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EFFECTS OF WOOD SPECIES AND RETENTION LEVELS ON REMOVAL OF COPPER, CHROMIUM AND ARSENIC FROM OUT-OF SERVICE CCA TREATED WOOD USING CALCIUM HYPOCHLORITE

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Abstract:
Chromated copper arsenate (CCA) has been one of the most widely used since the 1933's as a wood preservative to protect wood against decay and insects for exterior applications such as decks, housing, utility poles, play equipment and fences. Although its major use for consumer lumber products was replaced with chromium- and arsenic-free preservatives in the USA, Canada and European Countries by the end of 2003, large volumes of CCA-treated wood has been still coming out-of-service each year. Therefore, at present, the potential loss of heavy metals from CCA-treated wood waste after disposal has become an important problem. The disposal of out-of service CCA treated wood materials at the end of its useful life remains a concern, despite the reduction in CCA-treated wood production. Waste management options for out-of service CCA-treat wood are limited and include minor amounts of recycling and incineration with the remainder going to landfill disposal. Because of new regulations and the concerns about environmental contamination, there is a need in developing methods for recycling out-of-service CCA-treated wood products. Acid extraction, with or without bioremediation, has been extensively studied for removal of copper, chromium and arsenic from out-of service CCA-treated wood. However, none of the researchers addressed the problem about the effects of wood species and retention levels on remediation efficiency. The objectives of this study were to investigate the effects of wood species and retention levels on removal of copper, chromium and arsenic from CCA-treated wood samples using calcium hypochlorite. The results showed that $Ca(ClO)_2$ *was very effective to remove copper, chromium and arsenic from CCA-C treated milled wood samples for all three species used in this study.* $Ca(ClO)_2$ *may be very good option to remediate out-of-service CCA treated wood not only because of its high and relatively fast extraction efficiency but also because the chemical is relatively inexpensive. However, the results showed that wood species and initial retention levels of CCA-treated wood products played very important role in terms of removal of Cu, Cr and As. Therefore, whichever the remediation methods and chemicals are used for the removal of Cu, Cr and As, initial retention levels of the CCA treated wood products should be taken into account and CCA-treated wood products should be sorted according to their initial retention levels and wood species (if possible) before remediation process.*

Key words: *CCA; Calcium Hypochlorite; Remediation; Remediation efficiency; Wood species; Red pine; Aspen; Maple.*

INTRODUCTION

Chromated copper arsenate (CCA) has been one of the most widely used wood preservatives since the 1933's to protect wood products against decay and insects for exterior applications such as decks, housing, utility poles, play equipment and fences. CCA wood preservatives are formulated from chromium trioxide, copper oxide, and arsenic pentoxide (AWPA 1999). Copper and arsenic are excellent broad-spectrum fungicides against decay fungi, insects, and marine borers. Chromium acts as a ''fixing'' agent for these components. During the fixation process, chromium is reduced from the hexavalent state (Cr^{+6}) to the trivalent state (Cr^{+3}) and in the process reacts with wood and the other CCA components to form low solubility reaction products. The arsenic is fixed primarily as chromium arsenates (pentavalent) while the divalent copper is stabilized primarily by ion exchange to wood components. Retention levels in CCA treated wood range between 4.0kg/m^3 for above ground contact uses to 40kg/m^3 for marine piling. The average retention for all products treated in the USA was estimated to be 5.6kg/m^3 in 1990 (Kazi and Cooper 2006). On February 12, 2002, the US Environmental Protection Agency (EPA) announced a voluntary decision by the pressure-treated wood industry to phase out use of common arsenic-based wood preservative CCA in products destined for consumer markets. Since January 2004, the EPA has no longer allowed pressure treated wood containing CCA to be used for residential applications such as children's play structures, decks, picnic tables, landscaping timbers, residential fencing or walkways (Lin and Hse 2002, Mateus *et al.* 2002). However, CCA has still been allowed to treat utility poles and railroad sleepers. Although its major use for consumer lumber products was replaced with chromium- and arsenic-free preservatives in the USA, Canada and European countries by the end of 2003, large volumes of CCA-treated wood are still coming out of service each year. Some researchers already reported that the quantity of spent CCA-treated wood generated each year would reach significant levels within the next decades (Huang and Cooper 2000). Cooper (1993) estimated that CCA-treated wood being removed from service annually in the United States would increase up to 16x10^{6}m^3 by 2020. In Canada, approximately 2x10^{6}m^3 of CCA-treated wood will be taken out of service each year by 2020. Disposal of CCA-treated wood is also a growing problem in Europe. The total amount of wood waste is around 4x10^6 ton per year of which ~2.4x10^6 ton is toxic in Germany and France (Helsen *et al.* 1998). The disposal of out-of service CCA treated wood materials at the end of its useful life remains a concern, despite the reduction in CCA-treated wood production. Waste management options for out-of service CCA-treat wood are limited and include minor amounts of recycling and incineration with the remainder going to landfill disposal (Cooper 1993, Helsen *et al.* 1998, Kartal and Clausen 2001). Because of new regulations and the concerns about environmental contamination, there is a need in developing methods for recycling out-of-service CCA-treated wood products.

Acid extraction, with or without bioremediation, has been extensively studied for removal of copper, chromium and arsenic from out-of service CCA-treated wood. Extraction efficiencies depend on the extraction chemicals and conditions of extraction, but in general, extraction efficiencies higher than 90% for all three metals could be achieved after 2 – 6 hours for pure acid extractions. Treatment times of several days were needed for dual remediation processes that incorporated a biological treatment step evaluated methods of recovering the copper, chromium and arsenic components from acid extracts for reuse or disposal (Honda *et al.* 1991, Kazi and Cooper 1998, Clausen and Smith 1998, Shiau *et al.* 2000, Clausen 2000, Kazi and Cooper 2002, Clausen 2004a, Clausen 2004b, Helsen *et al.* 2005, Kakitani *et al.* 2006, Gezer *et al* 2006, Janin *et al.* 2009, Gezer and Cooper 2009). However, none of the researchers addressed the problem about the effects of wood species and retention levels on remediation efficiency.

The objectives of this study were to investigate the effects of wood species and retention levels on removal of copper, chromium and arsenic from CCA-treated wood samples using calcium hypochlorite.

MATERIALS AND METHODS

The detailed information about impregnation and fixation procedure of the wood samples used in this study was given in the study by Radivojevic and Cooper (2010). Particles were generated from three different retentions (4.0, 9.6 and 30kg/m^3) chromated copper arsenate Type C (CCA-C) treated red pine (*Pinus resinosa Ait*.), red maple (*Acer rubrum L*.) and trembling aspen (*Populus tremuloides Michx*.) and ground in a laboratory scale grinder to pass a screen of mesh size 20 (approximately 1mm). Ground CCA-C treated wood for each retention and species was stored in an airtight jar, and used in different studies. The treated sawdust samples were analyzed by x-ray fluorescence spectroscopy (XRF) using an OXFORD Lab-X-3000 spectrometer and also by ICP to determine the initial Cr, Cu and As contents in the wood.

Extraction experiments were designed to find suitable reaction conditions to maximize extraction of CCA fixation products from the wood matrix using aqueous $Ca(ClO)_2$ and to find the effects of wood species and initial retention levels on remediation. Experiments were carried out in 50ml. screw-capped test tubes at room temperature, 6.0% based on chlorine content, and for 3 reaction time intervals: 15, 30, and 60 minutes. For each series, 2g. wood sawdust was used, the other variables were kept constant and the ratio of liquid extractant to solid wood was kept at 15 to 1. At the end of each extraction reaction, the samples were vacuum filtered. Solid residues were washed with distilled water then dried overnight in an oven at 105±3°C.

Dried samples were digested with nitric acid/hydrogen peroxide (AWPA 2006) and analyzed for Cr, Cu and As content by ICP.

RESULTS AND DISCUSSIONS

The Effects of Retention Levels

Red Pine

The treated red pine sawdust contained, on an equivalent oxides basis, 0.40% CrO_3, and 0.19% CuO and 0.26% As_2O_5 for 4.0kg/m^3 retention level, 1.00% CrO_3, 0.41% CuO and 0.76% As_2O_5 for 9.6kg/m^3 retention level and 2.89% CrO_3, 1.1% CuO and 2.3% As_2O_5 for 30.0kg/m^3 retention level. Of the CCA-C components with 6% $Ca(ClO)_2$ extraction, while chromium was the most easily extracted followed by copper and then arsenic for 4.0kg/m^3 retention level, arsenic was the most easily extracted followed by chromium and then copper for both 9.6 and 30kg/m^3 retention levels. Extraction of all CCA components increased with extraction time up to 60 minutes for all retention levels. The most efficient extraction duration for all retention levels was 60 minutes. The Cu, Cr and As extraction efficiencies were 91%, 93% and 88% for 4.0kg/m^3 retention level, 90%, 87% and 92% for 9.6kg/m^3 retention level, 82%, 83% and 89% for 30.0kg/m^3 retention level, respectively. The efficiency of extraction with $Ca(ClO)_2$ decreased with increased retention levels (Fig.1). Especially, the amount of extracted copper decreased with increased retention levels.

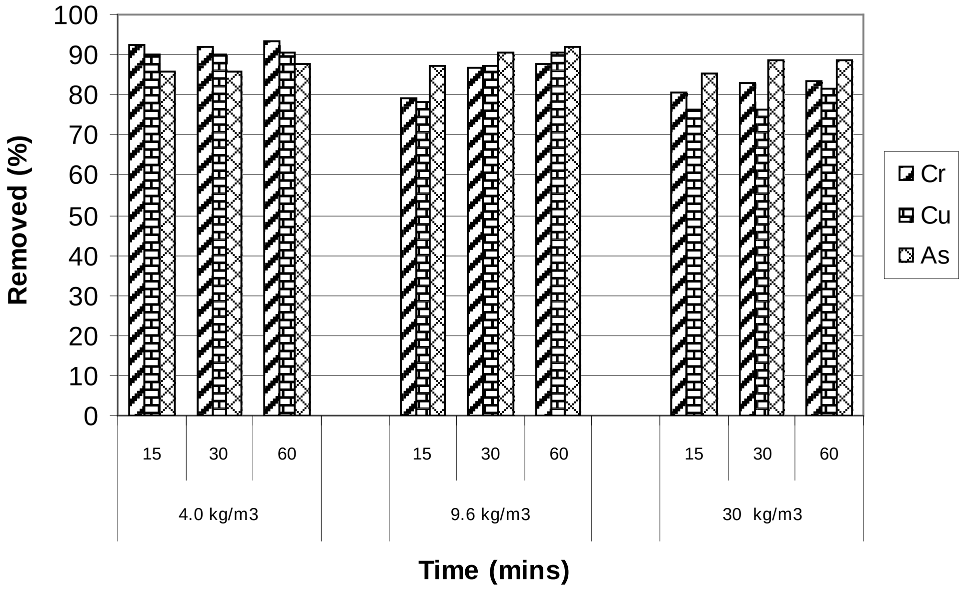

Fig. 1
Removal of Cu, Cr and As from CCA-treated red pine sawdust using $Ca(ClO)_2$.

Maple

The treated red maple sawdust contained, on an equivalent oxides basis, 0.29% CrO_3, 0.14% CuO and 0.19% As_2O_5 for 4.0kg/m^3 retention level, 0.72% CrO_3, 0.29% CuO and 0.54% As_2O_5 for 9.6kg/m^3 retention level and 2.30% CrO_3, 0.80% CuO and 1.93% As_2O_5 for 30.0 kg/m^3 retention level. Of the CCA-C components with 6% $Ca(ClO)_2$ extraction, arsenic was the most easily extracted followed by copper and then chromium for 4.0kg/m^3 retention level while arsenic was the most easily extracted followed by chromium and then copper for both 9.6 and 30kg/m^3 retention levels. While extraction of all CCA components increased with extraction time up to 60 minutes for 4.0kg/m^3 retention level, the most efficient extraction time for 9.6kg/m^3 and 30.0kg/m^3 retention levels was 60 minutes. After 60 minutes extraction, 75% Cu, 75% Cr and 81% As for 4.0kg/m^3 retention level, after 30 minutes extraction, 75% Cu, 82% Cr and 86% As for 9.6kg/m^3 retention level, 75% Cu, 78% Cr and 86% As for 30.0kg/m^3 retention level were removed from CCA-treated maple sawdust. The efficiency of extraction with $Ca(ClO)_2$ did not change dramatically with increased retention levels. The lowest removal of Cu, Cr and As was found for the CCA-treated maple sawdust which had 4.0kg/m^3 retention level (Fig. 2).

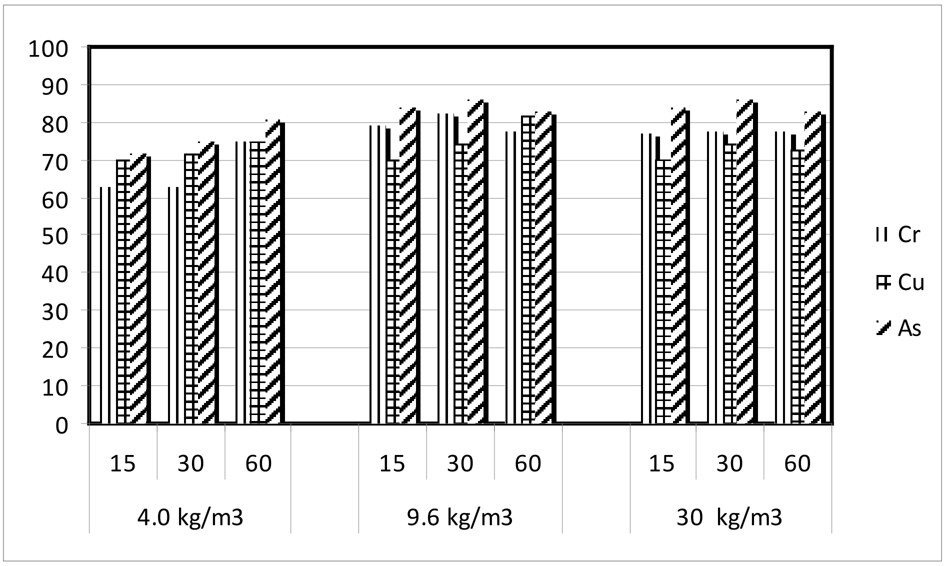

Fig. 2
Removal of Cu, Cr and As from CCA-treated maple sawdust using Ca(ClO)$_2$.

Aspen

The treated aspen sawdust contained, on an equivalent oxides basis, 0.22% CrO_3, and 0.17% CuO and 0.19% As_2O_5 for 4.0kg/m^3 retention level, 0.77% CrO_3, 0.39% CuO and 0.61% As_2O_5 for 9.6kg/m^3 retention level and 2.80% CrO_3, 1.14% CuO and 2.16% As_2O_5 for 30.0kg/m^3 retention level. Of the CCA-C components, with 6% $Ca(ClO)_2$ extraction, arsenic and copper were the most easily extracted followed by chromium for 4.0kg/m^3 retention level while arsenic was the most easily extracted followed by copper and then chromium for both 9.6 and 30kg/m^3 retention levels. While extraction of all CCA components increased with extraction time up to 60 minutes for 4.0kg/m^3 retention level, the most efficient extraction durations for 9.6kg/m^3 and 30.0kg/m^3 retention levels were 15 and 30 minutes, respectively. After 60 minutes extraction, 79% Cu, 71% Cr and 79% As for 4.0kg/m^3 retention level, after 15 minutes extraction, 81% Cu, 79% Cr and 87% As for 9.6kg/m^3 retention level, after 30 minutes extraction, 78% Cu, 77% Cr and 86% As for 30.0kg/m^3 retention level were removed from CCA-treated aspen sawdust. The efficiency of remediation with 6% $Ca(ClO)_2$ did not change dramatically with increased retention levels. The lowest removal of Cu, Cr and As was found for the CCA-treated aspen sawdust which had 4.0kg/m^3 retention level (Fig. 3).

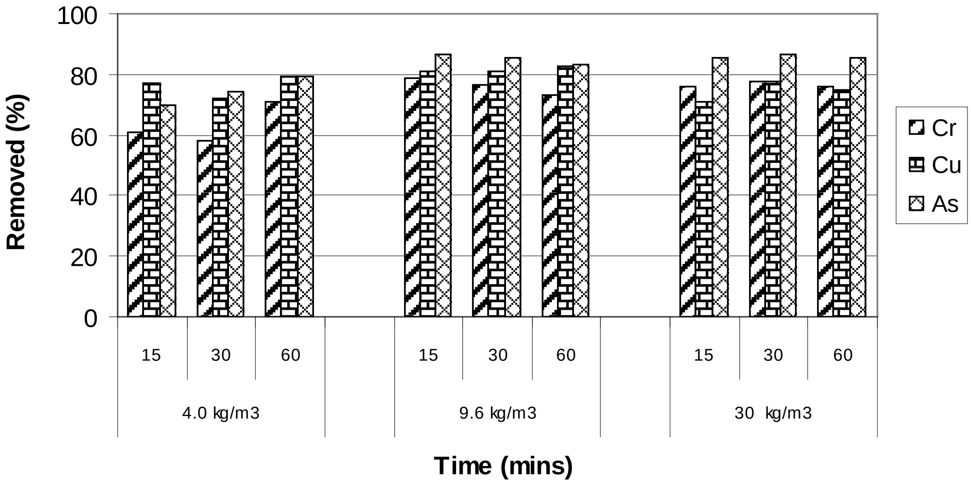

Fig. 3
Removal of Cu, Cr and As from CCA-treated aspen sawdust using Ca(ClO)$_2$.

The Effects of Wood Species

The effects of wood species on removal of Cu, Cr and As from CCA-treated red pine, maple and aspen at 4.0, 9.6 and 30kg/m^3 retention levels are shown on the Figures 4-6, respectively. The highest amounts of Cu, Cr and As were removed from red pine followed by maple and then aspen when the wood samples had 4.0 and 9.6kg/m^3 retention levels. However, when the three different wood species samples which had 30kg/m^3 retention level were remediated with 6% $Ca(ClO)_2$, wood species did not have so much effect on the remediation efficiency. At 4.0kg/m^3 retention level.

Water solubility of CCA components was determined by the extent of fixation and preservative retention. Availability of preservative components was profoundly affected by pH and ionic composition of the solution. Availability of chromium and arsenic from CCA was governed by anionic composition of the solution, increased toward extreme pH values, and was consistent with dissolution of nonstoichiometric Cr-As fixation products of variable composition. Alkaline conditions favor oxidation of insoluble and nontoxic Cr(III) to soluble and toxic Cr(VI) forms. Similar copper availability consistent with acid elution and cation displacement of Cu bound to wood by cation exchange mechanism was observed from CCA and ACQ treated wood. Composition of structural components in these three species used in this study is consistent with generally higher contribution of lignin, and lower contribution of carbohydrates in softwoods (e.g. red pine) in comparison to hardwoods (e.g. aspen and red maple). Contents of wood extractives are similar for all three species used in this study and within the range of 5-10% typical for wood species of the temperate zone (Fengel and Wegener 1984).

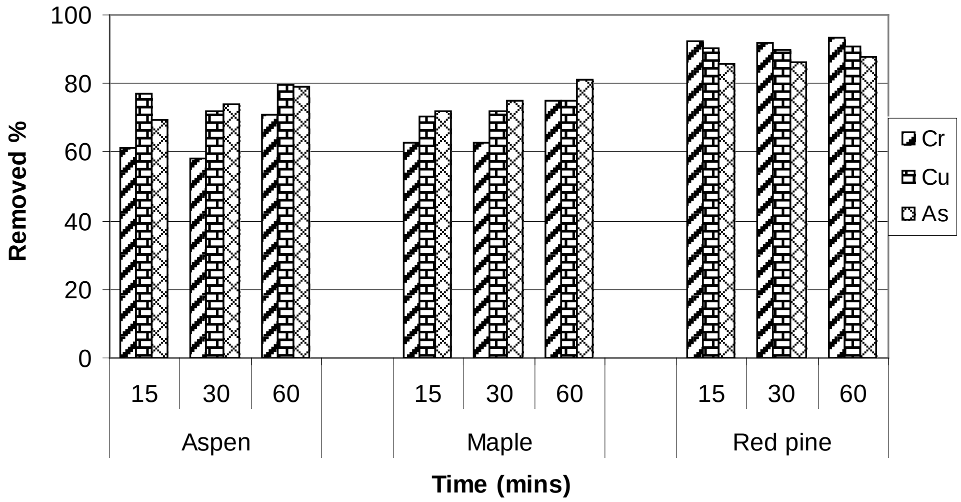

Fig. 4
Removal of Cu, Cr and As from CCA-treated aspen, maple and red pine sawdust at 4.0kg/m^3 retention level using $Ca(ClO)_2$.

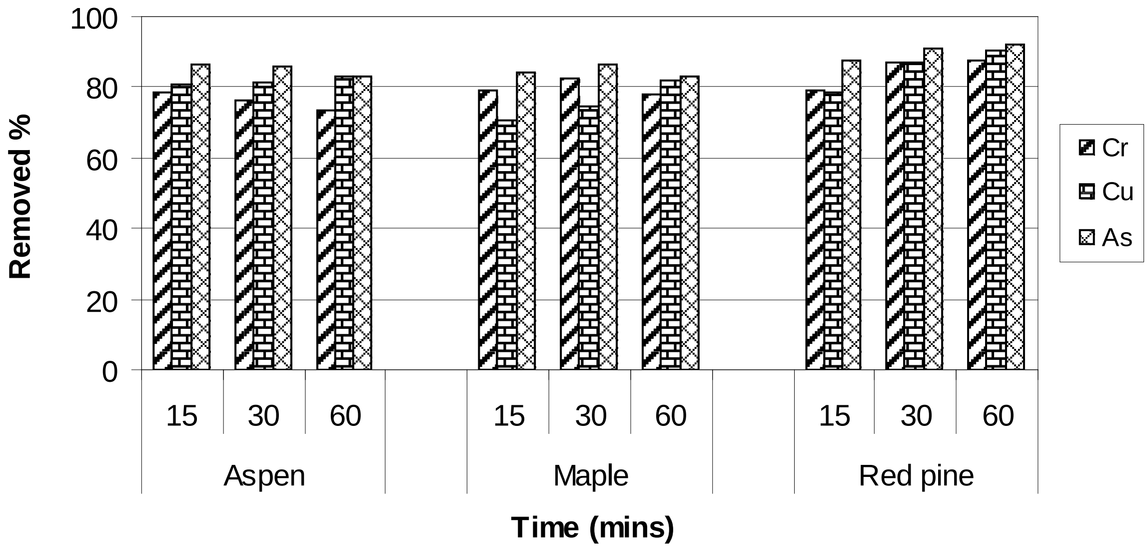

Fig. 5
Removal of Cu, Cr and As from CCA-treated aspen, maple and red pine sawdust at 9.6kg/m^3 retention level using $Ca(ClO)_2$.

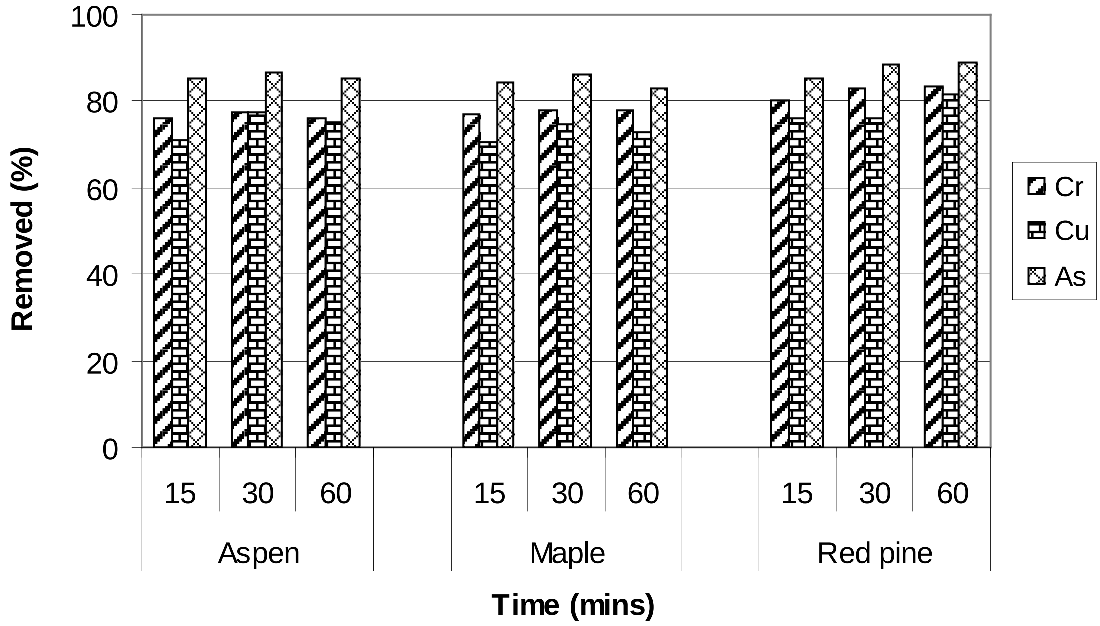

Fig. 6
Removal of Cu, Cr and As from CCA-treated aspen, maple and red pine sawdust at 30kg/m^3 retention level using Ca(ClO)$_2$.

The amount of Cu, Cr and As in wood samples after remediation

The amount of Cu, Cr and As in wood samples after remediation with 6% Ca(ClO)$_2$ for 60 mins are given Table 1. The results showed that initial retention level of CCA-treated wood samples was very important in terms of removal of Cu, Cr and As. At higher retention levels, although over 80% of Cu, Cr and As were removed from CCA treated wood samples, the significant amounts of Cu, Cr and As still remained in the wood samples after remediation. Therefore, whichever the remediation methods and chemicals are used for the removal of Cu, Cr and As, initial retention levels of the CCA treated wood products should be taken into account and CCA-treated wood products should be sorted according to their initial retention levels before remediation process.

Table 1

The amount of Cu, Cr and As remained in the wood samples after remediation

Retention levels	Aspen (ppm)			Maple (ppm)			Red pine (ppm)		
	Cu	Cr	As	Cu	Cr	As	Cu	Cr	As
4.0 kg/m3	447	243	499	70	87	38	284	145	312
9.6 kg/m3	1465	1036	1872	609	864	1080	1133	742	1425
30 kg/m3	3798	2944	5076	2030	3450	3474	3157	2189	3781

CONCLUSION

Ca(ClO)$_2$ was very effective to remove copper, chromium and arsenic from CCA-C treated milled wood for all three species used in this study. Ca(ClO)$_2$ may be very good option to remediate out-of-service CCA treated wood not only because of its high and relatively fast extraction efficiency but also because the chemical is relatively inexpensive. However, the results showed that wood species and initial retention levels of CCA-treated wood products played very important role in terms of removal of Cu, Cr and As. Therefore, whichever the remediation methods and chemicals are used for the removal of Cu, Cr and As, initial retention levels of the CCA treated wood products should be taken into account and CCA-treated wood products should be sorted according to their initial retention levels and wood species (at least hardwoods and softwoods should be sorted) before remediation process.

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