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Modeling CCA leaching

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Abstract

A physical model applicable to the leaching of any substance undergoing a first-order fixation reaction with wood is presented. Using this model and laboratory leaching experiments with small wood samples immersed in water, the diffusion coefficients and reaction rate constant of Cr^{6+} in unfixed CCA-treated red pine (*Pinus resinosa Ait.*) are measured. Modeled reaction rate constants are in agreement with pure fixation experiments except when determined from experiments involving small samples severely depleted by longitudinal leaching, but this effect is seen to decrease for larger sample sizes. The operation of the model for predicting intermittent Cr^{6+} leaching is explained through a visual demonstration. The model is shown to have good predictive ability when compared to a a leaching experiment involving intermittent immersion and changing temperatures.

1 Introduction

Although chromated copper arsenate (CCA) faces an uncertain future, it is presently the most widely used industrial wood preservative in the world (Gray 1991). In addition to its residential applications such as decks and fences which are being phased out in the U.S., CCA is likely to have continued usage in industrial applications such as utility poles and marine pilings. CCA has replaced other traditional organic preservatives in many applications due to its clean appearance, safety for human contact, resistance to leaching, and long-term durability. These desirable properties are due to a chemical fixation reaction which takes place after initial treatment, stabilizing it in the wood matrix and lowering its toxicity (Cooper, Alexander & Ung 1991). However before fixation is complete, CCA is readily leachable, toxic, and mobile in the environment. Thus fixation is an essential stage in the safe and effective production of CCA-treated wood.

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.

1.1 Why follow $\mathbf{Cr^{6+}}$?

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.

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

When red pine is treated with CCA at room temperature (22^{o}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.):

$$\left[Cr^{6+}(t)\right] = \left[Cr_0^{6+}\right] e^{-4.0\times10^{10}e^{-69811/(8.314*T)}t} \tag{1}$$

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

$\left[Cr_0^{6+}\right]$ 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 of other fixation rate experiments.

2 Theory

2.1 Analytical computation

The problem of first order reaction with diffusion can be solved analytically for simple boundary conditions. Analytical solutions are fast and accurate to compute, but are difficult to use or even unworkable for more complex boundary conditions. It is the method of choice for least squares calculations because many iterations can be done in a short period of time, and the minimization algorithm performs much better given accurate χ^2 calculations.

Crank (1975) shows that the the diffusion with reaction problem can be found from a solution to the corresponding pure diffusion problem. If the flux across the exposed surface area is constant, then the quantity of leachate M_t is related to the quantity in the pure diffusion problem M'_t by

$$M_t = k \int_0^t M'_t \exp\left(-kt'\right) dt' + M'_t \exp\left(-kt\right). \tag{2}$$

Crank (1975) also solves the pure diffusion problem in one dimension for a sample bound by two planes at $x = 0$ and $x = l$, with uniform initial concentration and equal, constant concentrations at each boundary, and gives the mass of leachate as

$$\frac{M'_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(-D\alpha_n^2 t\right) \cos \alpha_n x. \tag{3}$$

where $\alpha_n = \frac{(2n+1)\pi}{2l}$

Substituting equation 3 into equation 2 and integrating yields

$$\frac{M_t}{M_\infty} = \sum_{n=0}^{\infty} \frac{2D}{l^2(k + D\alpha_n^2)} \left[1 - \exp\left(-(k + \alpha_n^2 D)t\right)\right]. \tag{4}$$

This solution can be used for samples sealed on 4 sides, with 2 opposing sides exposed. The number of terms to include in the sum is chosen by how accurate an answer is required. In practice, for minimization calculations only terms larger than 10^{-3} affect the final values of k and D.

This same solution can be applied to the sample geometry where 5 sides are coated and only 1 side exposed. The solution for this geometry is identical to the solution for one half of a sample of twice the length with 2 opposing sides exposed (Crank 1975), as demonstrated in figure 1, and the mass leached is exactly one half the mass leached from the larger sample.

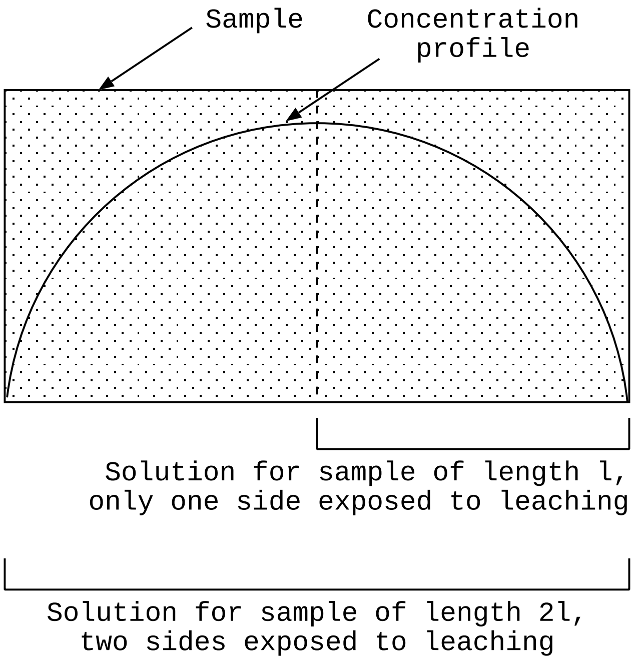

Figure 1: Equivalence of solutions for sample of length l exposed on 1 side and sample of length $2l$ exposed on 2 opposing sides

2.2 Finite difference computation

Solving the diffusion/reaction equation by finite differences is slower computationally and less accurate than the analytical solution. However, it is more flexible and easily adaptable to many different boundary and initial conditions. For non-iterative, predictive calculations, the speed and accuracy of numerical calculations are still more than adequate.

A finite difference form of the one-dimensional partial differential equation for diffusion with simultaneous reaction has demonstrated by Moldrup, Kruse, Yamaguchi & Rolston (1996). To use this form, 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 Cr^{6+} 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 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

$$\frac{dC}{dt} = -kC \tag{5}$$

where: C is the concentration of the substance under study, in this case Cr^{6+} (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 et al. 1996)

$$C_i^{t+\Delta t} = C_i^t + D\left(\frac{C_{i+1}^t - 2C_i^t + C_{i-1}^t}{(\Delta z)^2}\right)\Delta t - kC_i^t\Delta t. \tag{6}$$

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 6 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

$$C_2^{t=\Delta t} = C_2^{t=0} + D\left(\frac{C_3^{t=0} - 2C_2^{t=0} + C_1^{t=0}}{(\Delta z)^2}\right)\Delta t - kC_2^{t=0}\Delta t \tag{7}$$

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. Then from this concentration profile, the mass leached between two times T_1 and T_2 can be calculated:

$$M(leached)_i^{T_2} = [C_i^{T_2} - (C_i^{T_1} + C(fixed)_i^{T_2-T_1})]M(liquid)_i, \tag{8}$$

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

$M(liquid)_i$ 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.

$M(leached)_i^{T_2}$ 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.

This quantity can be directly compared to experimental values obtained by multiplying measured leachate concentration by volume of leachwater.

2.3 Finding k and D by χ^2 minimization

The analytical and finite difference procedures described 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. This can be done by either by finite differences as described in section 2.2 or analytically as described in section 2.1.

4. Compute the normalized χ^2 between calculated and measured Cr^{6+} leached quantities

$$\chi^2 = \sum_{i=1}^{N_{points}} \left(\frac{M_i^{expt} - M_i^{calc}}{\delta M_i^{expt}} \right)^2 . \tag{9}$$

   where δM_i^{expt} is the experimental error for each data point, and
   χ^2 is summed over all experimental measurements.

5. Make a new guess for k and D, and return to step 2. The values of the new guesses are determined by a optimization algorithm within the software package Minuit (Min n.d.), which was called as a subroutine from the author's Fortran program. In conjunction with the analytical leaching calculation a *Migrad* minimization technique was used. *Migrad* is a highly efficient algorithm with reliable parameter error estimations. However, it tends to fail when first derivative calculations are inaccurate, as with the least squares leaching calculation. With finite difference calculations, the more robust Simplex Downhill minimization algorithm had to be used, which is much slower and produces unreliable parameter error estimates.

6. The minimization algorithm converges when it finds unique values for k and D which minimize the the χ^2 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 General leaching method

The basic approach was to cut untreated, airdry samples to the same size for each treatment group. The samples were coated on 4 or 5 sides to restrict diffusion to one direction, using Mono "Window and Bathroom" flexible silicon. When applied to dry wood, this product adheres very well even after wetting and expands without cracking. The faces to be left uncoated were covered with duct tape for protection from stray silicon during the coating process. The samples were then treated with CCA using a full-cell process of 30 minutes of vacuum followed by 30 minutes at 100psi. After treatment, samples were rinsed to remove excess treating solution, stored in Ziploc bags for 2 hours to allow completion of the primary reaction, then immersed individually in jars of 200-400mL of distilled water. Extra samples were treated for measurement of initial [Cr^{6+}].

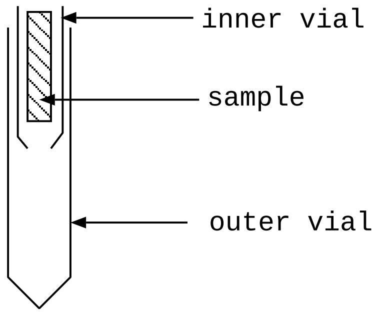

Figure 2: Setup for expressing samples by centrifuge. Note the hole in the bottom of the smaller vial.

At varying time intervals, the leachwater for each sample was tested for Cr^{6+} concentration using the diphenylcarbizide method (Coggins & Hiscocks 1978). Between 1g and 40g of leachwater, depending on the Cr^{6+} concentration, was weighed into a 50mL flask. 0.5mL of diphenylcarbizide was added then the flask was topped up to 50g of total liquid with 0.5N sulfuric acid. In acidic solution, Cr^{6+} undergoes a colour reaction with diphenylcarbizide to produce a purple solution which absorbs visible light in direct proportion to the Cr^{6+} concentration. The colour solutions were analyzed for light absorption in a spectrophotometer at 540nm, with at least three calibration standards.

Experimental error for measuring $[Cr^{6+}]$ by the diphenylcarbizide method was estimated to be $0.03M_i^{expt} + 0.005$mg - *i.e.*, 3% of the measured value plus a minimum error of 5 μg. This reflects error in spectrophotometer calibration, some instability in colour absorption and in spectrophotometer readings, and accuracy of the spectrophotometer digital readout. This error estimate was used to calculate χ^2 by equation 9.

Fixation was measured independently during the leaching experiments by storing extra samples in Ziploc bags with wet paper towels to help prevent evaporation. Slices of the samples were removed with a razor blade, taking care to sample several annual rings to avoid over-selecting earlywood or latewood. The slice was place in a small centrifuge vial, which had a hole in the bottom to hold the sample in place but allow liquid to escape. This vial was nested in a larger vial to collect the liquid after removal, as shown in figure 2.

3.1 Initial measurement of k and D

To measure the reaction constant and diffusion coefficients, for Cr^{6+} in red pine, 21mm cubic samples were coated on 4 sides to restrict diffusion to the radial, tangential, or longitudinal direction and allow leaching from opposing faces. Samples were pressure treated with 0.90% CCA-C with uptakes between 170% and 210% of dry sample weight, corresponding to CCA retentions of $6 - 6.4kg/m^3$. The individual uptake was input into the model for each sample when computing leaching quantities. Measurements of [Cr^{6+}] were made for radial, tangential, and longitudinal leaching at 23^oC and radial leaching at 13^oC. Samples were also taken to analyze for Cr, Cu, and As by ICP but those results are not discussed in this paper. Measurements were taken at t=0.26, 1.35, 2.3, 3.01, 4.13, 5.05, 6.07, 7.0, and 8.9 days, and the water replaced after all measurements except at t=0.80 days.

3.2 Effect of sample size

Samples were cut with a longitudinal cross-section of 20mm by 20mm, with lengths of 21mm and 42mm in the longitudinal direction. For each length, one set of samples was coated on 4 sides and one set coated on 5 sides, such as to restrict diffusion to the longitudinal direction. Thus there were 4 different treatment groups, with 3 replicates for each treatment as summarized in table 1

Group	Length	Number of open faces
A	21mm	2
B	21mm	1
C	42mm	2
D	42mm	1

Table 1: Sample treatments for varying length experiment

These samples were CCA-treated as in section 3.1 and leached continuously starting at t=0 days with [Cr6] measurements taken at t=0.10, 0.94, 1.4, 1.9, 3.0, 3.9, 5.0, 5.9, 7.2, 8.3, 10.4, 11.2, and 13.2 days.

3.3 Intermittent leaching test

20mm red pine samples were coated to allow radial leaching from 2 opposing sides. Samples were treated as in section 3.1 and exposed to the leaching scenario detailed in table 2. At each time listed, the samples were exposed to the conditions described on that row of table 2 until the next time. Whenever the samples were not being leached, they were sealed in a Ziploc bag to reduce evaporation. When the temperature was changed at $t = 3.02$ days, the samples were placed in water already equilibrated to 13^oC to ensure a rapid temperature change within the samples. The concentration of Cr^{6+} in the leachate was measured at the end of each period of leaching.

Time (days)	T(^{o}C) (after this time)	Leaching? (after this time)
0	23	N
0.80	23	Y
1.39	23	N
1.76	23	Y
2.30	23	N
3.02	13	Y
4.14	13	N
6.07	13	Y
7.03	23	N
8.51	23	Y
8.91	23	N

Table 2: Intermittent Leaching Schedule

4 Results and discussion

4.1 Determination of k and D

Leaching experiments were carried out in the radial, tangential, and longitudinal directions at 23C and in the radial direction at 13C. Figures 3 and 4 show the first order reaction constants and diffusion coefficients calculated by the model. In each group, 1 of the 5 replicates was taken from a sapstained pole; in each case this replicate had the highest reaction rate constant. Average values and standard deviations of k and D for the non-sapstained samples of each group are also summarized in table 3.

The reaction rate constant has been measured in the absence of leaching directly by expressing unfixed solution from the samples by Kazi, Cooper & Chen (2000) to be $2.3 \times 10^{-6} s^{-1}$ for 1% CCA-C and $1.5 \times 10^{-6} s^{-1}$ for 3% CCA-C at 22^{o}C. The reaction constants calculated from the radial and tangential leaching experiments at 23^{o}C are in agreement with these fixation experiments. The model of longitudinal leaching, however, produced significantly higher reaction coefficients. This may be due to reaction processes more complex than first-order reaction as assumed by the model, which are significant under such extreme leaching conditions on such a small sample. In section 4.2, the leaching model is applied to longer samples leaching in the longitudinal and this effect is seen to decrease with longer samples where the amount of Cr^{6+} leached relative to the initial retention is less.

It should be noted that during this experiment room temperature was checked several times and found to be 23 ± 1^oC, but it was not continuously monitored. A decrease in temperature of 1^oC would, according to published activation energies for Cr^{6+} fixation, decrease the reaction rate by 12%. A measurement of reaction rate or activation energy more accurate than this would require temperature control with a tolerance less than 1^oC.

Sample	D ($\times 10^{-7} cm^2/s$)	k ($\times 10^{-6} s^{-1}$)
Radial 23C	1.70 ± 0.6	2.25 ± 0.3
Tangential 23C	1.55 ± 0.2	2.90 ± 0.6
Longitudinal 23C	41 ± 11	6.20 ± 0.7
Radial 13C	2.0 ± 0.4	1.30 ± 0.3
Kazi et al. (2000) 1% CCA, 22^oC		2.3
Kazi et al. (2000) 3% CCA, 22^oC		1.5

Table 3: Best fit values of k and D

4.2 Effect of sample size

Figure 6 shows experimental and analytically modeled Cr^{6+} longitudinal leaching rate for the 3 replicates of 4 different sample geometries in this experiment. The model fits experimental leaching data closely except for the first point, which is typical of all experiments. In previous experiments where the samples were not rinsed with water after treatment but before leaching, the first leachate concentration was higher than the model prediction. In this experiment, all samples were rinsed with water before leaching, and the first data points are equal or lower than the model prediction for initial leaching. It appears that this initial effect is due to excess CCA on the surface and in exposed lumens near the surface being rinsed away. Lumens cut open at the surface could release CCA much more readily than intact lumens, and could be completely depleted by the rinsing.

The samples exposed on 2 sides initially leached twice as much as those exposed on 1

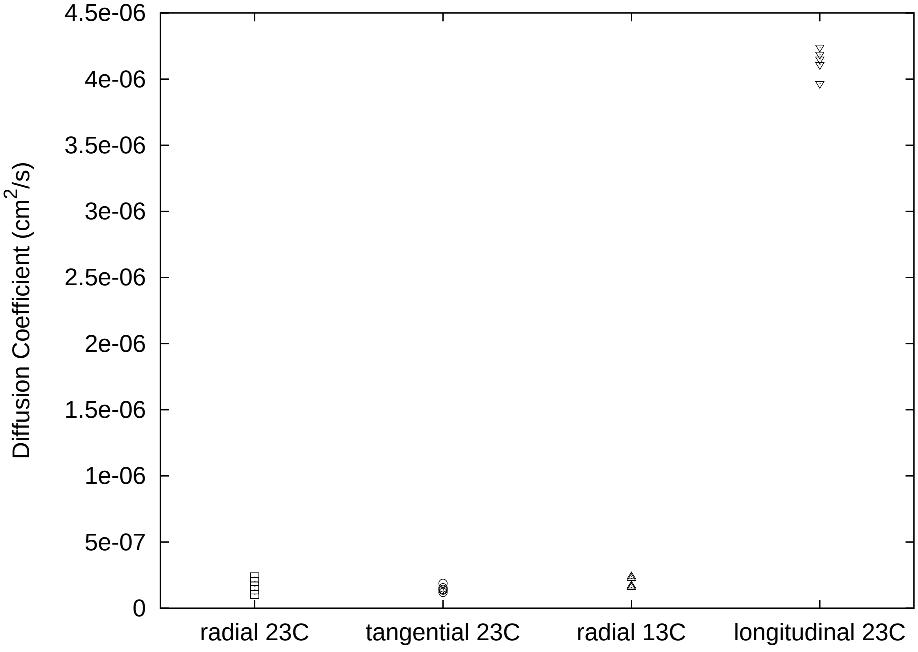

Figure 3: Diffusion Coefficients

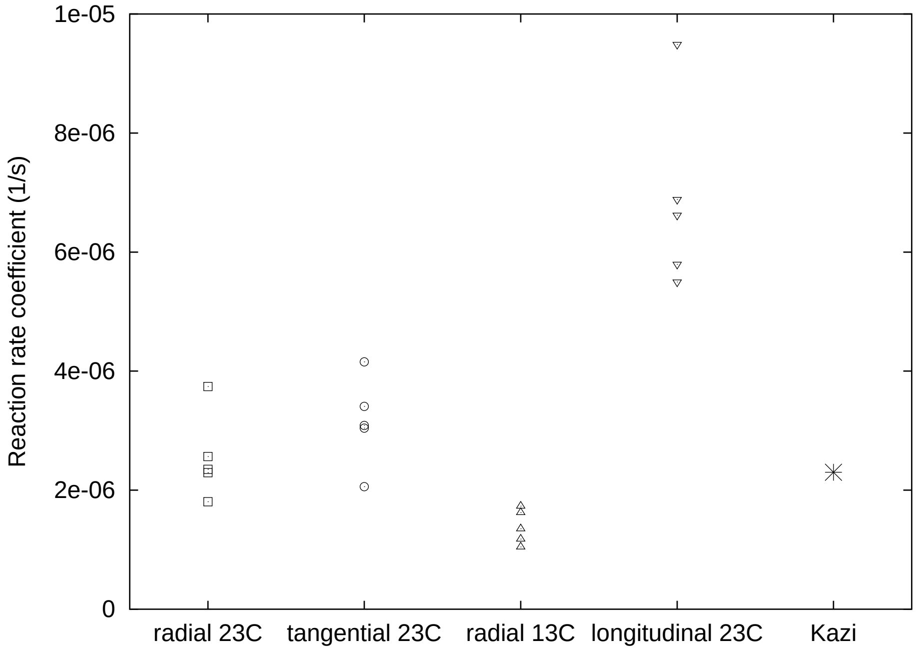

Figure 4: Reaction rate coefficients

side, but this difference is reduced as Cr^{6+} is depleted from the centre of the samples. This effect is seen in theoretical leaching calculations, which are demonstrated in figure 5. The 21mm samples exposed on both sides are actually depleted significantly enough that leaching goes to zero before any of the other geometries.

The values of k and D resulting from least squares fits are shown in figures 7 and 8. The 21mm samples leaching from 2 ends show a much greater variation and standard error than the other samples. This may be caused by collecting only 5 leaching data points before the leaching became unmeasurable, or by complex reaction and diffusion processes which become significant during such significant depletion which are not accounted for by the first order reaction and single component diffusion of the model. Thus, the results from these 21mm samples leaching longitudinally from 2 ends should be considered unreliable, and longer samples should be used to measure k and D from longitudinal leaching experiments. The other samples show a general trend towards reaction constants closer to that calculated in the pure fixation experiment by Kazi et al. (2000) as the proportion of total chromium leached becomes less. That is, while the model fits the leaching data points well for all sample geometries, the modeled reaction constant matches the pure fixation experiment best for the 42mm samples leaching on one side and worst for the 21mm samples leaching from two sides. The fixation experiment was performed using the centrifuge method described in section 3, and the results are shown as a semi-log plot in figure 9. This plot does not appear to be a good straight line as expected for first order fixation. This may be an experimental artifact caused by drying during fixation, or possibly by the small sample volumes extracted by the centrifuge. However, the reaction constant calculated from the best fit line matches the published value by Kazi et al. (2000). Further work will be required to compare the centrifuge expressing method to the traditional hydraulic press method.

The modeled diffusion coefficient is relatively constant for all the sample geometries tested, but again with greater variation and standard error for the 21mm samples leaching from both ends.

4.3 Model demonstration and testing

In order to predict Cr^{6+} leachate concentration at one particular point in time, it is necessary to calculate the internal Cr^{6+} and fixed Cr concentration everywhere within the sample continuously from the initial treatment to the time when leachate concentration is needed. Figure 10 shows the calculated concentration profiles for a 21mm sample treated at $t = 0$ and allowed to fix until $t = 1$ day, then leached in the radial direction from 2 exposed faces until $t = 2$ days, then removed from the water until fixation is complete. From $t = 0$ to $t = 1$

(figure 10a), the total Cr retention is 100% everywhere in the sample. Cr^{6+} concentration is constant an decreasing, fixed Cr is constant and increasing. At $t = 1$ the sample is immersed (figure 10b), and immediately the Cr^{6+} concentration at the exposed surfaces drops to zero, as specified by the boundary condition. During leaching the region of Cr^{6+} depletion extends toward the centre of the sample, and fixed Cr continues increasing in the interior but remains unchanged at the surfaces, creating a retention gradient. At $t = 2$ the sample is removed from the leachwater (figure 10c), but fixation is still affected by the gradients created during leaching. The mobile Cr^{6+} begins redistributing to reduce its concentration gradient, but the rate of fixation near the surface is still lessened because of reduced Cr^{6+} concentration, further increasing the difference in fixed Cr between the centre and surfaces of the sample. As time passes the mobile Cr-VI finally redistributes itself to approximately constant concentration and fixation rate becomes constant throughout the sample, but the gradient in fixed Cr remains. As fixation nears completion (figure 10d), fixed Cr and total Cr become the same as $[Cr^{6+}]$ goes to zero.

The predictive ability of the model was tested under the more complex intermittent leaching scenario with changing temperature described in section 3.3. Modeled values were calculated using reaction constants and diffusion coefficients and standard errors summarized in table 3, which were obtained from modeling the leaching experiment of section 3.1. Maximum leaching quantities were calculated from minimum k and maximum D using one standard error ($k - \Delta k$, $D + \Delta D$), minimum leaching leaching quantities were calculated using maximum k and minimum D ($k + \Delta k$, $D - \Delta D$). The computed results are compared to experimental results in figure 11. As with the leaching experiments of section 4.1, the first time the sample is leached it releases somewhat less Cr^{6+} than predicted by the model, but the difference is less than 25%. Good agreement is seen for all subsequent leaching tests, although the range of uncertainty in the calculations is as much as 45% of the mean value.

5 Conclusion

A numerical diffusion-reaction model was used to calculate the first order reaction constant and diffusion coefficient of Cr^{6+} 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 able to accurately represent Cr^{6+} leaching rates observed in the leaching experiment. Reaction constants calculated by the model for transverse diffusion at room temperature were in agreement with published values measured directly from fixation experiments. For longitudinal diffusion, better agreement was found for samples with less overall depletion, *i.e.*, longer samples with only one side exposed to leaching. Diffusion coefficients for Cr^{6+} in red pine were found to be least in the tangential direction and greatest in the longitudinal, with a tangential:radial:longitudinal ratio of 1:1.1:26.

Since this is a physical model, based on what is actually occurring within the wood, it can used to make predictions for arbitrary intermittent conditions not tested in the lab. This was checked against a leaching experiment where samples were immersed and removed from water 5 times and the temperature changed twice, and the model successfully predicted Cr^{6+} leaching quantities over the 9-day duration of the experiment. This model can in the same way be applied to other intermittent leaching scenarios for many different sized samples.

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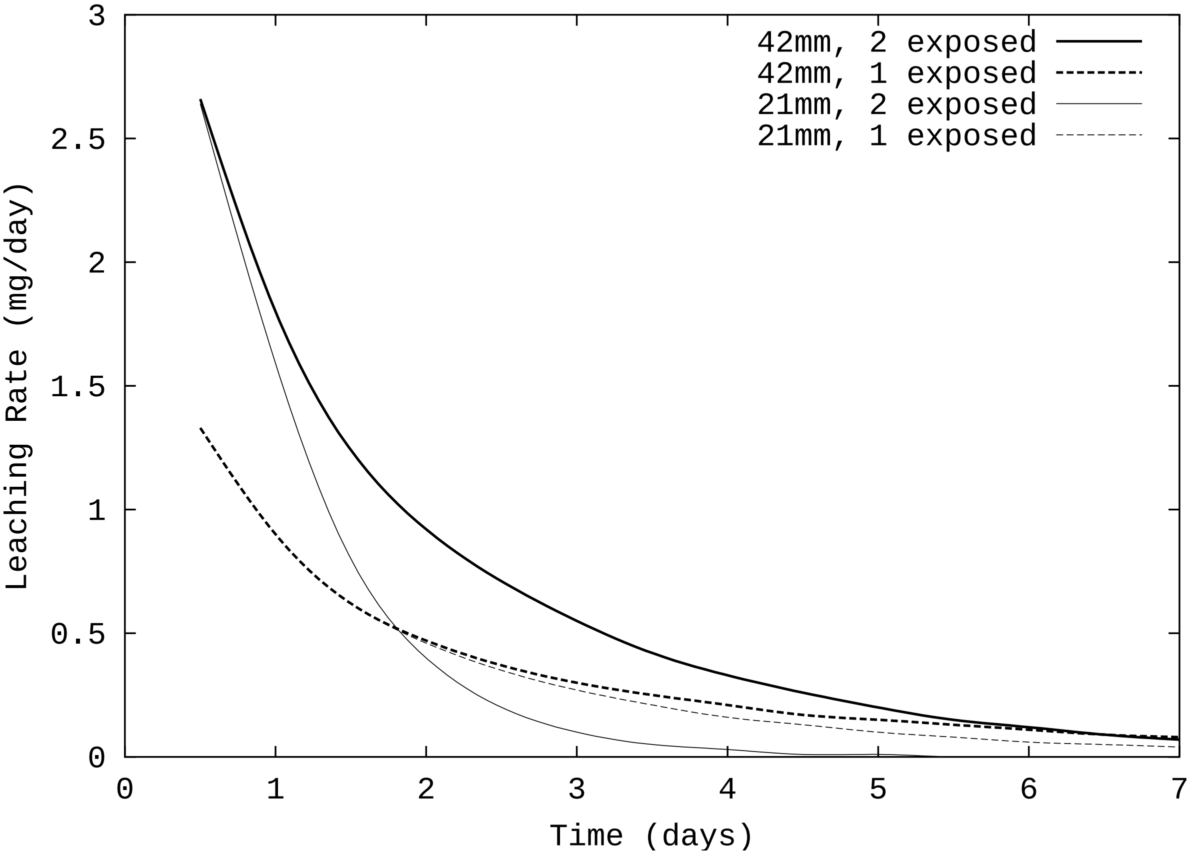
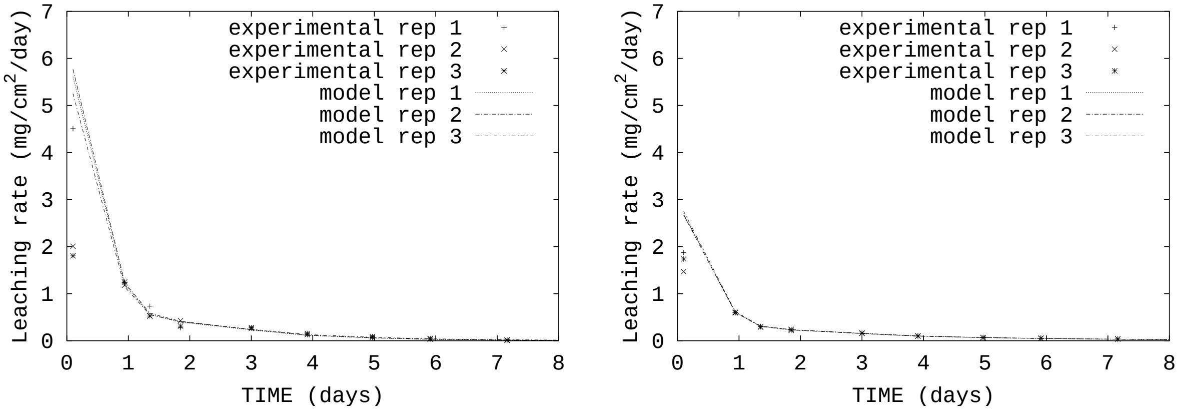
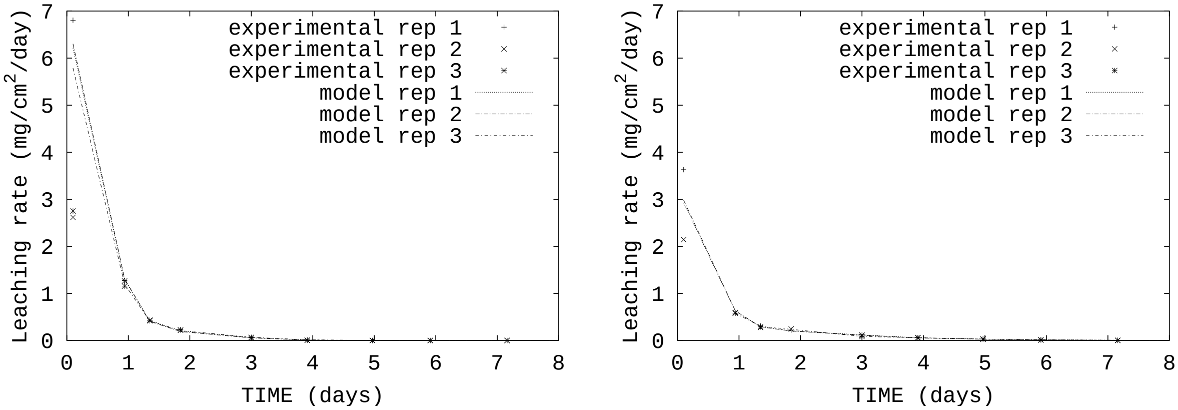


Figure 5: Theoretical leaching calculation for several different sample geometries



(a) 42mm, 2 ends exposed

(b) 42mm, 1 end exposed



(c) 21mm, 2 ends exposed

(d) 21mm, 1 end exposed

Figure 6: Experimental and modeled longitudinal leaching rate for 3 replicates of 4 sample geometries

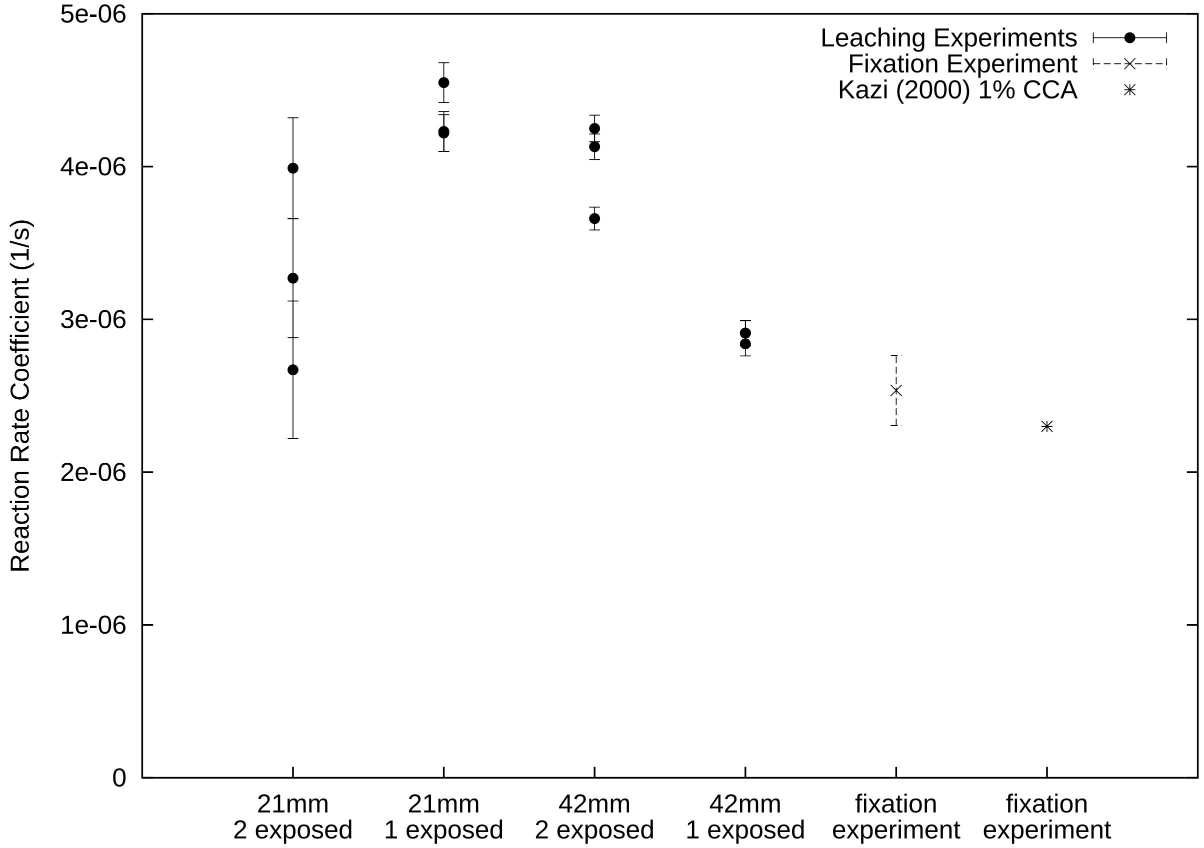


Figure 7: Reaction rate coefficient, calculated from leaching experiments on 4 different block geometries and from a pure fixation experiment

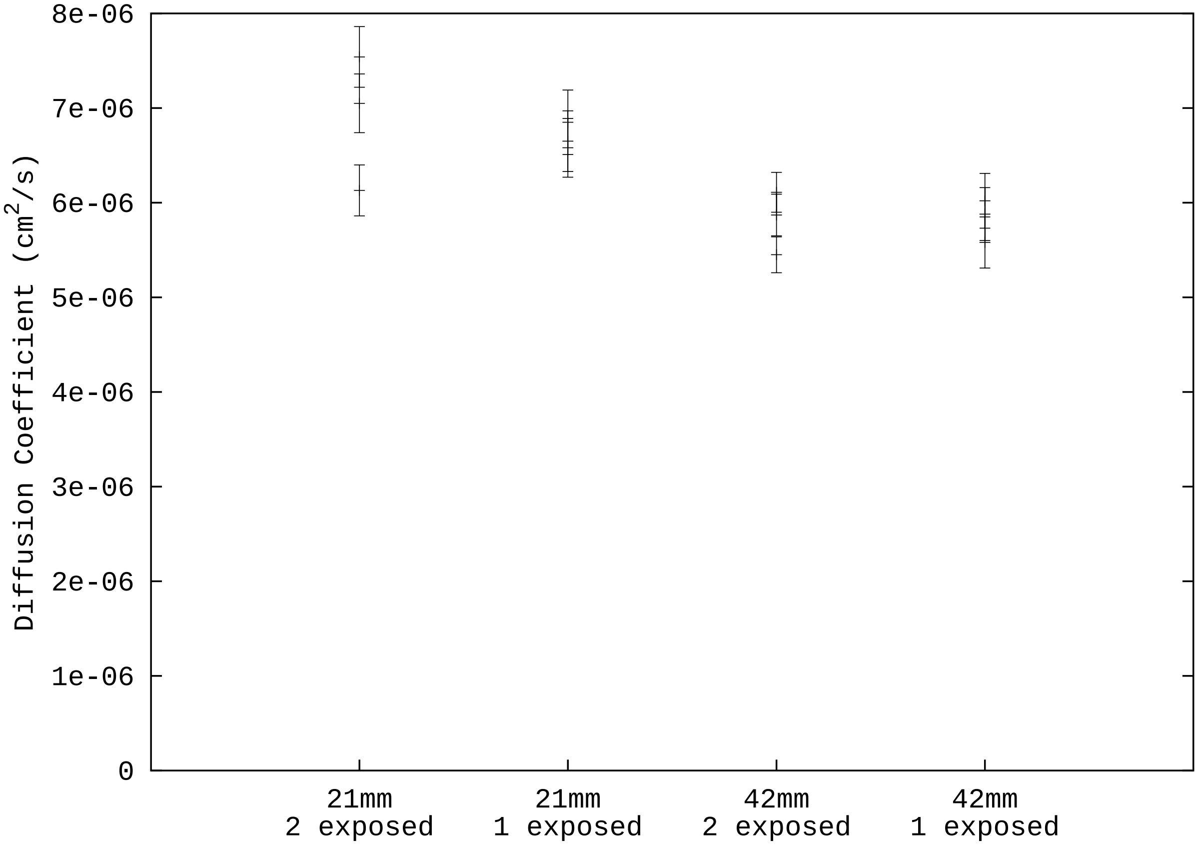


Figure 8: Diffusion coefficient, calculated from leaching experiments on 4 different sample geometries

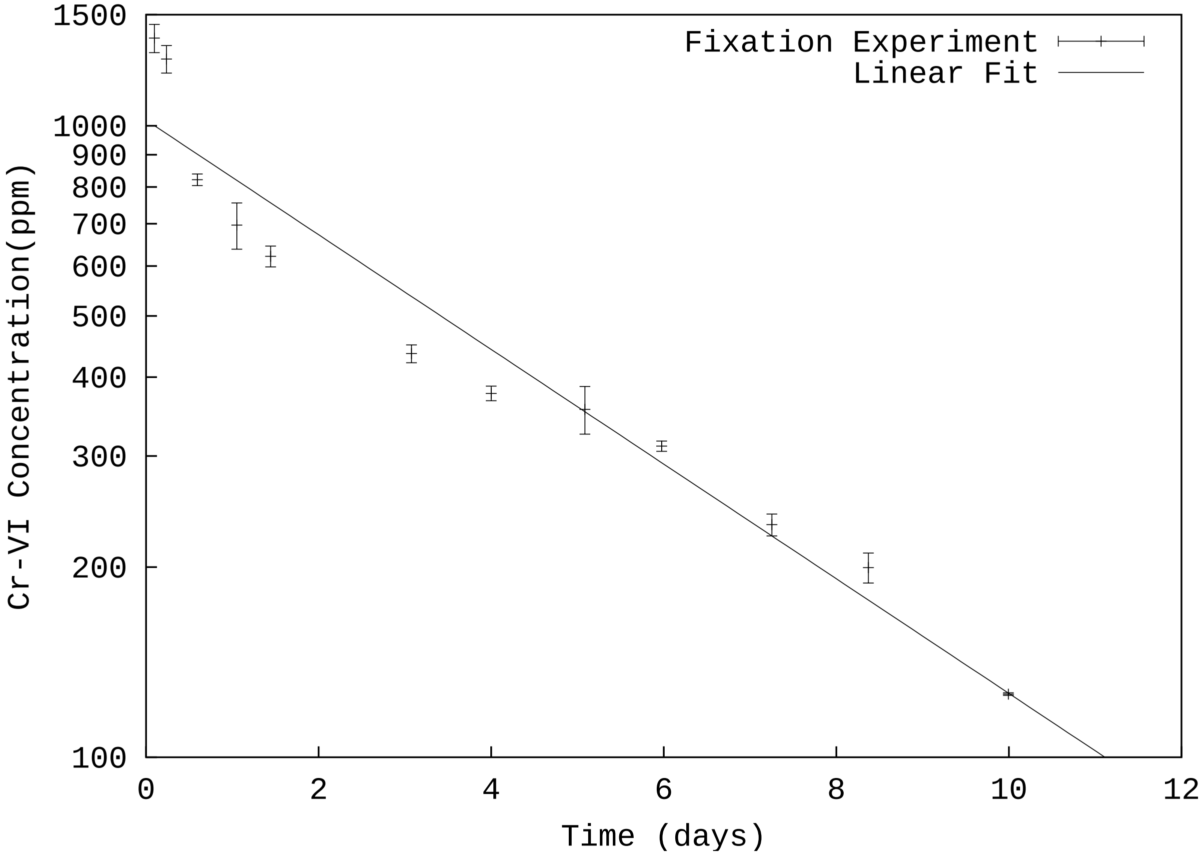
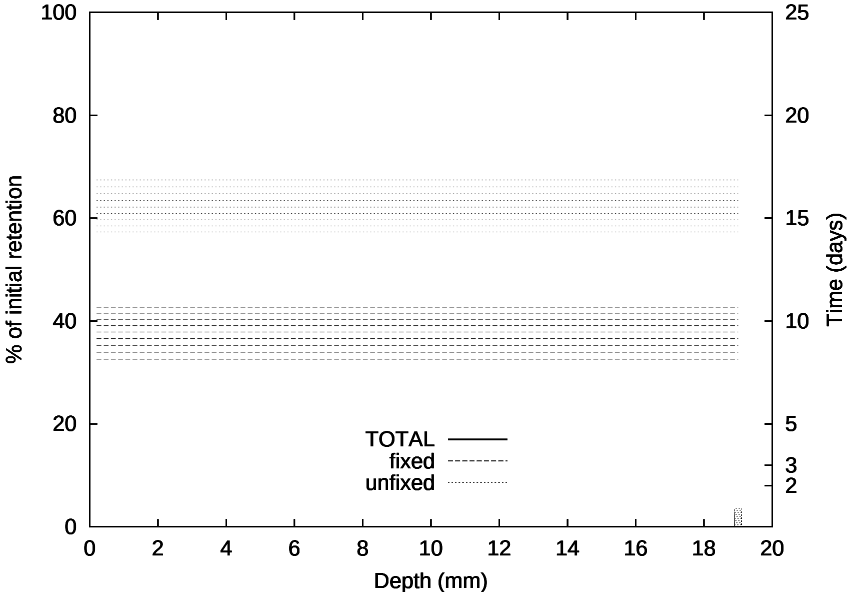
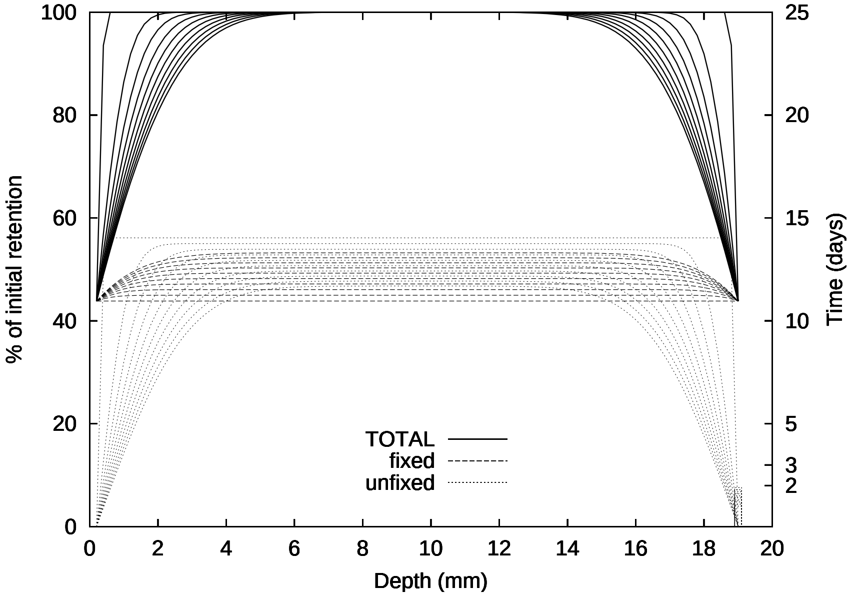


Figure 9: Pure fixation experiment using centrifuge expressing method

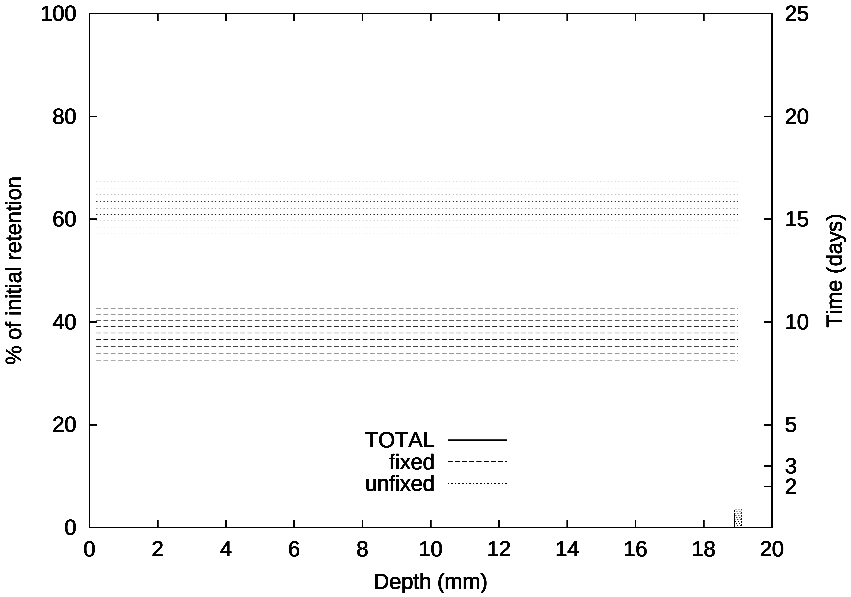


(a) t=0-1 days, no leaching. Total Cr is 100% of original retention, Cr^{6+} is decreasing from 67% to 58% of the total, fixed Cr is increasing from 33% to 42%.

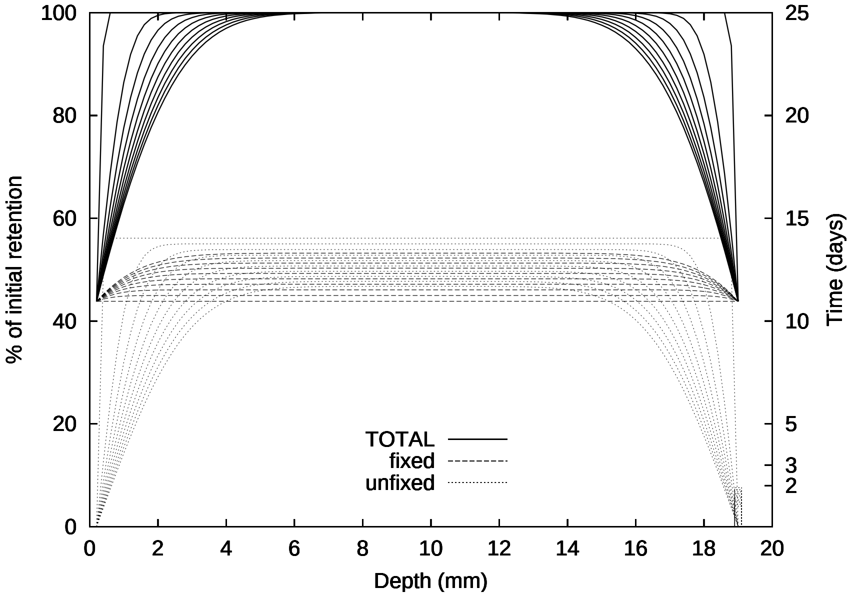


(b) t=1-2 days, leaching. Total Cr is still 100% near centre, but depletion moves inward with time. Cr^{6+} is completely depleted right at the surface, as required by the boundary condition. Fixed Cr remains constant at the surface, and increases towards the centre.

Figure 10: Model prediction of internal concentration profiles for a sample being leached between 1 and 2 days, just undergoing fixation the rest of the time.



(c) t=0-1 days, no leaching. Total Cr is 100% of original retention, Cr^{6+} is decreasing from 67% to 58% of the total, fixed Cr is increasing from 33% to 42%.



(d) t=1-2 days, leaching. Total Cr is still 100% near centre, but depletion moves inward with time. Cr^{6+} is completely depleted right at the surface, as required by the boundary condition. Fixed Cr remains constant at the surface, and increases towards the centre.

Figure 10: Model prediction of internal concentration profiles for a sample being leached between 1 and 2 days, just undergoing fixation the rest of the time.

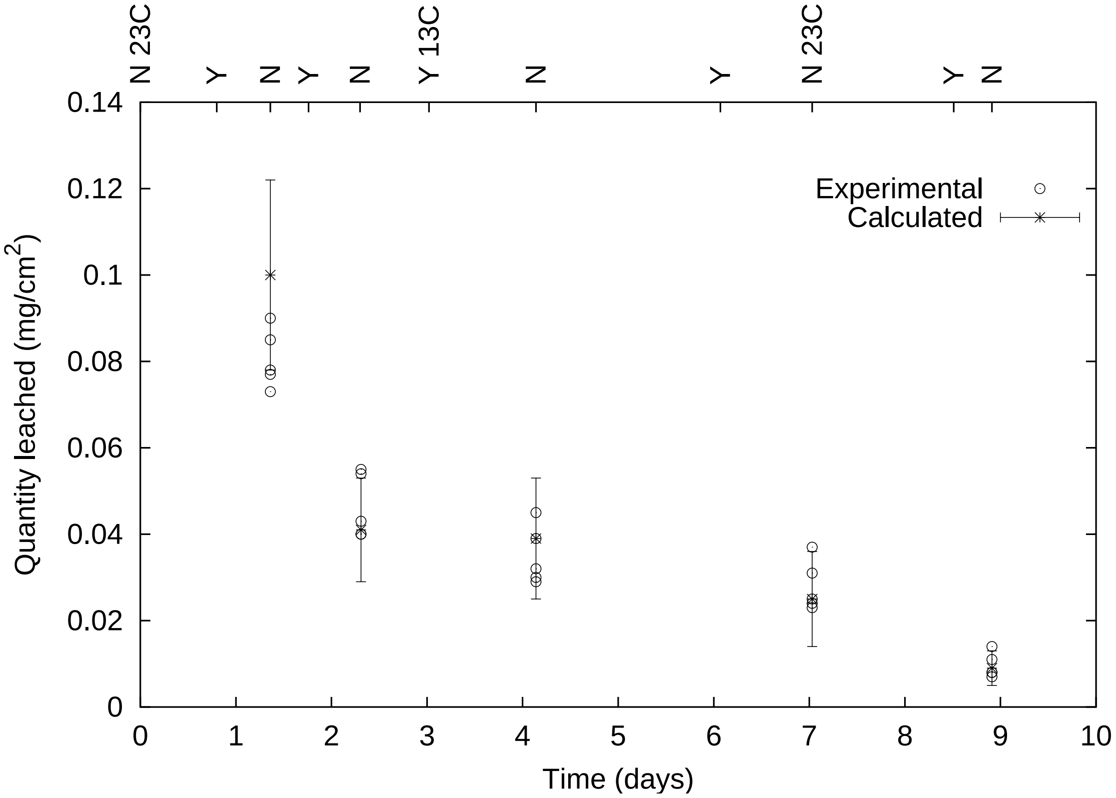


Figure 11: Intermittent leaching test. Along the top of the graph, "Y" indicates that the samples were immersed in water at this time and "N" indicates that they were removed at this time. The temperature indicated is from this time to the next time a temperature change is indicated.