

THE INTERNATIONAL RESEARCH GROUP ON WOOD PROTECTION

Section 5

Sustainability and environment

PRACTICAL EXTRACTION OF METALS FROM CCA-TREATED WOOD

Bin Yu¹, Chung Y. Hse², Todd F. Shupe¹

¹Louisiana State University Agricultural Center, Baton Rouge, La 70803

²USDA Forest Service, South Research Station, Pineville, La 71360

Paper prepared for the 45th IRG Annual Meeting
St George, Utah, USA
11-15 May 2014

Disclaimer

The opinions expressed in this document are those of the author(s) and are not necessarily the opinions or policy of the IRG Organization.

IRG SECRETARIAT
Box 5609
SE-114 86 Stockholm
Sweden
www.irg-wp.com

PRACTICAL EXTRACTION OF METALS FROM CCA-TREATED WOOD

Bin Yu¹, Chung Y. Hse², Todd F. Shupe¹

¹Louisiana State University Agricultural Center, Baton Rouge, La 70803

²USDA Forest Service, South Research Station, Pineville, La 71360

ABSTRACT

The extraction effects of acid concentration, reaction time and temperature in a microwave reactor on recovery of chromated copper arsenate (CCA)-treated wood were evaluated. Extraction of copper, chromium, and arsenic metals from CCA-treated southern pine wood samples with three different wood particle sizes (i.e., (1) 0.5 cm³, (2) 0.5x0.5x1.0 cm, and (3) 0.5x0.5x1.5 cm) was investigated using a microwave reactor. Experiments were performed at three reaction times (i.e., (1) 10, (2) 30, and (3) 50 min. and two levels of phosphoric acid concentration (i.e., (1) 2.5, (2) 3.5%).

The recovery of all three metals at all particle sizes was significantly affected by reaction time for short reaction periods but not at long durations. As expected higher acid concentration greatly facilitated greater metal recovery rates. The recovery of chromium was much less than the other metals and the best recovery was 64.47% with an acid concentration of 3.5%, 50 min. reaction time, and 0.5 cm³ particle size. The recovery of arsenic and copper was 93.52% and 94.89%, respectively, at similar reaction conditions.

Keyword: CCA, extraction, microwave, wood particle size

1. INTRODUCTION

Chromated copper arsenate (CCA) was the most commonly used waterborne wood preservative in the world until its removal from the U.S. residential market on December 31, 2003. However, large volumes of CCA-treated wood remain in service and accordingly large amounts will continue to be decommissioned in coming years. Traditionally, CCA-treated wood has been primarily disposed in construction and demolition (C&D) debris landfills, with municipal solid waste (MSW) landfills as alternative disposal options. It is estimated that about 3 to 12 million tons of spent preserved wood will be removed from service in the United States and Canada in the next 20 years (Kazi and Cooper, 2006).

Disposal of the spent CCA-treated wood has become an important concern because of its residual heavy metal content, in particular the arsenic and chromium. Traditional waste disposal options for spent preserved wood, such as burning and landfilling, are becoming more costly or even impractical because of increasingly strict regulatory requirements (Townsend *et al.*, 2004). The burning of treated wood can be extremely dangerous and even more so when the wood has been treated with CCA. Studies have shown that burning of preservative –treated wood waste emits highly toxic smoke and fumes in the environment (Solo-Gabriele, 2002). In the case of landfills, studies have shown that CCA compounds can be gradually leached out (Townsend, 2005 *et al.*; Moghaddam and Mulligan, 2008). There is an imperative need for developing techniques to recycle CCA-treated out of service wood.

Several chemical methods have been proposed to extract the metals from CCA-treated wood. Solvent extraction will dissolve the preservatives and partially remove them from the wood. The use of acid extraction to remove CCA components from wood has been extensively studied (Kartal and Clausen, 2001; Son *et al.*, 2003; Clausen, 2003; Clausen, 2004; Gezer *et al.*, 2006; Kakitani *et al.* 2006). One of the advantages for acid extraction is its potential ability to reverse the CCA fixation process, thereby converting CCA elements into their water-soluble form (Kartal and Clausen, 2001).

One disadvantage of this recycling method is the huge amount of chemical solvents used and the long duration of the process. The prevailing treatment times reported ranged from 16 hours for sawdust (Clausen and Smith, 1998) to 24 hours for chips (Kartal and Clausen, 2001), which are considered to be major factors hindering commercial development. Therefore, to develop an economically viable industrial process, the focus of our previous study was on treatment time and acid concentration (Yu *et al.* 2009). One other variable that needs to be resolved before commercialization is the proper wood particle size from both a technical and economical perspective. We know that a reduction in particle size will provide an increase in surface area on a mass basis and thus facilitate metal extraction but the ideal particle size is yet unknown. Therefore, the focus of this study was to determine the effect of particle size on the metal recovery of copper, chromium, and arsenic from CCA-treated wood. The recovery rates were also examined with regards to extraction time and phosphoric acid concentration.

2. MATERIALS AND METHODS

2.1 Preparation of CCA-Treated Wood Samples

A southern pine (*Pinus sp.*) pole was obtained from Arnold Forest Products Co. in Shreveport, La, USA and used as the raw material. The pole was treated with CCA type C preservative (CCA-C, chromium as CrO_3 , 45%-50%; copper as CuO , 17-21%; arsenic as As_2O_5 , 30-37%) solution using a full-cell process. The pole was cut into strips, air dried, and cut to different sample sizes. Three length sizes of matched wood chips were prepared and used without further treatment i.e., (1) 0.5 cm³, (2) 0.5x0.5x1.0 cm, and (3) 0.5x0.5x1.5 cm). The last number denotes the longitudinal direction.

2.2 Acid Extraction in Microwave Reactor

The temperature of the microwave reactor (Milestone, Shelton, CT) was set at 130 °C and the concentration of phosphoric acid was 2.5 or 3.5% w/w. The reaction time was 10, 30, and 50 min. Each combination of variables was replicated three times. The ratio of sawdust to diluted acid or mixed acid solution was fixed at 1g to 20 ml. The vessel was sealed and placed into the microwave reactor (Milestone, Shelton, CT). The solution was filtered after the reaction by Whatman No.4 filter paper then diluted to 100ml in a volumetric flask.

2.3. Determination of Copper, Chromium, and Arsenic Concentrations

Digestion. Solid wood residue was digested according to American Wood Protection Association Standard A7-13 (AWPA 2013). The procedure required that the CCA-bearing solid residues be accurately weighed into 100 ml test tubes. For each gram of solid residue, 15ml of nitric acid was added. A digestion blank along with the samples was also prepared. The test tubes were placed into an aluminium heating block and slowly warmed. The temperature was increased to 120 °C after the initial reaction of brown fumes subsided. The temperature was maintained until a transparent liquid was obtained. The transparent liquid was cooled to room temperature and 5ml of hydrogen peroxide was drop-wise added. If the solution was not clear after this treatment, the temperature was increased and another 5ml of hydrogen peroxide was added. The sample was continually heated until approximately 1 ml sample solution was left in

the test tube. The sample was carefully transferred into a 25ml volumetric flask and then diluted with distilled water to a 25ml solution.

Analysis of Cu, Cr, and As. Quantitative elemental analysis of copper, chromium and arsenic was conducted according to American Wood Protection Association Standard A21-08 (AWPA 2013). After digestion, the concentrations of copper, chromium, and arsenic in the samples were determined by inductive coupled plasma atomic emission spectroscopy (ICP-AES).

3. RESULTS AND DISCUSSION

3.1 Behaviour of CCA elements in different length size in microwave oven.

Table 1 shows the recovery of copper, chromium, and arsenic from three different wood chip sizes. As expected, the largest ($0.5 \times 0.5 \times 1.5 \text{ cm}^3$) particles typically yielded the lowest recovery for all metals. It is well known that lower particles sizes can increase the kinetics of any chemical reaction by increasing the effective surface area. However, the recovery of metals for the larger particles was in some instances comparable or even greater than $0.5 \times 0.5 \times 1.0 \text{ cm}^3$ particles.

Chromium is well known for its role in fixation in CCA-treated wood and hence has consistently proven difficult to completely extract, particularly for larger particle sizes. For the extreme reaction condition of 3.5% phosphoric acid at 130°C for 50 min. the recovery rate ranged from 54.76-64.47%. However, at the same reaction condition the recovery rate of arsenic and copper was 85.30-93.52% and 85.55-94.89%, respectively.

Figure 1 shows the CCA elements recovery rate affected by wood chip size and reaction time using 3.5% phosphoric acid. Arsenic and copper displayed a similar extraction trend and recovery rate for different wood chip sizes. From a reaction time of 10min. to 30min., particle size had a significant effect on arsenic and copper recovery rate. However, after 50min. the recovery rate for all three sizes was similar. The recovery rate trend for chromium did not indicate an obvious sudden change from 10min. to 50min. for all particle sizes. Additional extraction time may be advantageous for additional chromium recovery at these reaction conditions. However, such additional time will also decrease the economic viability of the process.

Figure 2 shows the CCA elements recovery rate affected by wood chip size and reaction time using 2.5% phosphoric acid. The general trends for all metals are similar to that in Figure 1. It is interesting to note that the largest particles provided the best recovery for arsenic and copper for 10 min. Many of the same factors previously discussed (e.g., wood permeability and variability) are certainly in play. In addition, Figure 2 indicates the effectiveness of the microwave system of heating. Due to the nature of microwave heating, it can provide favourable results in short reaction periods, particularly with larger particles, but the advantages are less obvious with longer reaction periods.

Another factor impacting these results is the inherent permeability of southern pine wood. In addition to high radial and tangential permeability, southern pine wood has high longitudinal permeability (Koch 1972). For all particle sizes, the samples are all uniform in the radial and tangential dimensions and only the longitudinal dimension varies. Although the permeability of these samples was not determined, we know from previous research that there is inherent variability in wood permeability (Koch 1972). At longer treatment times, the variability appears

to be less critical in determining metal recovery. This is evidenced by similar recovery rates for all particle sizes for longer reaction periods.

Table 1. CCA recovery in three reaction times, three wood chip sizes and two acid concentrations.

H ₃ PO ₄ (%)	Time (min)	0.5×0.5×0.5cm	0.5×0.5×1.0cm	0.5×0.5×1.5cm
			---As(%)---	
2.5	10.00	42.11	41.17	51.48
2.5	30.00	84.36	71.61	58.65
2.5	50.00	91.26	74.40	73.74
3.5	10.00	68.22	67.79	58.01
3.5	30.00	87.70	70.68	71.91
3.5	50.00	93.52	89.91	85.30
			---Cr(%)---	
2.5	10.00	12.95	10.23	22.93
2.5	30.00	43.28	37.81	26.45
2.5	50.00	52.10	40.94	34.19
3.5	10.00	33.69	33.85	26.72
3.5	30.00	52.49	37.96	34.59
3.5	50.00	64.47	60.31	54.76
			---Cu---	
2.5	10.00	48.33	41.86	55.82
2.5	30.00	88.28	71.42	59.03
2.5	50.00	93.84	77.79	76.13
3.5	10.00	71.38	69.80	58.17
3.5	30.00	89.84	72.36	74.25
3.5	50.00	94.89	89.81	85.55

The current results with a single acid are not as promising as our previous results with a dual acid system which showed that diluted phosphoric acid (PA) mixed with acetic acid (AA) was very effective to recover CCA elements in a microwave reactor within a short period. A binary acid solution consisting of 2.75 % PA and 0.5 % AA (10-min reaction time at 130 °C) was optimal to achieve the maximum recovery rate of all CCA elements (Hse *et al.* 2012). The current data is in agreement with previous results by Fleischer and Thurow (2013). These researchers used microwave digestion and ICP-OES of treated and untreated wood samples to quickly determine low levels of total mercury.

4. CONCLUSIONS

The extraction effects of acid concentration, reaction time, and temperature in a microwave reactor on recovery of chromated copper arsenate (CCA)-treated wood were evaluated. Extraction of copper, chromium, and arsenic metals from CCA-treated southern pine wood samples with three different wood particle sizes (i.e., (1) 0.5 cm³, (2) 0.5x0.5x1.0 cm, and (3) 0.5x0.5x1.5 cm) was investigated using a microwave reactor. The recovery of all three metals at all particle sizes was significantly affected by reaction time for short reaction periods but not at long durations. As expected higher acid concentration greatly facilitated greater metal recovery rates. The recovery of chromium was much less than the other metals and the best recovery was 64.47% with an acid concentration of 3.5%, 50 min. reaction time, and 0.5 cm³ particle size. The recovery of arsenic and copper was 93.52% and 94.89%, respectively, at similar reaction conditions.

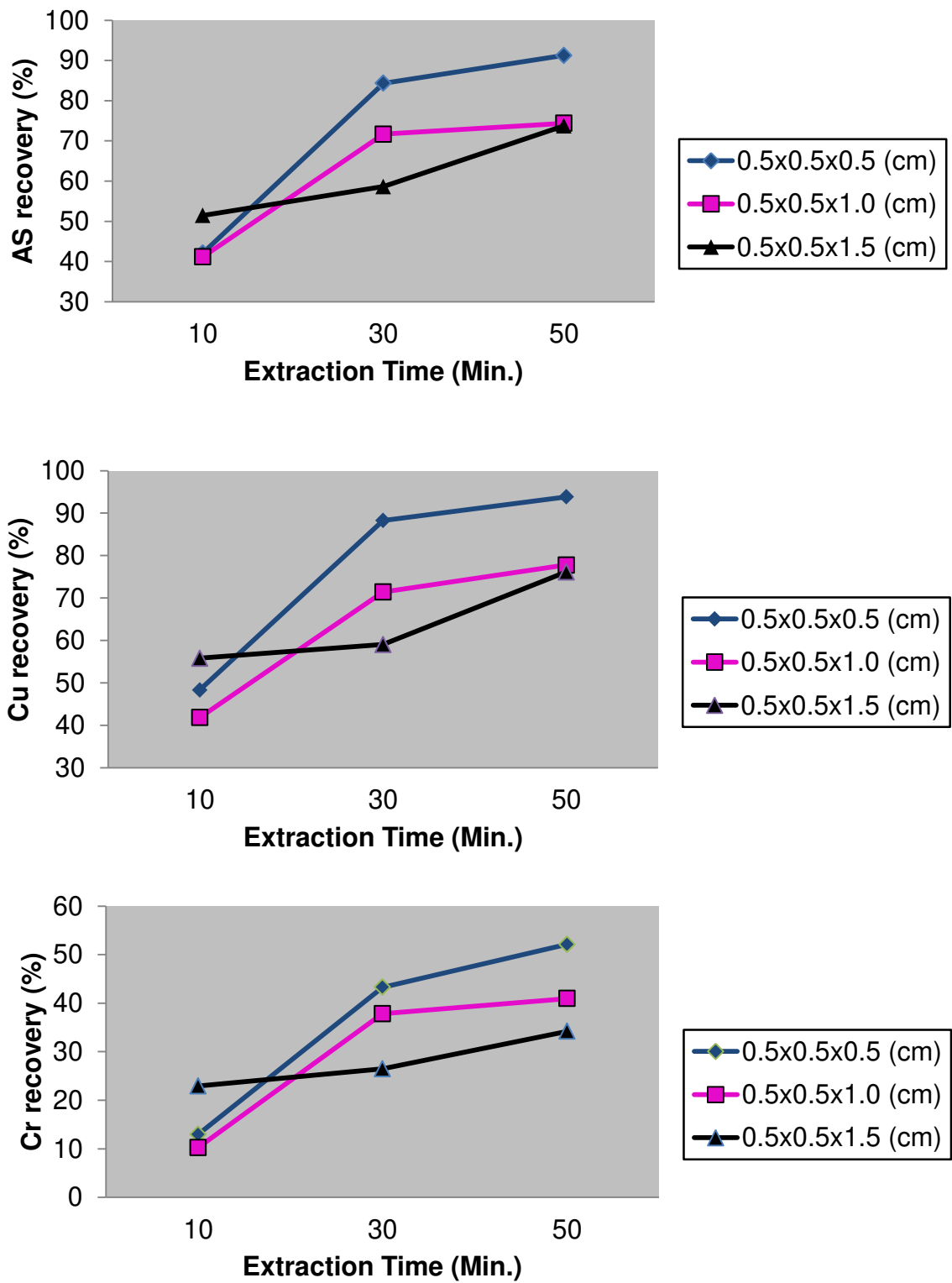


Figure 1. CCA recovery rate with 3.5% phosphoric acid as a function of time and particle size.

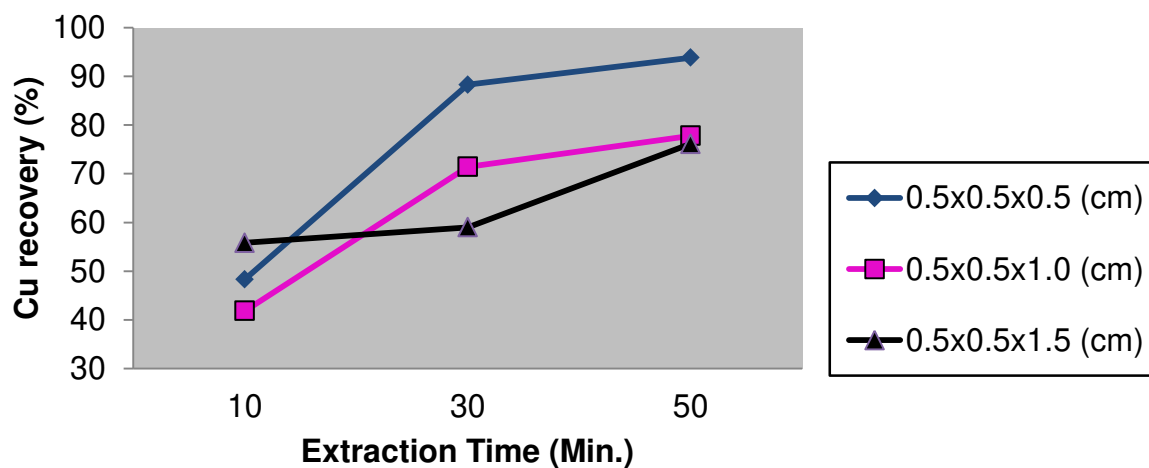
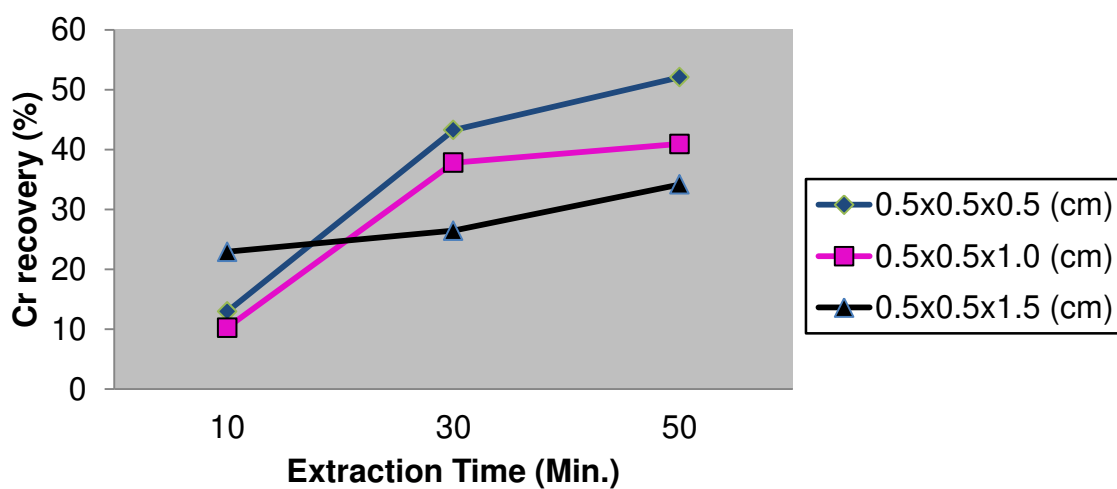
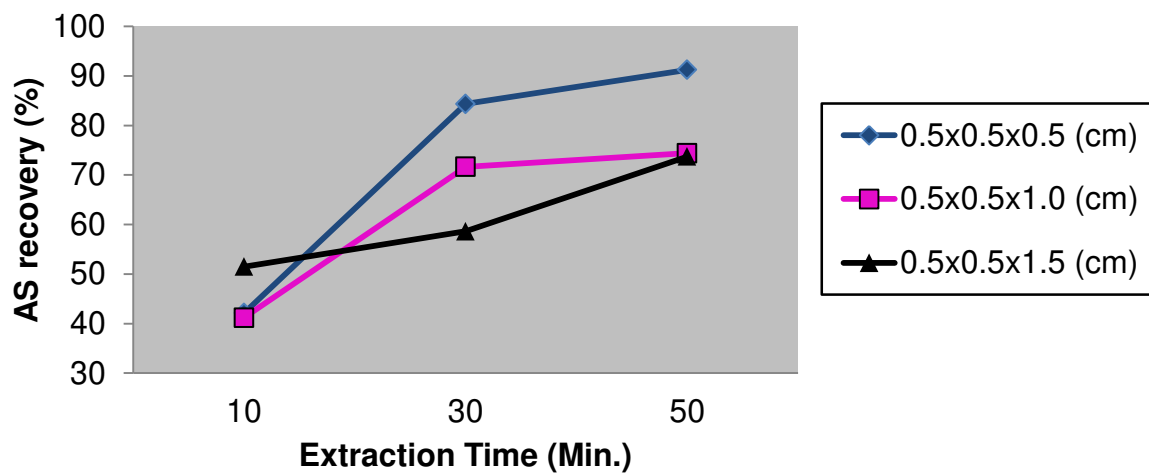


Figure 2. CCA recovery rate with 2.5% phosphoric acid as a function of time and particle size.

5. REFERENCES

- American Wood Protection Association (2013). Annual book of standards. Birmingham, AC, USA.
- Clausen, C A (2003) Improving the two-step remediation process for CCA-treated wood: Part I. Evaluating oxalic acid extraction. *Waste Management*, **24**(4), 401-405.
- Clausen, C A (2004). Improving the two-step remediation process for CCA-treated wood: Part II. Evaluating bacterial nutrient sources. *Waste Management*, **24**(4), 407-411.
- Clausen, C A., Smith R L (1998). Removal of CCA from treated wood by oxalic acid extraction, steam explosion, and bacterial fermentation. *Journal of Industrial Microbiology & Biotechnology*, **20**(3-4), 251-257.
- Fleischer, H, Thurow, K (2013). Determination of total mercury content and trace metal analysis in wood materials – Part 1: ICP-OES using mercury cold vapour. American Laboratory, South San Francisco, CA, <http://www.americanlaboratory.com/914-Application-Notes/142521-Determination-of-Total-Mercury-Content-and-Trace-Metal-Analysis-in-Wood-Materials-Part-1-ICP-OES-Using-Mercury-Cold-Vapor/>
- Gezer, E D, Yildiz, U, Yildiz, S (2006). Removal copper, chromium and arsenic from CCA-treated yellow pine by oleic acid. *Building and Environment*, **41**(3), 380-385.
- Hse, C Y, Shupe, T F, Yu, B (2012). Rapid microwave-assisted acid extraction of southern pine waste wood to remove metals from chromate copper arsenate (CCA) treatment, DOI 10.1515/hf-2012-0073.
- Kakitani, T, Hata, T, Kajimoto, T (2006). A novel extractant for removal of hazardous metals from preservative-treated wood waste. *Journal of Environmental Quality*, **35**(3), 912-917.
- Kakitani, T, Hata, T, Katsumata, N (2007). Chelating extraction for removal of chromium, copper, and arsenic from treated wood with bioxalate. *Environmental Engineering Science*, **24**(8), 1026-1037.
- Kartal, S N, Clausen, C A (2001). Leachability and decay resistance of particleboard made from acid extracted and bioremediated CCA-treated wood. *International Biodeterioration & Biodegradation*, **47**(3), 183-191.
- Kazi, F K M, Cooper P A (2006). Method to recover and reuse chromated copper arsenate wood preservative from spent treated wood. *Waste Management*, **26**(2), 182-188.
- Koch, P (1972). Utilization of the southern pines. *Ag Handbook 420*. USDA. Washington, DC.
- Moghaddam, A H and Mulligan, C N (2008). Leaching of heavy metals from chromate copper arsenate (CCA) treated wood after disposal. *Waste Management* **28**, 628-637.
- Solo-Gabriele, H, Townsend, T, Messick, B, Calitu, V (2002). Characteristics of chromated copper arsenate treated wood ash. *Journal of Hazardous Materials*, **B89**, 213-232.

Son, D W, Lee, D H, Kang, C H (2003). Proceedings of International Conference on Forest Products, 30th Anniversary of the Korean Society of Wood Science and Technology (IAWPS2003), 1059-1064.

Townsend, T , Tolaymat, T, Solo-Gabriele, H (2004). Leaching of CCA-treated wood: implications for waste disposal, *Journal of Hazardous Materials*, **B114**, 75-91.

Townsend, T, Dubey, B, Tolaymat, T, Gabriele, H S (2005). Preservative leaching from weathered CCA-treated wood. *Journal of Environmental Management*, **75**, 105-113.

Yu, B, Hse, C Y, Shupe, T F (2009). Rapid microwave-assisted acid extraction of metals from chromated copper arsenate (CCA)-treated southern pine wood. *Proceedings IRG Annual Meeting IRG/WP 09-50262*. 10 pp.