known concentration each time.

2.3 Finite Difference Computation

Analysis was based on the one-dimensional partial differential equation for diffusion with simultaneous reaction. This equation and the derivation of the numerical finite difference solution used here are given in appendix A.

To compute the finite difference solution, we imagine the sample divided into thin slices of equal thickness Δz . The slices are made parallel to the two exposed faces, so that the concentration of Cr⁶⁺ is approximately constant throughout each slice. The slices are labelled by an integer i , which varies between $1 \leq i \leq N$, where N is the total number of slices. For the computations presented in this paper, the 19mm blocks were divided into $N = 95$ slices, so $\Delta z = 0.2mm$.

For a first order reaction rate of the form

$$\frac{dC}{dt} = -kC \quad (2)$$

where: C is the concentration of the substance under study, in this case Cr⁶⁺ (ppm),

t is the time (days),

k is the reaction rate coefficient (days⁻¹),

and $\frac{dC}{dt}$ is the rate of change of concentration, in the absence of diffusion (ppm/day), the finite difference form of the diffusion-reaction equation is (Moldrup, Kruse, Yamaguchi & Rolston 1996)

$$C_i^{t+\Delta t} = C_i^t + D \left(\frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{(\Delta z)^2} \right) \Delta t - kC_i^t \Delta t. \quad (3)$$

where: C_i^t is the concentration at time t and position i , and

Δt is the time interval of each iteration, in days ($\Delta t = 0.002$ days in this computation).

Δz is the slice thickness ($\Delta z = 0.2$ mm in this computation)

The second term on the right hand side of equation 3 is the change in concentration of slice i over one timestep due to diffusion alone. The last term is the loss in concentration due to reaction.

Carrying out the finite difference computation requires a knowledge of:

- the reaction rate k ,
- the diffusion coefficient D ,
- $C_i^{t=0}$, $1 \leq i \leq N$, *i.e.*, the initial concentration distribution throughout the sample, and
- $C_{i=1,N}^t$, $0 \leq t \leq T$, where T is the final time of the computation. *I.e.*, the concentration at the boundaries from time $t=0$ to the latest time in the computation.

A Fortran program was written to carry out the actual computation. The first step of the first iteration is to calculate

$$C_2^{t=\Delta t} = C_2^{t=0} + D \left(\frac{C_3^{t=0} - 2C_2^{t=0} + C_1^{t=0}}{(\Delta z)^2} \right) \Delta t - kC_2^{t=0} \Delta t \quad (4)$$

This is repeated until all $C_i^{t=\Delta t}$ have been calculated for $2 \leq i \leq N - 1$. At this point the first time iteration of the computation is complete, as we know the complete concentration profile for the next time $t = \Delta t$. Thus the concentration at each interior slice at the next time is calculated from the concentration of that slice and the two adjacent slices at the previous time. Concentration at the boundaries ($i=1$ and $i=N$) must be known as a boundary condition.

This time iteration is repeated for $t = 2\Delta t, 3\Delta t$, and so on until the latest time of interest $t = T$. We then know the concentration everywhere in the sample for all times between 0 and T .

2.4 Finding k and D

The procedure described in the previous section can be used to calculate future concentration profiles within a sample given the reaction rate k and diffusion coefficient D . However, in this experiment the concentration of Cr^{6+} in the leachwater is measured at various time intervals but k and D are unknown. k and D are calculated by an optimization procedure of choosing a series of educated guesses and choosing the values which cause the finite difference model to reproduce experimental data the closest. The steps of this iterative optimization procedure are:

1. Make an initial guess of the values for k and D .
2. Carry out the finite difference computation to the time of the last experimental measurement.
3. For the time of each experimental measurement, calculate the total mass of Cr^{6+} leached since the previous measurement.

For a measurement at time T_2 , where the previous measurement was at time T_1 , calculate for each slice

$$M(\text{leached})_i^{T_2} = [C_i^{T_2} - (C_i^{T_1} + C(\text{fixed})_i^{T_2-T_1})]M(\text{liquid})_i, \quad (5)$$

where: $C(\text{fixed})_i^{T_2-T_1}$ is the mass of Cr^{6+} which was fixed to slice i between times T_1 and T_2 , and

$M(\text{liquid})_i$ is the mass of solution retained in each slice, which is assumed to be the same for all slices and all times. It is calculated by dividing the CCA retention of the whole sample during pressure treatment by the number of slices N .

$M(\text{leached})_i^{T_2}$ is summed over the entire sample, $1 \leq i \leq N$ to give the total mass of Cr^{6+} leached since the previous experimental measurement.

4. Compute the square of the fractional difference between calculated and measured Cr^{6+} leached for each experimental measurement:
 $\text{diff}^2 = \left(\frac{M_{\text{expt}} - M_{\text{calc}}}{M_{\text{expt}}} \right)^2$. Sum this quantity over all experimental measurements. This fractional difference was used instead of the standard sum of squares to give equal weighting to data points whose quantity of Cr^{6+} leached varied by orders of magnitude between the beginning and end of the leaching experiment. Using just a sum of squares of differences, the first few leaching measurements dominated the rest because of the rapid falling off of quantities leached.
5. Make a new guess for k and D , and return to step 2. The values of the new guesses are determined by a Simplex Downhill optimization algorithm within the software package Minuit (Min n.d.), which was called as a subroutine from the author's Fortran program.

6. The Simplex Downhill algorithm converges when it finds unique values for k and D which minimize the sum of squares calculated in step 4.

Using this method, the reaction constant k and the diffusion coefficient D were calculated individually for each sample in the leaching experiment.

3. Results and Discussion

The leaching model produced relatively good fits to experimental data for quantity of Cr^{6+} leached over the duration of the experiment, for all cases where the Simplex Downhill optimization converged. Figure 3 shows the Cr^{6+} leaching rate measured for a sample in group A as modeled. This fit is typical of the rest in that the model matches experiment closely except for the first data point. Although the samples were wiped off with a paper towel before immersion, this may be due to excess Cr^{6+} residue on the surface of the sample or to some other effect not accounted for in the model. Additional insight could be gained in a future experiment by taking a leaching measurement very early in the experiment, *i.e.*, less than an hour after the samples are immersed.

Figure 1 and 2 show the first order reaction constants and diffusion coefficients calculated by the model. Samples for which the Simplex Downhill minimization did not converge are not shown. The averages and standard deviations of k and D for each group are summarized in table 2. T-Tests for significance of the difference between means were conducted for k and D for each pair of groups and are summarized in table 3.

In general, the diffusion coefficients showed a much greater variation than reaction constants. This may be due to inherent wood properties or to slight failures of the coatings. Any failure of the coating which allowed Cr^{6+} to escape through the end grain would show up as an increase in diffusion coefficient but should not affect the reaction rate.

Group B, for which diffusion was in the tangential direction, showed a significantly lower diffusion rate than all groups with radial diffusion. It also showed a small but statistically significant increase in reaction rate over groups A, C, and D. Since the wood used for groups A, B, C, and D were all from the same pole, we would not expect the reaction rates to be different unless it were affected by the lower leaching rates for group B.

Group E, from a higher density pole, showed significantly higher diffusion coefficients and reaction constants than all other groups. The magnitude of the increase in reaction rate is surprising as it is a much larger difference than previous studies of the effect of wood density on reaction rate have found. These samples have been saved and further study may help to determine the reason for the very high reaction rates.

Groups C and D did not show a significant difference from group A for reaction constant or diffusion coefficient. This information will be of help for future experiments where changing the water with every measurement or use of a shaker are impractical.

The reaction constants for groups A, B, C, and D are in close agreement with the constant measured by Kazi & Cooper (n.d.) of 0.20 day^{-1} for 1% CCA-C and 0.13

day⁻¹ for 3% CCA-C at 22°C. These reaction constants were measured in the absence of leaching directly by expressing unfixed solution from the samples. It should be noted that during this experiment room temperature was checked several times and found to be 22°C, but it was not continuously monitored. A decrease in temperature of 1°C, for example, would decrease the reaction rate by 12%. A measurement of reaction rate or activation energy more accurate than this would require continuous or frequent temperature measurements.

4. Conclusions

A numerical diffusion-reaction model was used to calculate the first order reaction constant and diffusion coefficient of Cr⁶⁺ in unfixed CCA-treated red pine from the results of a laboratory leaching experiment. By adjusting only two variables for the reaction constant and diffusion coefficient, the model was made to accurately represent Cr⁶⁺ leaching rates observed in the leaching experiment. Reaction constants calculated for one pole were found to match closely with previous values measured directly from fixation experiments, but constants calculated from a higher density pole were much greater. Radial and tangential diffusion coefficients for Cr⁶⁺ in red pine were also presented. These values were not found to differ significantly at a 95% confidence level whether the samples were on a shaker or not, or whether the leachwater was replaced infrequently or with every concentration measurement.

Since this is a physical model, based on what is actually occurring within the wood, it can be applied over a wider range of conditions and to calculate different quantities than those observed. For example, the model was used to calculate a profile of fixed chromium retention, and could be used to calculate fixed chromium retention and leaching quantities if the samples had been immersed in water at a different time after initial treatment or been exposed to intermittent leaching conditions. By performing similar leaching experiments, this model can be applied in its present form to any substance which undergoes a first order fixation reaction in wood. With some further development and experiments, this model could be expanded over a wide range of temperatures and be applied to fixation in hot water or under outdoor atmospheric conditions.

Appendix: Derivation of the forward-time discretization of the diffusion-reaction equation

The one-dimensional differential equation for simultaneous diffusion and first-order reaction is (Moldrup et al. 1996)

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC, \quad (6)$$

where: C is the concentration of the diffusing substance,

- D is the diffusion coefficient, and

- k is the first-order reaction constant.

Now, we divide the wood sample into slices of equal thickness Δz which are numbered in sequence by the integer variable i . i varies between 1 and N , where N is the total number of slices in the sample. Converting the true differentials of equation 6 to discrete differences yields

$$\frac{\Delta C}{\Delta t} = D \frac{\Delta}{\Delta z} \left(\frac{\Delta C}{\Delta z} \right) - kC. \quad (7)$$

We then explicitly expand the time differential as

$$\frac{\Delta C}{\Delta t} = \frac{C_i^{t+\Delta t} - C_i^t}{\Delta t}, \quad (8)$$

and the spatial differential as

$$\begin{aligned} \frac{\Delta}{\Delta z} \left(\frac{\Delta C}{\Delta z} \right) &= \frac{\Delta}{\Delta z} \left(\frac{C_{i+1}^t - C_i^t}{\Delta z} \right) \\ &= \left(\frac{(C_{i+1}^t - C_i^t) - (C_i^t - C_{i-1}^t)}{(\Delta z)^2} \right) \\ &= \frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{(\Delta z)^2}. \end{aligned} \quad (9)$$

Substituting these explicit expansions into equation 7, the discretized diffusion-reaction equation becomes

$$\frac{C_i^{t+\Delta t} - C_i^t}{\Delta t} = D \left(\frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{(\Delta z)^2} \right) - kC_i^t. \quad (10)$$

By multiplying through by Δt and adding C_i^t to both sides,

$$C_i^{t+\Delta t} = C_i^t + D \left(\frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{(\Delta z)^2} \right) \Delta t - kC_i^t \Delta t. \quad (11)$$

This is the forward-time discretization of the diffusion reaction equation which was used in the model, and is referred to as equation 3 in section 2.3.

5. Literature

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Tables

Table 1: Description of sample groups used in the leaching experiment

Group	Direction of diffusion	On shaker? (60rpm)	Sample density	Leachwater changed every time?
A	radial	yes	low	yes
B	tangential	yes	low	yes
C	radial	yes	low	no
D	radial	no	low	yes
E	radial	yes	high	yes

Table 2: Calculated mean and standard deviation of reaction constants and diffusion coefficients

	# of samples	D (mm ² /day)	Δ D (mm ² /day)	k (day ⁻¹)	Δ k (day ⁻¹)
Group A	3	2.34	0.73	0.23	0.02
Group B	5	0.27	0.21	0.29	0.03
Group C	4	1.51	0.79	0.23	0.03
Group D	5	1.85	0.76	0.20	0.02
Group E	2	3.31	0.15	0.86	0.04
(Kazi & Cooper n.d.) 1% CCA-C	-	-	-	0.20	-
(Kazi & Cooper n.d.) 3% CCA-C	-	-	-	0.13	-

Table 3: Results of the t-Test for significance of difference between means. "Yes" means that the null hypothesis that the two means are equal can be rejected with a 95% confidence, "No" means that it cannot.

	Group B k / D	Group C k / D	Group D k / D	Group E k / D
Group A	Yes / Yes	No / No	No / No	Yes / No
Group B	-	Yes / Yes	Yes / Yes	Yes / Yes
Group C	-	-	No / No	Yes / Yes
Group D	-	-	-	Yes / Yes

Figures

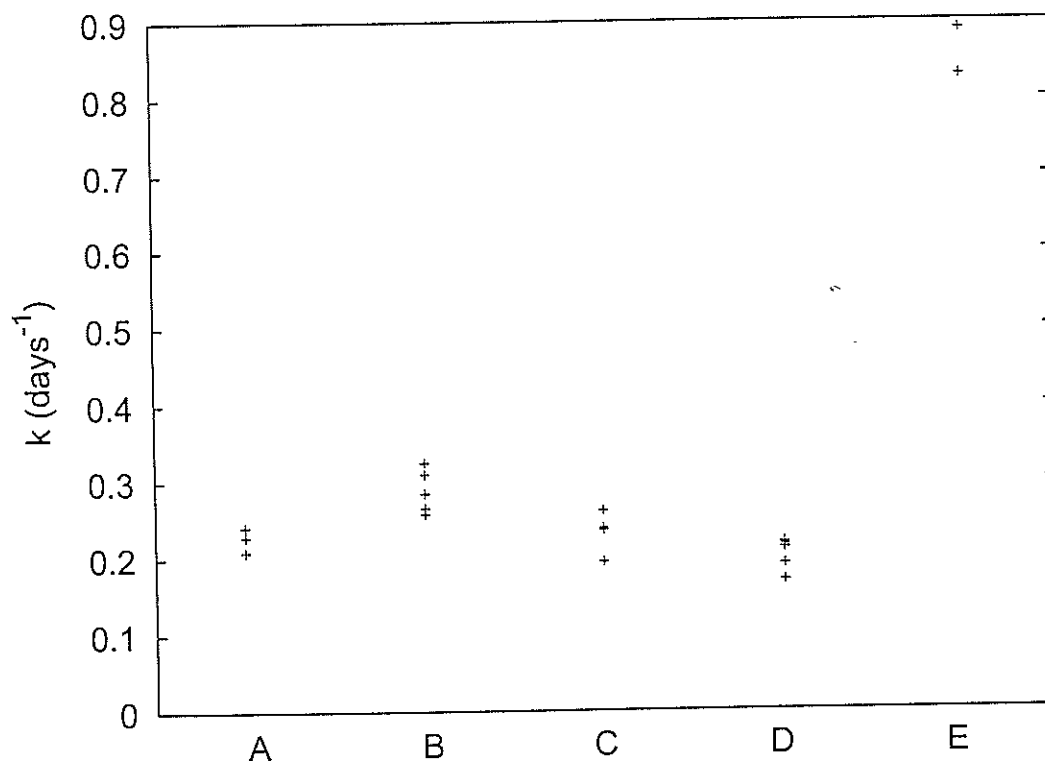


Figure 1: Calculated first order reaction constants for sample groups A to E

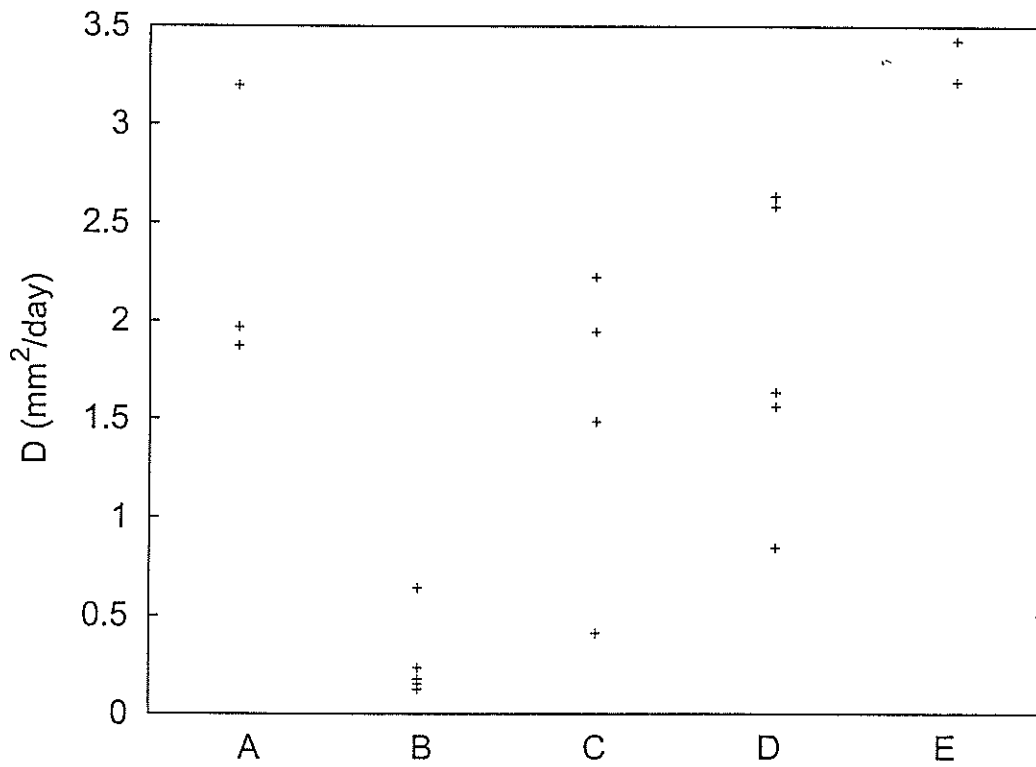


Figure 2: Calculated diffusion coefficients for sample groups A to E

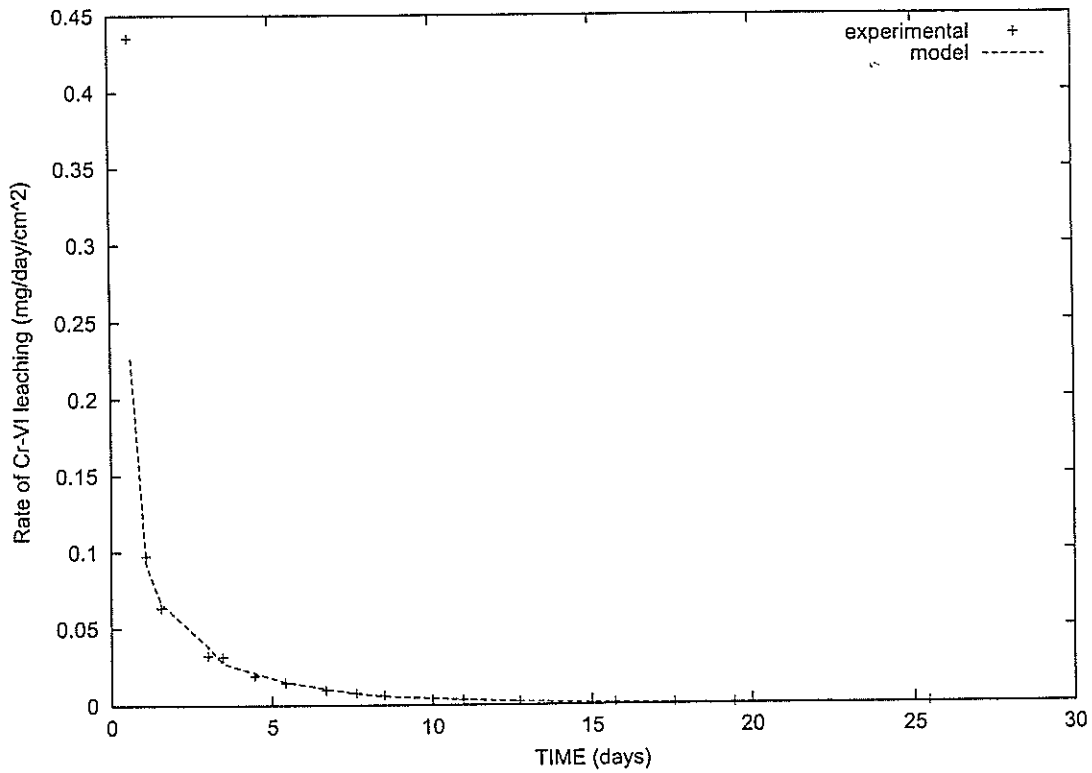


Figure 3: Experimental and modeled rate of Cr^{6+} leaching from a 19mm cube of freshly treated red pine from group A, coated on 4 sides, immersed in water.

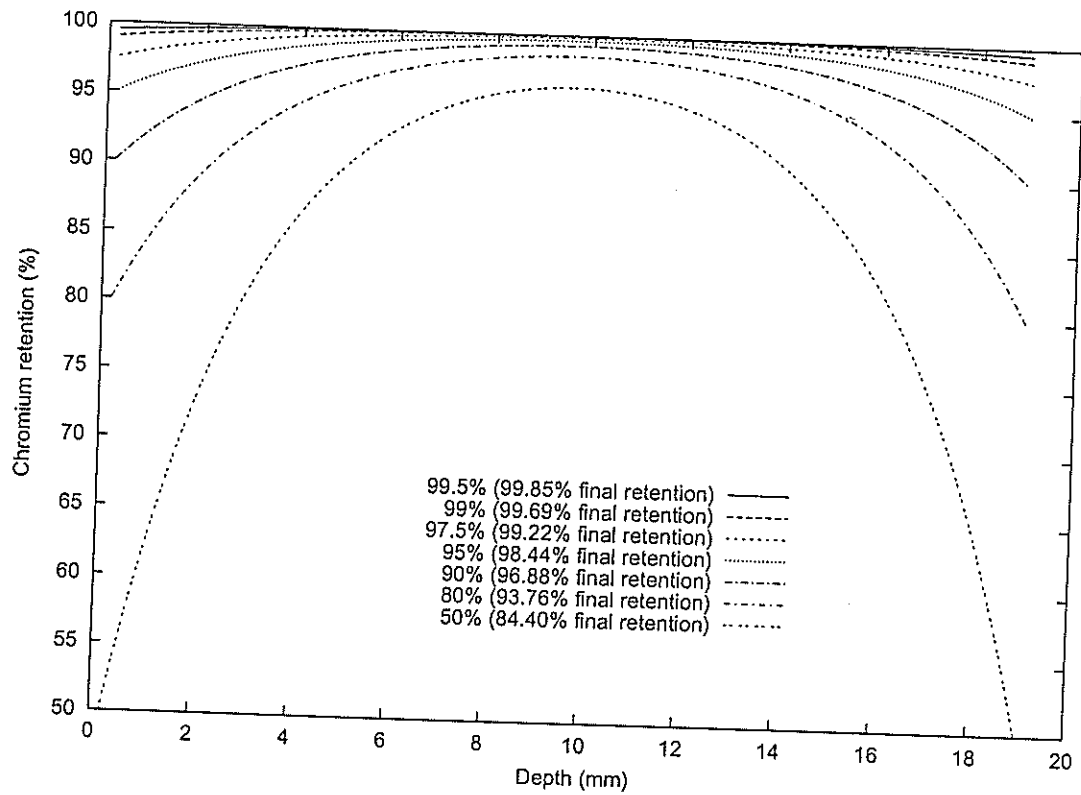


Figure 4: Calculated final chromium retention of a sample from group A as a percentage of initial treatment retention after 3 weeks of continuous immersion in water. The different lines represent different degrees of fixation at the start of leaching, between 50% and 99.5%. Final retention refers to the overall chromium retention in the sample after complete fixation.