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# INVESTIGATION OF ANOMALOUS FIXATION AND LEACHING OF CCA TREATED RED MAPLE

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## Abstract

The fixation of CCA-C preservative was investigated in red maple sawdust (*Acer rubrum* L.) at target retentions of 4.0, 6.4, 9.6 and 30.0 kg/m$^3$. The effect of water-soluble extractives on the course of fixation was evaluated comparing the non-extracted with pre-extracted samples treated to 6.4 and 30 kg/m$^3$. Leaching of the CCA components was monitored after complete fixation for all retentions. Fixation results show rapid chromium reduction, with the formation of a significant amount of water-soluble chromium complexes at lower retentions. Copper fixation was extremely fast while substantial amount of arsenic remained unreacted. Leaching at the lower retentions was characterized by exceptionally high losses of arsenic and moderate losses of copper and chromium. Strength of the CCA solution had consistent effect on fixation and leaching. The observed anomalies were more pronounced for low retention levels. The presence of water-soluble low molecular weight carbohydrates and phenolic extractives is likely the prominent factor responsible for the observed irregularities.

## Introduction

The outstanding mechanical properties of red maple (*Acer rubrum* L.) and its overall abundance in Northeastern American region qualify it as a potential softwood alternative for structural purposes. Due to the low natural decay resistance (Anagnost and Smith 1997), the prospects of its use for the outdoor applications such as railroad ties and bridges rely greatly on adequate preservative treatment. AWPA standards presently recommend creosote treatment for preservation of red maple (AWPA 1996). However, the treatment with water-borne preservatives would improve versatility of possible applications and design of structural value added products using this traditionally underutilized species.

In contrast to most refractory hardwoods, red maple sapwood can be adequately pressure treated with CCA-C to meet AWPA minimum retention requirement for ground contact (Kamdem *et al*. 1994; Smith *et al*. 1996). However, a number of anomalies regarding the performance of CCA treated red maple were reported in literature. Low effectiveness against fungus decay especially soft rot (Smith *et al*. 1996), also observed in some other hardwoods, was suggested to be caused by nonuniform distribution of fixation components among different cell types (Dickinson 1974). Inadequate quality of CCA fixation and depletion of active preservative components through leaching were observed by Stevanovic-Janezic *et al*. (2001). Also, exceptionally high leaching of arsenic reported in literature (Cooper *et al*. 1997, Stevanovic Janezic *et al*. 2001) give rise to environmental concerns about the use of red maple products treated with CCA.

Compared to softwoods, CCA fixation varies considerably among hardwood species (Stevanovic Janezic *et al*. 2000), and is accompanied with high leaching of active components. This variability can be explained by the effect of chemical composition rather than anatomical differences among investigated species. Cooper *et al*. (1997) reported extremely fast CCA fixation rates in red maple. The fast fixation in red maple sawdust was associated with high initial chromium adsorption and reduction from the treating solution, high initial copper fixation, while substantial amounts of arsenic remained water-soluble and thus unfixed throughout the course of fixation (Radivojevic and Cooper 2001, Cooper *et al*. 1997; Stevanovic-Janezic *et al*. 2001). These effects were more pronounced for lower than for higher preservative retentions.

The interference of the wood extractives with the course of fixation has been identified and characterized for polyflavonoid tannins in eucalyptus species (Pizzi *et al*. 1986; Bariska and Pizzi 1986), red oak, and red maple (Stevanovic-Janezic *et al*. 2000).

It has been hypothesized (Stevanovic-Janezic *et al*. 2000) that low molecular weight, reducing sugars present in red maple extractives can undergo faster oxidation reactions compared to large polymers of carbohydrates and lignin involved in fixation reactions in softwoods. Supporting evidence to the hypothesis was reported by Ung *et al*. (1998) who showed that both fixation rates and high arsenic leaching of red maple were affected by the seasonal variations in extractive content. It has also been shown that water-soluble extractives, which comprise mainly carbohydrates, had influence on the course of fixation (Stevanovic-Janezic *et al*. 2001; Kamdem *et al*. 1997), while the acetone-soluble fraction did not (Cooper *et al*. 1997).

This study was undertaken in order to further investigate the influence of red maple extractives on the course of CCA fixation with regard to preservative loading. It is hypothesized that certain groups of extractives compete with wood structural components and preferentially react with CCA. Since the content of wood extractives is significantly lower in comparison to the structural wood constituents, their contribution is expected to be more pronounced at lower preservative retentions. Knowing that the extractives render chromium unavailable for arsenic fixation, better treatment quality would be expected at higher CCA retentions.

## Materials and Methods

Wood sawdust, used in experiments to monitor fixation and leaching, was prepared from red maple (*Acer rubrum* L.). The tree was cut in spring and air-dried for two months. Sapwood free of stained wood was milled in a Willey mill and 25-40 mesh fraction was collected. Samples were treated with commercial CCA type C preservative (approximately 19.0% CuO, 47.0% $CrO_3$, 34.0% $As_2O_5$) at total four retention levels: 4.0, 6.4, 9.6 and 30.0 kg/m$^3$. CCA treating solutions (Table 1) were prepared in order to maintain wood to solution mass ratio of approximately 2:1. Precise concentrations of Cr, Cu and As in treating solutions were determined by ICP-AES according to AWPA Standard A21-93 (1996), and the content of hexavalent chromium by spectrophotometry using diphenylcarbazide as color developing reagent (Coggins and Hiscocks 1978).

Table 1. CCA treating solution parameters

| Target retention ($kg/m^3$) | CCA (%), oxide based | pH |
|---|---|---|
| 4 | 0.36 | 2.38 |
| 6.4 | 0.58 | 2.26 |
| 9.6 | 0.87 | 2.14 |
| 30 | 2.72 | 1.86 |

Wood sawdust was mixed with the preservative solution, homogenized, placed in polyethylene bags, closed, and conditioned at temperature of 30°C and high relative humidity for the duration of fixation. Two replicates of approximately 2g of each sample were being taken at close time intervals and extracted. Based on the preliminary experiments, 20 min extraction time was chosen to assure complete dissolution of unfixed CCA elements, soluble in water, leaving fixation products intact. Depending on the concentration of unfixed components, samples were extracted at least twice with 100 ml aliquots of deionized water on oscillating shaker for 20 minutes. The extracted samples were filtered through a Buchner funnel by vacuum filtration and additionally washed with 50 ml of water. The unfixed ingredients collected in the filtrate were analyzed for the content of hexavalent chromium and total chromium, copper and arsenic, according to standard methods mentioned above.

In order to evaluate the influence of water-soluble extractives on the course of fixation and leaching of red maple, sample of wood sawdust was pre-extracted with hot water. Content of hot-water soluble extractives was determined according to ASTM D1110-50T standard. The extracted wood sawdust was air dried and handled during treatment / fixation in similar way to unextracted samples. CCA fixation in extracted samples was investigated for the target retentions of 6.4 and 30 $kg/m^3$.

Unextracted red maple was investigated for the long term leaching losses at the four retentions. Leaching was performed on samples acquired from the same batches used for the fixation monitoring, after the fixation was completed. Duplicate samples of approximately 2 g of treated sawdust were extracted with 100 ml of deionized water for 20 min to allow removal of unfixed components, mixed with 100 ml of deionized water, and leached for total 35 days on orbital shaker at 100rpm. Water was exchanged and analyzed for leached CCA elements after 4, 8, 12, 17, 21, and 35 days by ICP-AES.

The treated and untreated samples were observed under the light microscope in order to possibly allocate the fixation products. Due to the apparent color of fixation products, no extra preparation of samples was necessary.

## Results

### CCA Fixation

The effect of the treating solution concentration on the CCA fixation rates of unextracted red maple is shown in Figures 1-4 for the four evaluated preservative retentions. The time required for the complete reduction of hexavalent chromium increased with the preservative retention, ranging from 1.5 hours for retention of 4.0 $kg/m^3$ to 168 hours for retention of 30 $kg/m^3$. These data show a good correlation with those reported by Stevanovic-Janezic *et al.*

(2000) for low retention treatments, and confirm fast chromium fixation in red maple compared to slowly fixing species such as aspen or red pine (Radivojevic and Cooper 2001).
The general trend of decreasing rates of chromium reduction in aspen and red pine with increase in solution strength is accompanied by a decrease in cooper fixation rate and increasing arsenic fixation rates (Radivojevic and Cooper 2001). These effects are largely explained by the decrease of treating solution pH with increase in CCA concentration. Decreased solution pH increases the rate of chromium reduction and precipitation of chromium arsenates, and decreases level of dissociation of cation exchange sites believed to be responsible for copper fixation. However, the fixation of red maple for the studied range of preservative retentions reveals different reaction patterns compared to aspen and red pine.
Fixation of arsenic was not only slower than chromium fixation at lower retentions (4.0, 6.4 and 9.6 kg/$m^3$), but also significant amounts of arsenic were observed to remain unfixed. The amount of unfixed arsenic at these retentions decreased with the increase in retention in terms of percents of treatment load and absolute amounts (mg per gram of wood substance). Approximately 35% of arsenic was extracted by the end of chromium fixation for retention of 4.0kg/$m^3$. Contrary to low retention, for the 30 kg/$m^3$ treatment, arsenic was completely and rapidly fixed. High molar ratios of chromium to arsenic (Fig. 8) clearly show low contribution of chromium arsenates at low retention levels.
The level of total extractable chromium was noticeably higher than that of hexavalent chromium throughout and at the end of the fixation. Fixation studies in most of other investigated species show negligible differences between these two (Radivojevic and Cooper 2000). Approximately 14% of total chromium was extractable with water at the point of complete chromium reduction for 4.0kg/$m^3$ treatment. The level of water-soluble total chromium decreased toward higher retentions, and only small amounts were found at the retention of 30kg/$m^3$.
Instantaneous fixation of copper was observed for 4.0 and 6.4kg/$m^3$. The trend of time dependant copper fixation became slightly apparent for 9.6 kg/$m^3$ and pronounced for 30kg/$m^3$. However, regardless of retention, distinct amounts of copper remained soluble in water, to as much as 10 % at the retention of 4.0 kg/$m^3$.
Except for the high initial fixation of all three components, CCA fixation at the retention of 30kg/$m^3$ followed the similar fixation patterns to those observed for slow fixing species such as red pine and aspen (Radivojevic and Cooper 2001).
The fixation curves are essentially different for the three “lower” retentions in comparison to one of 30kg/$m^3$ referred to as “high” and this distinction will be applied throughout the discussion of results.
*Pre-extraction:* The content of hot-water extractives in red maple was 4.24%. The pre-extraction affected the CCA fixation at both, lower (6.4kg/$m^3$) and high retention (30 kg/$m^3$) treatment as shown in Figures 5 and 6. Chromium fixation rates were lower than in un-extracted counterparts as already observed by others (Stevanovic-Janezic et al. 2000; Kamdem et al (1997). In addition, the amount of unfixed arsenic was significantly lower for the retention of 6.4 kg/$m^3$, while the divergence between hexavalent and total chromium was virtually eliminated. 6-7 % of unfixed copper observed in unextracted wood at this retention, was not found in the pre-extracted sample. Pre-extraction for the retention of 30kg/$m^3$ resulted in moderately faster fixation of arsenic and significantly slower fixation of copper.

**Leaching**

Data on 35 days leaching of CCA components for all four retentions are presented in Table 2 and Figures 9-11, respectively. Total losses (Table 2) represent sum of initially extracted components and those leached during the extended leaching period. Bars in Figures 9-11 show losses during extractions for 20 minutes and the following period of 35 days.

In terms of percent leached from the sample, the losses of all three components decrease with increase in the preservative retention. The absolute values, expressed as milligrams of a particular CCA element leached per gram of oven-dry wood substance, show that chromium leaching declines, while copper and arsenic increase with preservative loading. Since the presented values are based on the leaching of treated sawdust, they overestimate the losses from the solid wood that would be expected in service. However, they quantify the inherent chemical leaching potentials of the wood species, and can be used for projections and modeling of leaching from solid wood, with correction factors for other leaching variables.

In general, it can be understood that leaching of red maple is characterized by moderate copper and slightly higher chromium leaching. However, excessive arsenic leaching accounts for 60% loss from red maple treated to low retention (4.0kg/$m^3$). These results are of practical importance, since they indicate that one to two thirds of arsenic can potentially be depleted from wood treated to low retentions. The absolute values provide the estimation of maximum component losses into the environment.

Regardless of the preservative retention, 0.1 mg of copper per gram of wood substance is leached easily with water indicating the formation of peculiar fixation product. In general, copper is tightly bound and the total in terms of absolute amounts increases with retention. The amount of unfixed arsenic decreases with retention, as sufficient amounts of chromium are present for the formation of fixation products.

During the microscopic investigation of treated sawdust, dense dark-color deposits originating from CCA fixation products in unextracted samples were observed, while the color was persistent in the cell walls and remote regions of parenchyma even in pre-extracted samples. The opaque green color characteristic of chromium arsenates was intense in samples treated to high retentions.

## Discussion

The above fixation results demonstrate the marked irregularities in CCA fixation of red maple and indicate the interference of wood extractives as a prominent parameter affecting the CCA fixation mechanism. Presence of sugars was already suggested as an explanation of high chromium fixation rates in red maple (Cooper et al. 1997; Stevanovic-Janezic et al 2000). Rapid chromium reduction confirms the presence and competing action of compounds other then holocellulose and lignin.

However, high residual arsenic contents suggest that reduced chromium was unavailable for the formation of chromium arsenates, which are the major arsenic fixation products in softwoods. This is supported by the fact that extracted chromium fixation products at lower retentions are highly water soluble while chromium arsenates are not. Instead, fixation results indicate that chromium preferentially reacts with some compounds other than arsenic. The effect of pre-extraction indicates that the water-soluble fraction of wood extractives is at least partly involved in these reactions. These extractives are expected to contain mainly low molecular weight carbohydrates and polyphenols which are expected to react with chromium to the extent limited by their relative amounts. In presence of a surplus of chromium, their

reaction potential is exhausted and considerable amounts of chromium remain for normal reactions with holocellulose and lignin, the effect of which becomes noticeable at retention of 9.6 kg/m$^3$ and higher. However, the speciation of water soluble chromium is needed to determine whether the chromium is complexed with extractives in trivalent form, or if it is present as transitory pentavalent species.

It is evident that pre-extraction resulted in only partial removal of extraneous chemicals species potentially responsible for characteristic fixation. Besides the water soluble fraction, red maple extractives comprise numerous and chemically different groups of compounds (Rowe and Conner 1976). Levitin (1972) reported that extractives capable of forming complexes with metal ions, found within the parenchyma cells, would be only removed by NaOH following the extraction with acetone and ethanol-benzene in addition to hot water. He identified it as lignin-associated material of the same solubility that is to a degree retained in the cell walls.

Almost instantaneous copper fixation at low retentions indicates a sufficient number of reaction sites inherent in wood. However, in excess of copper such as during 30kg/m$^3$ treatment, the provision of additional reaction sites by oxidative action of chromium is evident. Copper is capable of forming organometallic complexes with reducing sugars such as those present in maple sap, but also with polyphenols. Pizzi et al (1986) presented solid evidence of competing action of polyflavonoid tannins in *Eucalyptus* species responsible for under-treatment of the structural wood constituents. They reported rapid reaction rates for copper and chromium complexing with ortho-diphenols such as catechol and pyrogallol B-rings of flavonoid tannins. Work of Ryan and Plackett (1987) suggested that tannins solely do not account for under-treatments in other species such as beech.

From the above it can be hypothesized that extractives react preferentially with copper and chromium. Despite comparable copper and chromium affinities for the complexation reactions with the extractives, copper will react preferentially, because of its initial excess compared to trivalent chromium. As the fixed chromium to copper molar ratios for the lower retentions, increase with the fixation progress, the formation of chromium complexes increases as well (Fig. 7). At retention of 30kg/m$^3$, the effect of extractives is hindered due to the high concentration of copper and chromium.

The highly colored deposits in parenchyma cells are probably fixation products originating from extractives. That would lead to the suggestion that CCA components are localized within parenchyma cells causing severe under-treatment of other wood cells types. The level of under-treatment would be much higher at low preservative retentions.

Conclusions

CCA fixation and leaching in red maple show abnormal characteristics, namely: rapid rates of chromium reduction followed by inadequate low arsenic fixation and formation of water soluble chromium species. Water soluble extractives, mainly located within the parenchyma cells are identified as significant but not the only contributing factors, as confirmed by the analysis of pre-extracted samples. Low retention treatments result in poor fixation, high losses of active components, and significant untder-treatment of red maple. High retention treatments are more adequate for the preservation of red maple, since efficacy will be impaired while environmental impacts will not be substantially affected.

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## Figures and Tables

Fig. 1 Fixation of Red Maple, Rtn 4.0 kg/m$^3$

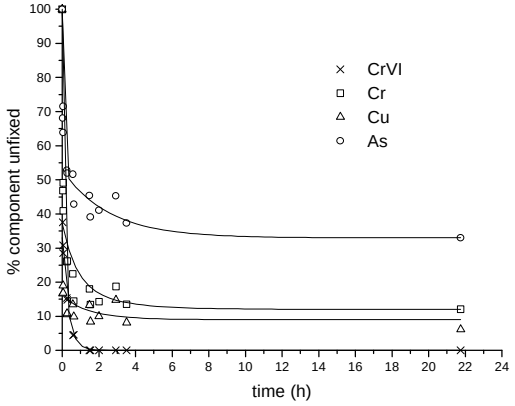


Fig. 2 Fixation of Red Maple, Rtn 6.4 kg/m$^3$

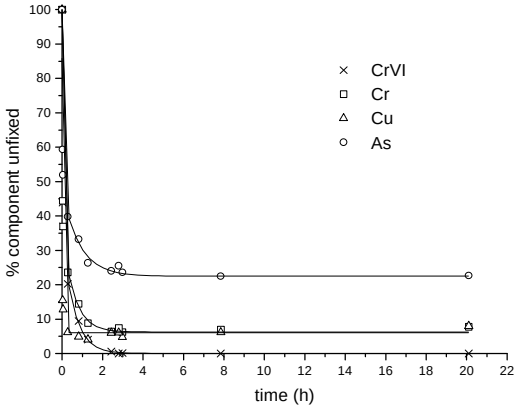


Fig. 3. Fixation of Red Maple, Rtn 9.6 kg/m$^3$

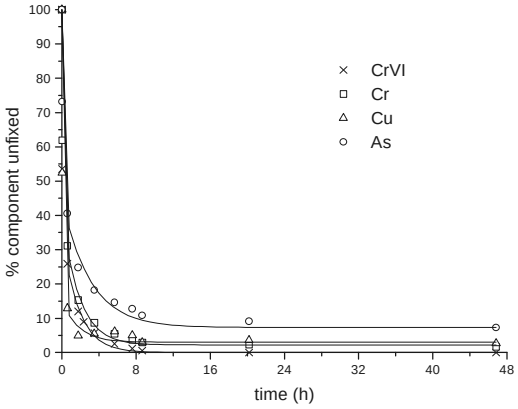


Fig. 4. Fixation of Red Maple, Rtn 30.0 kg/m$^3$

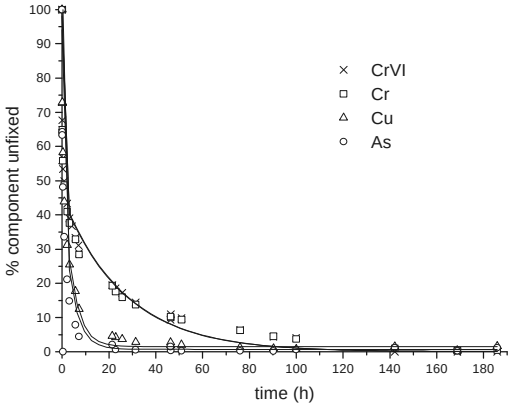


Fig. 5. Fixation of Extracted Red Maple, Rtn 6.4 kg/m$^3$

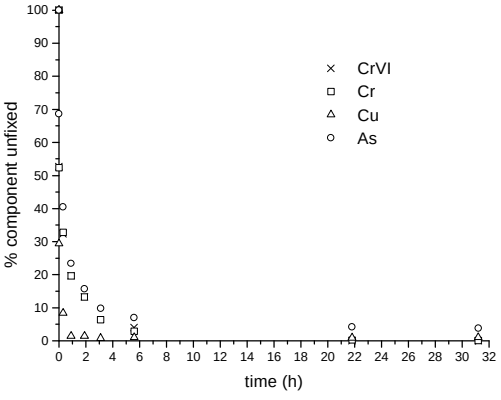


Fig. 6. Fixation of Extracted Red Maple, Rtn 30.0 kg/m$^3$

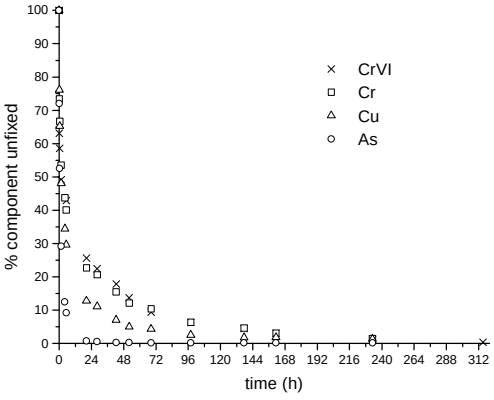

Figure 7. Chromium vs. Copper in Red Maple

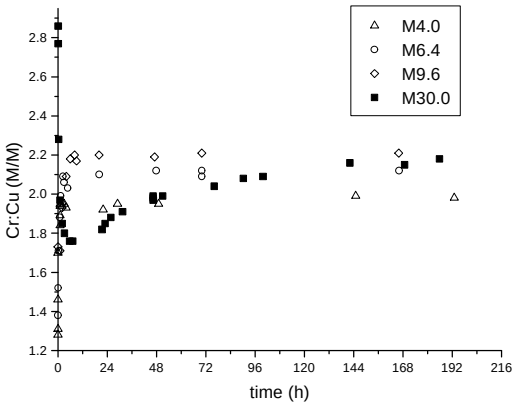


Figure 8. Chromium vs. Arsenic in Red Maple

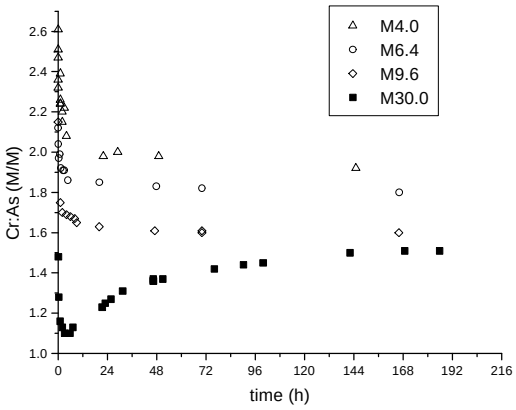


Table 2. Total Leaching from CCA treated Red Maple

| Retention | Leaching time (days) | Loss of CCA components | | | | | |
|---|---|---|---|---|---|---|---|
| | | % ot total | | | mg/godw* | | |
| | | Cr | Cu | As | Cr | Cu | As |
| 4.0 kg/m$^3$ | *35* | 23 | 16 | 61 | 0.40 | 0.16 | 1.01 |
| 6.4 kg/m$^3$ | *35* | 13 | 12 | 47 | 0.33 | 0.18 | 1.10 |
| 9.6 kg/m$^3$ | *35* | 6 | 9 | 33 | 0.26 | 0.23 | 1.38 |
| 30.0 kg/m$^3$ | *35* | 1 | 4 | 5 | 0.18 | 0.30 | 0.70 |

* - mg of CCA component per gram of o.d. wood excluding CCA

Figure 9. Leaching of Chromium in Red Maple

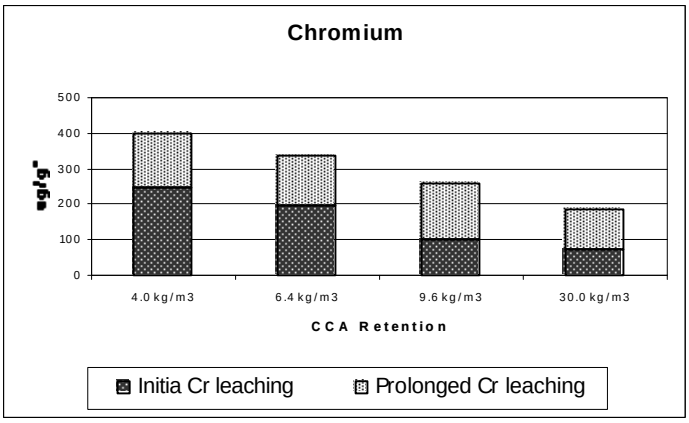


Figure 10. Leaching of Copper in Red Maple

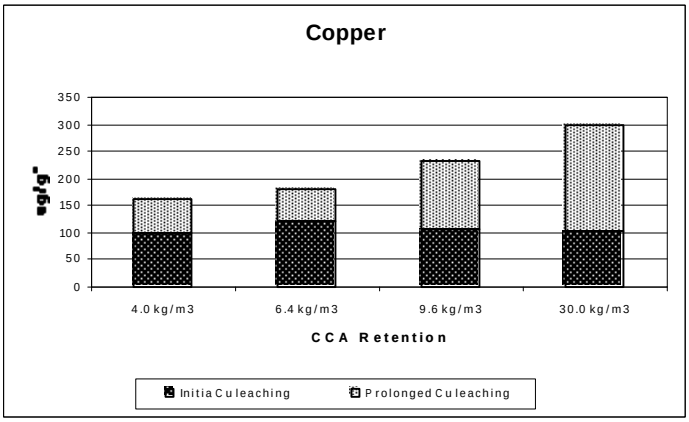


Figure 11. Leaching of Arsenic in Red Maple