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# RELEASE OF IRON FROM BONDING NAILS IN TORRENT CONTROL CHECK DAMS AND ITS EFFECT ON WOOD DECOMPOSITION BY *FOMITOPSIS PINICOLA*

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## ABSTRACT

Wooden check dams for torrent control consist of logs nailed with steel fastenings, which are subject to corrosion. We studied the distribution of iron adjacent to bonding nails within the wood by energy dispersive x-ray microanalysis (EDX) and atom emission spectroscopy (AES). The effect of iron on wood decomposition was tested using the brown rot fungus *Fomitopsis pinicola*. The zone of iron accumulation surrounding the nails exceeded 10 cm in most cases. In the wood adjacent to the nail surface, an iron concentration of 0,5-6% of the dry mass was found. In the wood decomposition experiment, iron had an inhibitory effect on decay at concentrations above 0,5%. At lower concentrations, wood decay was significantly enhanced. The implications of these findings for constructive improvements of crib dams and further research needs are discussed.

KEY WORDS: crib dams, nails, iron, *Fomitopsis pinicola*, wood decay

## INTRODUCTION

In torrent control, wooden check dams generally rely considerably on metal fastenings for structural integrity. Usually, the logs are nailed with reinforcing steel (Rickli 1997). Those steel

fastenings are subject to a particular type of corrosion, called crevice corrosion (Baker 1974). The corrosion products of the steel nails may considerably alter the chemical characteristics of the surrounding wood as well as its strength. In an experiment the tensile strength of wood samples in contact with rusting iron during nine months decreased about 50%, which is caused by the decomposition of both hemicellulose and cellulose (Marian and Wissing 1960).

Moreover, wood inhabiting fungi use metals and, in particular, iron present in the wood to degrade it and for maintaining their metabolism (Assmann et al. 2003, Goodell 2003). The availability of ferrous iron in an oxidizing environment is limited by the extreme insolubility of Fe $(OH)_3$ (Winkelmann and Winge 1994). In general, decay fungi produce high affinity chelating compounds to scavenge metal ions for their metabolic needs (Qian et al. 2002, Rodriguez et al. 2003).

The limited size of pores in the intact cell walls does not allow enzymes, including cellulase, to penetrate. Therefore, brown rot fungi rely on non-enzymatic oxidative systems (Henry 2003) and use Fenton type mechanisms in the early stages of wood cell wall depolymerization involving the participation of iron chelators (Goodell et al. 1997, Goodell and Jellison 1998, Rodriguez et al. 2003). To carry out the Fenton reaction, the fungi have developed different systems to reduce Fe (III) (Goodell 2003, Wang and Gao 2003, Shimokawa et al. 2004).

Based on these facts it is hypothesized that an increasing iron concentration in wood enhances decomposition of wood by brown rotting fungi. Investigations on wood decay by fungi related to iron are rare and the findings are inconsistent. A positive effect on the growth of several decay fungi in cultures was reported by Negrutzkiy et al. (1998). However, Ruddick and Kundzewicz (1991) did not observe an increase in decay at higher amounts of iron. No information on iron concentrations in the vicinity of steel nails of in-service wood could be found in literature.

The aim of this study was to analyse the distribution of iron adjacent to bonding steel nails of wooden check dams. In addition, the influence of iron on the wood degrading activity of the brown rot fungus *Fomitopsis pinicola* was tested experimentally. This species was found to be the most common brown-rot fungus on wooden check dams made of logs of *Picea abies* and *Abies alba* in Switzerland (Nötzli 2002).

## MATERIAL AND METHODS

### Preparation of the source material

The iron content was analyzed around bonding steel nails of fifteen-year-old wooden check dams of a catchment in the canton of Schwyz (Langenrainbach, Vorderthal) situated on the northern slopes of the Swiss Alps. The check dams were heavily damaged due to severe sliding processes in the area and, therefore, the destructive investigation was admissible. Ten check dams – all made of norway spruce (*Picea abies* L. Karst) – were selected for detailed analysis. One log section of 50 cm around a steel nail conjunction was taken from each of the 10 different check dams. The diameter of the logs varied between 25 and 40 cm. They were either part of the lateral parts of the check dams (wings) or of its longitudinal protection structure, which were built in order to stabilise the lateral slopes of the channel. All logs were split longitudinally near the plane of the bonding steel nail and the latter was removed (Fig. 1). With a band saw, a series of wood samples of the dimension 10x10x50 mm was taken along the grain of all 10 logs keeping a minimum space of 5 cm from the surface of the log and from its core (Fig. 2).

Six samples were taken each at intervals of 5, 15, 25, 35, 45, and 95 mm, respectively, measured between the original nail surface and the centres of the samples (Fig. 2). From seven randomly selected logs analoguous sample series were prepared perpendicular to the grain direction. Consequently, 17 sample series consisting of six samples each were produced.


*Fig. 1: Log after splitting along the steel fastening*

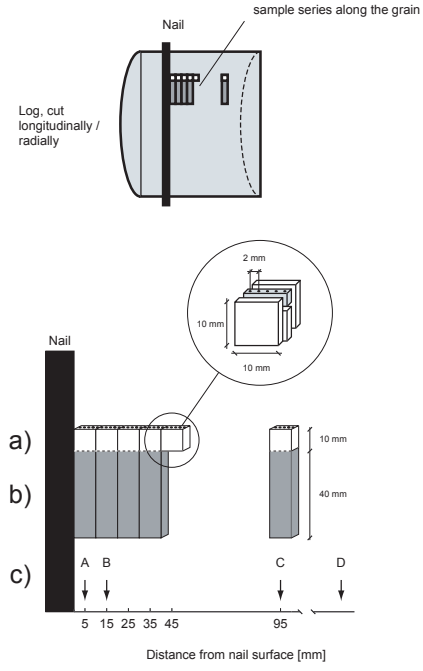


*Fig. 2: Above: scheme of a nail in a log and sample series longitudinal to the grain*
*Below: Detail of sample series:*
*a) Sample for EDX-analysis (white). Scaled up: Cutting of samples and arrangement of spot measurements*
*b) Samples for AES-analysis (grey): Analysed samples (specimens in a distance of 45 mm were not analysed)*
*c) Distances of which the iron contents (AES-analysis) were used for the decomposition experiment. Distance D represents an unknown iron concentration in a greater distance than 95 mm*

## Detection of iron in wood

### *Energy Dispersive X-ray Microanalysis (EDX)*

The samples of four series along and of two series perpendicular to the grain direction were dried at 70°C during 72 h. Of each sample, a small specimen (3x10x10 mm) with a smooth surface tangential to the grain direction was prepared using a razor blade (Fig. 2 below, a). Subsequently, all specimens were cleaned with compressed air. The EDX analysis was conducted with a low-temperature scanning electron microscope (Philips SEM 515). Preparation and cooling of the specimens followed Frey et al ( 2000). The specimens were sputter-coated with platinum (coating thickness 8 nm). On the tangential cut surface spot measurements were carried out at intervals of 2 mm at a magnification of x 300. All spectra were acquired for 60 s (live time) and a dead time of about 30%. Therefore, at the distance of 0 to 50 mm from the nail surface, series of measurements at intervals of 2 mm were performed (Fig. 2 below, a). The investigation of the area between 90 and 100 mm off the nail surface was restricted to two sample series along and one sample series perpendicular to the grain direction. For each measurement, a specimen surface of about 290 x 290 µm was analysed. Thus, an average measurement included 5 to 10 xylem cells. The spectra were processed using the Voyager software package (Noran Instruments Inc., Middleton, WI) for automatic background subtraction which calculates net counts of elements of interest (Brunner and Frey 2000, Frey et al. 2000, Cosio et al. 2005). Data generated by the X-ray micro analyzer are at best semi-quantitative (Van Steveninck and Van Steveninck 1991). The values were not converted to concentrations due to the difficulties associated with obtaining quantitative results from specimens of undefined thickness. Furthermore, the counts of non-standardized specimens may be subject of variance, depending on the angle of the specimens surface and the distance of the detector. Therefore, in place of the net counts of iron, the ratio of the net counts of iron and carbon (Fe/C) was taken. The detection limit for iron was set at 50 counts within 60 s. In order to check for possible iron contamination due to the use of a steel razor blade, 25 measurements on specimens of freshly cut norway spruce were analogously performed.

### *Atomic Emission Spectroscopy (AES)*

Based on the results of the EDX analysis the samples at the intervals 5, 15, 25, 35, and 95 mm of the nail surface of all series (10 along and 7 perpendicular to the grain direction) were subjected to quantitative spectroscopic iron analysis (Fig. 2, below, b). The dimension of the samples was 10x10x40 mm. After drying at 70°C during 72 h and cleaning with compressed air, they were grinded in a vibration-grinding mill (Retsch MM 2000) during 240 s at a frequency of 30 Hz. The grinding vessel and –balls were of zircon-oxide (vessel volume: 25 ml, ball diameter: 20 mm). Subsequently, the samples were dried again at 70°C during 24 h. The iron content of the samples was measured with an inductively coupled plasma atomic-emission spectrometer (IPC-AES Optima 3000, Perkin Elmer). Five control samples of freshly cut norway spruce were analogously prepared in the same way and checked for possible iron contamination due to sample preparation techniques.

## Wood decomposition depending on the iron concentration

### *Fungal cultures*

Heterokaryotic cultures of *Fomitopsis pinicola* (Fr.) Karst. (strain 011002.1) were produced in Petri dishes (diameter: 145 mm, height: 20 mm) on malt agar (20 g/l malt extract, 15 g/l agar, 1000 ml demin. $H_2O$) and incubated at room temperature during 10 days. After this period the cultures had a diameter of about 80 mm.

### *Preparation of $FeCl_3$ solutions*

The concentration *c* of a $FeCl_3$ solution that results in a distinct iron concentration *k* in the wood was calculated according to equation [1].

$$c = k \cdot \frac{\rho_L}{u \cdot M \cdot (w_{(Fe)} - k)} \; [mol/l]$$

c: Required concentration of the $FeCl_3$-solution [mol/l]

k: Iron-content of wood [g/g], from AES-Analyse

ρL: Density of the solution [g/l] ≈ 1000 g/l

u: Solution-content in % of dry mass (wood) ≈ 190%

w(Fe): Proportion of Fe in $FeCl_3$ (water-free) [g/g] ≈ 0.34

M: Mol mass of $FeCl_3$ [g/mol]

The maximum error that is made by considering the density $\rho_L$ of the $FeCl_3$ solution as 1000 g/l is about 2.5% (in series A with $c_A$ = 0.2 mol/l) and was ignored.

The iron concentrations of the samples after soaking were calculated after transformation of equation [1] and under consideration of the absorbed $FeCl_3$ solution. It was further arithmetically checked if the iron concentration within the wood blocks of the series A, B, and C corresponded to those measured with AES at the intervals 5, 15, and 95 mm of the nail surface, respectively. The pH of each solution was determined with an universal colour indicator (Merck, Darmstadt, D).

### *Wood sample preparation and soaking*

Following the concept of Jellison et al. (1997a), the decomposition experiment was conducted with wood samples soaked in $FeCl_3$-solution of different concentrations. The samples were prepared from the same scantling (80x80 mm; 10 m off the base cut) of an 80-year old Norway spruce. The length of the samples along the grain direction was fixed to 10 mm to guarantee good soaking. All samples (80x80x10 mm) were dried at 103°C until weight equilibrium (DIN 52183 1977) and the dry weight was determined with an accuracy of 0.001 g. Subsequently, the samples were soaked during 88 h under vacuum conditions and continuous stirring. The vacuum was interrupted for 30 min every 24 h to improve the soaking process.

Five different $FeCl_3$ concentrations (A: 0.2, B: 0.05, C: 0.01, D: 0.001, E: 0.000 mol/l) were applied to 23 samples each. The solutions were prepared in distilled water with dehydrated $FeCl_3$. The concentrations of the series A, B, and C approximately corresponded to the average total amount of iron resulting from the AES analysis at the intervals 5, 15, and 95 mm of the nail surface along the grain direction, respectively (Fig. 2, below, c). Series D represented an unknown larger distance of the nail surface, and series E was the zero control.

After the soaking process, the samples were drained, weighted and the amount of $FeCl_3$ absorbed was calculated. The samples were then dried at 70°C until the water content was set on about 80%. Subsequently, each sample was put directly on the mycelium of a Petri dish and sealed with Parafilm®. After an incubation time of 6 months at room temperature, the fungal mycelium was carefully removed from the surface of the samples that were then kiln dried and weighted again.

The loss of mass of the wood was calculated after equation [2].

$$MV = \frac{P_0 - P_1}{P_0} \cdot 100\ [\%]$$

whereas

$$P_0 = m_0 + m_L [g]$$

MV: Mass loss of sample [%]

$P_0$: Weight of sample before the experiment [g]

$P_1$: Weight of sample after the experiment [g]

$m_0$: Dry mass of sample before the experiment [g]

$m_L$: Absorbed mass of $FeCl_3$ [g]

***Statistical analysis***

The data were statistically analysed with non-parametric tests (Hollander and Wolfe 1973) of the software package R 2.0.0 (R Development Core Team 2004). In a first step a Kruskal-Wallis rank sum test was performed with the data of the AES analysis to test the null hypothesis that the iron concentrations are the same in each group (distances off the nail). The alternative hypothesis was that they differ in at least one location. Likewise, the data of the decomposition experiment were tested with the null hypothesis that the proportional mass loss through fungal decay was the same in each group (iron concentrations).

In a second step the pairwise Wilcoxon rank sum test was applied to calculate pairwise comparisons between group levels of the distances off the nail and the iron concentrations, respectively, considering the correction of Holm (1979) for multiple testing. Furthermore, this latter test design was applied to compare the iron concentrations of the AES analyses with those of the samples artificially soaked in corresponding $FeCl_3$ solutions.

## RESULTS

The EDX measurements indicated a strong decrease of the iron concentration in the wood (net count ratio of Fe/C) within only a few millimetres off the nail surface (Fig. 3). Along the grain direction high variation between the series was observed within the interval of 0 and 20 mm. From about 20 mm onwards, the measurements of the series were closely together. At the largest measurement distance of about 100 mm off the nail surface the iron concentration was still above the detection limit in one series. The distribution of the net counts (ratio Fe/C) of the series perpendicular to the grain direction was similar to the longitudinal one, however, with a considerably lower frequency (Fig. 3). The control measurements of the freshly cut Norway spruce only twice exceeded the detection limit with a net count ratio (Fe/C) of 0.01 each.

The iron concentrations measured by AES analyses confirmed the assumed distribution based on the EDX measurements. In all series, the highest iron values were detected in the samples 5 mm off the nail surface. Within this interval, the iron concentration varied from 0.5 to 6% of the dried mass with a median of 1.9% (Fig. 4a). From 5 mm onwards, a remarkable decrease of the iron concentration was observed. Nevertheless, along the grain direction still substantial iron contents were measured several centimetres off the nail surface. Comparable to the EDX analyses, the distribution of the iron concentrations perpendicular to the grain direction was similar to the longitudinal one, however, on a noticeably lower level (Fig. 4b). The control samples of the freshly cut Norway spruce had concentrations of about 10 ppm and correspond to values found in literature for this tree species very well (Young and Guinn 1966).

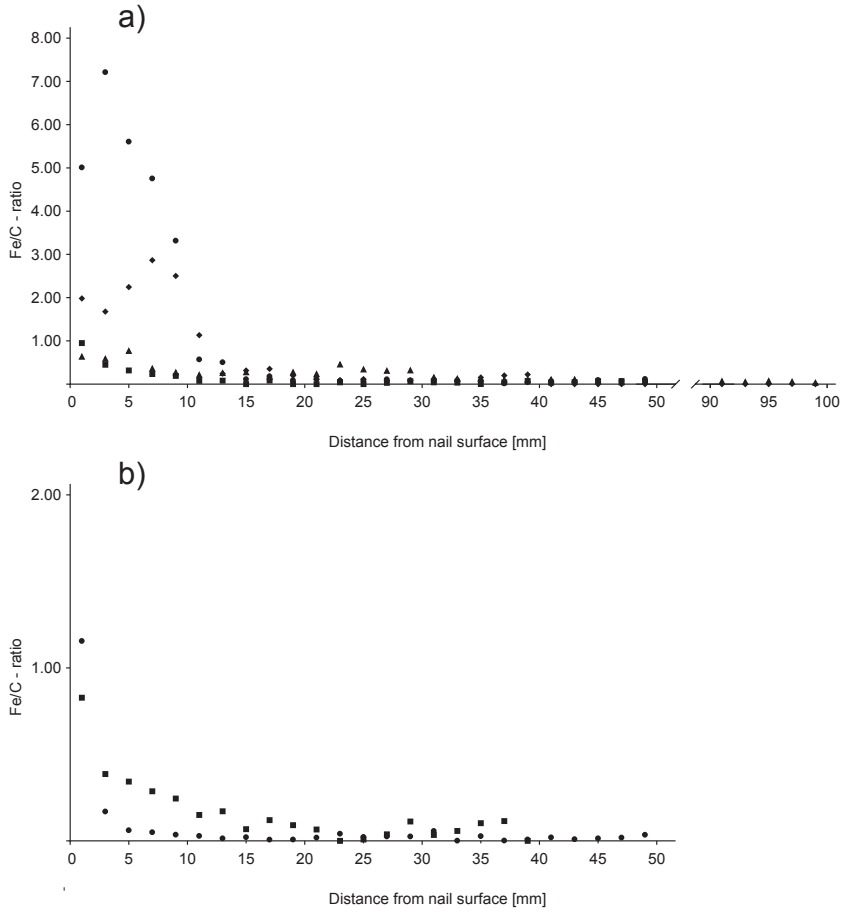


*Fig. 3: Iron content from EDX-analysis in function of the distance to the nail surface (Fe/C-Ratio). a) values of the four series along the grain. b) values of the two sample series perpendicular to the grain. Different symbols represent different sample series*

The distribution of the iron concentration significantly depended on the distance in the series along and perpendicular to the grain direction (Tab. 1). The pairwise comparison tests further revealed significant differences between the iron concentration at 5 mm off the nail surface and those of all other intervals as well as between the concentrations at 15 and 95 mm, respectively, again for all series along and perpendicular to the grain direction (Tab. 2).

*Tab. 1: AES-analysis: Kruskal-Wallis rank sum test. Data: iron by distance off the nail*

| grain direction | $\chi^2$ | df | p-value |
|---|---|---|---|
| along | 30.5187 | 4 | 3.838e-06 |
| perpendicular | 23.742 | 4 | 8.997e-05 |

*Tab. 2: AES-analysis: Pairwise comparisons using Wilcoxon rank sum test (p-value adjustment method: Holm). Data: iron by distance off the nail (along / perpendicular to the grain direction)*

| | 5 mm | 15 mm | 25 mm | 35 mm |
|---|---|---|---|---|
| 15 mm | 0.011 / 0.018 | -- | -- | -- |
| 25 mm | 0.002 / 0.006 | 0.424 / 0.286 | -- | -- |
| 35 mm | 0.002 / 0.018 | 0.164 / 0.230 | 0.424 / 0.572 | -- |
| 95 mm | 0.002 / 0.018 | 0.019 / 0.018 | 0.077 / 0.230 | 0.164 / 0.572 |

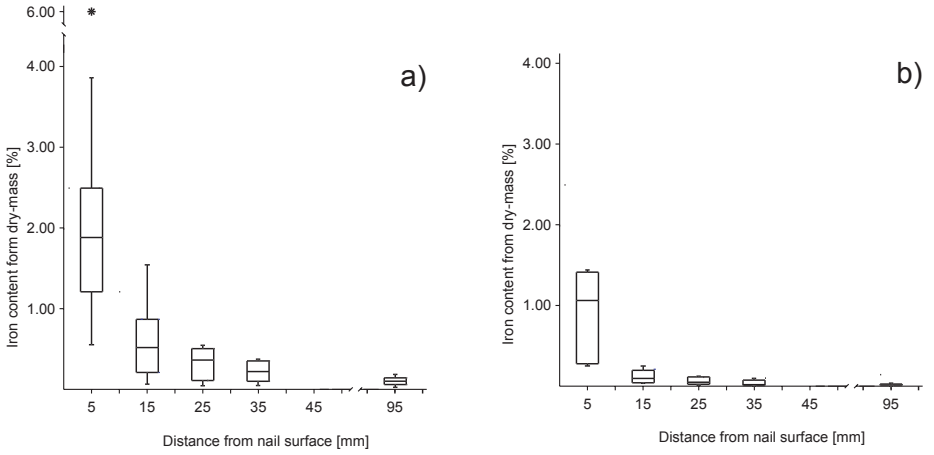


*Fig. 4: Iron content from AES-analysis in different distances from nail surface. a) along the grain (N = 10), b) perpendicular to the grain (N = 7). The box plots show the variation within and between the sample series*

## Decomposition experiment

### *Iron content of the wood samples*

Iron concentrations A, B, and C that were artificially adjusted in the wood blocks with different $FeCl_3$-solutions did not differ significantly from the corresponding values (AES analysis) along the grain direction at 5, 15, and 95 mm from the nail surface (Tab. 3).

*Tab. 3: Iron solution $FeCl_3$: Pairwise comparisons using Wilcoxon rank sum test (p-value adjustment method: Holm). Data: iron (AES) by iron ($FeCl_3$-solution). Bold values indicate non-significant differences*

| | 5 mm | 15 mm | 95 mm | A | B |
|---|---|---|---|---|---|
| 15 mm | 0.0075 | -- | -- | -- | -- |
| 95 mm | 0.0013 | 0.0127 | -- | -- | -- |
| A | **0.6167** | 7.9e-05 | 7.9e-05 | -- | -- |
| B | 7.9e-05 | **1.0000** | 7.9e-05 | 9.4e-08 | -- |
| C | 7.9e-05 | 0.0021 | **0.2601** | 9.4e-08 | 9.4e-08 |

## Fungal wood decomposition

After six months of incubation with *Fomitopsis pinicola*, a considerable variation of the loss of dry mass was observed between the different series (Tab. 4). The highest decomposition rate with a median of 20.5% was measured at an iron concentration of 0.11% (series C) corresponding to the AES measurements at 95 mm off the nail surface (Fig. 2). At iron concentrations above 0.5% of wood dry mass (series A and B, according to iron concentration at 5 mm and 15 mm off the nail surface) virtually no mass loss was observed except for one sample of series B. In these series, virtually no decay was observed, and the fungus could not be reisolated after the incubation period.

The influence of the iron concentration on the loss of dried mass was highly significant (Kruskal-Wallis: $\chi^2 = 87.5491$, df = 4, p-value < $2.2e^{-16}$). Furthermore, all pairwise comparisons were significantly different, except the one between the iron concentration D with 0.01% and the control E (0%) (Tab. 5). The decomposition rate of the latter was lower (median = 13.2%) than the one of the former (median = 15.6%). However, this difference was not significant.

*Tab. 4: Results of decomposition experiment: All values except those of the concentrations c are medians of the sample series. c: concentrations of the $FeCl_3$-solutions [mol/l]; u: absorbed solution in % of dry mass of the sample; k: experimentally provided iron content of the samples [% of dry mass]; MV: mass loss of the samples in % of sample weight (dry mass + absorbed $FeCl_3$-solution)*

| Serie | c | u | k | MV |
|---|---|---|---|---|
| A | 0.20 | 188.09 | 1.99 | 3.33 |
| B | 0.05 | 172.40 | 0.48 | 1.79 |
| C | 0.01 | 202.34 | 0.11 | 20.48 |
| D | 0.001 | 196.08 | 0.01 | 15.60 |
| E | 0.00 | - | - | 13.20 |

*Tab. 5: Fungal wood decomposition: Pairwise comparisons using Wilcoxon rank sum test (p-value adjustment method: Holm). Data: decay by iron concentration. Bold values indicate non-significant differences*

| | A | B | C | D |
|---|---|---|---|---|
| B | 4.7e-07 | -- | -- | -- |
| C | 6.6e-08 | 6.6e-08 | -- | -- |
| D | 1.4e-07 | 8.9e-08 | 0.029 | -- |
| E | 1.0e-07 | 1.2e-07 | 0.029 | **0.428** |

# DISCUSSION

## Iron content of the wood surrounding steel fastenings

The wood in the vicinity of steel nails showed a distinctly raised iron content, although a remarkable variation was observed. In a distance of 10 cm along the grain from the nail surface the concentration of iron was still about 100x higher compared to the control samples. Considering the normal distance of steel fastenings in crib dams of about 1.5 m, it can be supposed that the iron content would be raised in the bigger part of the log during the life-time of the dam. The great variation of the iron concentration between the samples and also along one nail may be caused by irregular crevice geometry along the nail. Unequal pH, electrolyte-concentration and

oxygen transport finally lead to an irregular corrosion and to an unequal distribution of corrosion products (Baker 1974, Wranglén 1985, Tostmann 2001). Another reason for the considerable variation may be the different humidity regimes of the analysed logs.

Other important reasons for an unequal distribution of the iron content are probably growth characteristics of the wood as well as damage caused during the construction of the dams. These factors influence each other as well as the activity of fungi and other microorganisms, which again influence porosity of the wood and the pH of the electrolyte.

## Influence of iron on *Fomitopsis pinicola*

In general, the decomposition rate of the wood samples was rather small. This could have been caused by a reduced gas exchange in the Petri dishes. Furthermore, the malt agar was an additional nutrient-source for the test fungi during the initial phase of the experiment. In previous studies, decomposition rates of 30 (Schwarze 1995) up to 70% (Srebotnik and Messner 1991) were reported from experiments with *Fomitopsis pinicola* after an incubation time of three months. Other authors found a decomposition rate of only 2% after 8 months (*Fomitopsis pinicola* on *Picea rubens,* Ostrofsky et al. 1997).

The lack of any decomposition in the test-series A and B (2 and 0.5% iron content) is most likely due to the fact, that the test fungi could not colonise the whole woodblock and died during the experiment.

In series C (0.11% iron content) the decomposition rate was significantly higher than in all other test series, indicating that this iron content enhances the activity of *F. pinicola*. This is in accordance with previous findings (Danninger 1980, Ritschkoff 1996). Most likely, the iron increased the non-enzymatic cracking of the ligno-cellulose complex (Fenton's reaction). However, the detailed mechanisms that are involved in the reduction of iron from its trivalent to its bivalent form are not understood. Nevertheless, *Fomitopsis pinicola* is able to reduce $Fe^{3+}$ from a $FeCl_3$ solution to $Fe^{2+}$ (Lundborg 1988) and we assume that this fungus can use different corrosion products of iron.

Even when the iron concentrations in the decomposition experiment did not differ significantly from those measured in the wood around steel nails in logs, a direct comparison is difficult, because in the case of the logs, the overall-concentration of iron was measured. In the decomposition experiment, at least at the beginning, iron was dissolved in its trivalent form. Even though the high concentration of $Fe^{3+}$-chloride applied in the sample series A and B seems to be toxic to the test fungi, it cannot be assumed that the same total concentration of iron (including other corrosion products such as rust) has the same effect to fungi in logs.

The pH in the wood samples varied from 2.5 in series A up to 4 in series D respectively. In crevice corrosion processes pH values of the electrolyte solution are reported to decrease to values between 2 and 3 (Fontana and Greene 1978). So the provided pH values in the experiment do not differ much from those along the shaft of a nail in wood. Nevertheless, the lack of decomposition in series A and B is probably not only due to the low pH: Brown rot fungi are well known to reduce pH values of their substrates to 2.5-3.8 (Hintikka 1969, Hyde and Wood 1997, Jellison et al. 1997b).

In the present study we investigated wood samples from the wings and longitudinal protection structures of the crib dam. Decomposition of permanently water saturated parts of crib dams seems to be of less practical importance, as water saturated conditions are

inhibitory for most decay fungi. However, some white rot fungi are able to decompose also water saturated wood (Metzler and Hecht 2004).

The use of fungicides to seal the surrounding wood of the nails proposed by Yang (2001) can not be recommended here for reasons of water pollution. Our results indicate that it is most important to prevent the diffusion of the corrosion products into the longitudinal direction of the wood. Pre-drilling of the holes and pointing of the nails are the simplest methods to prevent additional damages to the wood which might act as diffusion channels for corrosion products(Rickli 1997, Böll et al. 1999). But this method cannot reduce crevice corrosion along the shaft of the nail.

## CONCLUSIONS

Our data show, that the activity of *Fomitopsis pinicola* in the wood of norway spruce is influenced by the iron content of the wood. Steel nails raise the iron content of the adjacent wood up to a distance of several centimetres. Close to the nail, mycelial growth is probably suppressed, whereas low concentrations at larger distances might enhance decay. However, the actual significance of this process in crib dams remains to be studied under field conditions.

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