

RECOVERY AND REUSE OF CHROMATED COPPER ARSENATE (CCA) WOOD PRESERVATIVE FROM CCA TREATED WASTES

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Summary

CCA impregnated waste materials are generated during the treating process and from wood removed from service. The volume of chromated copper arsenate (CCA) treated wood products coming out of service is expected to increase dramatically over the next ten years. This material is currently land-filled, which creates concerns because of the bulky nature of wood and the potential for leaching of some Cr, Cu and As components of the preservative. Contaminated sludges generated during the treating process are disposed of as hazardous wastes by waste disposal companies. In the present study we have developed recycling processes whereby most of the CCA components are extracted from the waste material. The "clean" wood and other residues can be used for paper or composite products or disposed of by normal landfill. The extracted solution, containing Cr^{III}, Cu^{II} and As^V was oxidized to a condition where it was compatible with CCA treating solutions and could be re-used for treating new wood.

1. Introduction

There was a rapid expansion of the use of chromated copper arsenate (CCA) wood preservative between 1975 and 1990, as a result of high consumer acceptance of the product for decks, fences and other residential applications (Cooper 1993). It is therefore expected that in the next two decades, the amounts of CCA treated wood that will be removed from service will expand greatly to approximately 12 million m³ per year in Canada and the USA.

Currently Canadian and American environmental regulations allow the disposal of CCA treated lumber in landfills and most of the out-of-service or "spent" treated wood ends up in landfills. In the future, treated wood will use increasing volumes of landfill space.

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The cost of disposal varies greatly with the municipality responsible for the site and the type of site (e.g., lined vs unlined). However the disposal of CCA treated wood is becoming an increasing concern with regulators (Solo-Gabriele *et al.* 1999) and alternative disposal options are required.

The increased production of CCA treated wood was accompanied by expansion of the CCA treating capacity in North America. This, in combination with improved environmental controls to recycle dripped chemical and to collect all contaminated residues has resulted in significant amounts of contaminated plant wastes that are listed as hazardous wastes and require more costly disposal in hazardous waste sites. If it is assumed that each of the approximately 55 CCA plants in Canada disposes of 6-300kg drums per year, there are about 100 Tonnes of this waste generated per year in Canada. Wastes from treating plants consist of used filters, solution tank sludges, sump sludges, dirt, sawdust and plant sweepings. This material is collected, dried and disposed of by hazardous waste companies at a higher cost because of the extra controls required on transportation and containment security of the disposal site. In Canada, typical cost for disposal of this material is \$ 300/drum.

An environmentally sound and cost effective recycling method for CCA treated wood and other wastes will help alleviate the landfill and potential chromium and arsenic contamination problems. A number of alternative approaches have been evaluated:

- Burning/incineration of spent CCA treated wood in incinerators (Nurmi 1996; Hirata *et al.* 1993) or cement kilns (Bernardin 1995);
- Reuse of spent CCA treated wood to make composites such as wood-cement, OSB boards, etc. (Huang and Cooper 1999, Cooper *et al.* 1998; Vick *et al.* 1996);
- Use of biological or biotechnological method to detoxify spent treated wood (Burgstaller and Schinner 1993; Stephan and Peek 1992);
- Chemical extraction of CCA from spent treated wood (Kamdem *et al.* 1998; Kazi and Cooper 1998; Smith and Shiau 1997; Pasek and McIntyre 1993; Honda *et al.* 1991) prior to disposal or reuse.

In the present studies, we are looking at chemical extraction methods where we extract CCA salts from spent wood or sludge using a suitable reagent. The extract, containing mostly Cr^{III} , Cu^{II} and As^{V} can be treated to oxidize the chromium to Cr^{VI} resulting in material that is compatible with fresh CCA treating solution. Thus, the rejuvenated CCA solution can be used to treat wood in a closed loop treating process.

Generally a catalyst or an oxidizing agent is needed to accelerate the oxidation process. Commonly used catalyst or oxidizing agents are: Ozone (O_3) (Schroeder and Lee 1975); Mn(III,IV) (hydro)oxides (Bartlett and James 1979; Amacher and Baker 1982; James and Bartlett 1983); persulfuric acid (Franco 1997); NaOH, hydrogen peroxide (H_2O_2) and perchloric acid (Pal and Tarafder 1996). Aqueous hydrogen peroxide could be a convenient oxidizing agent where solid-liquid interface poisoning can be avoided. Commercially hydrogen peroxide is available at a concentration of 30-

90% suitable for oxidation in water or water miscible solvents. It is generally very stable to active oxygen loss and is a powerful oxidizing agent in acid media. The redox potential of H_2O_2 in acid media is 1.76 V (Ardon 1965) which is favourable for Cr^{III} oxidation (Blessa *et al.* 1994). Sodium hypochlorite was also recognized as a relatively low cost reagent that can significantly convert Cr^{III} to Cr^{VI} (Taylor *et al.* 1999).

In this study, we used hydrogen peroxide to extract fixed CCA components from treated wood at a moderately low temperature to minimize the extraction of wood components. Freshly extracted leachates containing Cr^{III} , Cu^{II} and As^V were oxidized shortly after extraction to avoid aging by dilute aqueous hydrogen peroxide in acidic or neutral media. The oxidation of Cr^{III} by hydrogen peroxide was conducted at elevated reaction temperature in a multistage oxidation reaction process to maximize the conversion of Cr^{III} to Cr^{VI} . For sludges, hydrogen peroxide consumption was excessive, so a different extraction and oxidation procedure was used. Sludge was treated with sodium hypochlorite to simultaneously oxidize chromium and extract chromium and arsenic. The remaining sludge was extracted with phosphoric acid to remove copper and some residual chromium and arsenic and the extract oxidized with sodium hypochlorite.

2 Materials and Methods

2.1 Extraction of treated wood

In a preliminary study (Kazi and Cooper 1998) a number of organic and inorganic acids and oxidizing agents were evaluated for their ability to extract CCA components. The effects of extractant concentration, temperature and time of extraction on efficiency of copper, chromium and arsenic removal were determined (Figures 1 – 3). Based on these results, we decided to focus on hydrogen peroxide, since it was an efficient extracting agent, and under certain conditions, could also oxidize the trivalent chromium to soluble hexavalent chromium, necessary to recycle the solution for wood treatment.

Part of the treated portion of a chromated copper arsenate Type C (CCA-C) treated Southern Yellow Pine (SYP – various *Pinus* species) lumber was removed with a power planer. Dry treated sawdust samples were analyzed by x-ray fluorescence spectroscopy (XRF) using an OXFORD Lab-X-3000 spectrometer 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 salts fixed on wood matrix using aqueous H_2O_2 solution. Experiments were carried out at 4 different reaction temperatures - 30, 50, 70 and 90°C, 5 different H_2O_2 concentrations - 0.62, 1.25, 2.5, 5.0 and 10.0%, and for 8 reaction time intervals - 0, 0.5, 1, 2, 3, 4, 5 and 6 hours. For each series, 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 filtered and leachate for oxidation experiments and for chemical analysis. The extracted wood samples were washed, dried

and re-analyzed by XRF. Samples that showed almost complete extraction of CCA components by XRF were digested with a mixture of 30% H₂O₂ and concentrated H₂SO₄ (Piper 1950) and the digested fluid analyzed for Cr, Cu and As content by Inductively Coupled Plasma Emission Spectrometer (ICP-ES).

The oxidation of chromium with aqueous H₂O₂ was optimized for time, temperature and H₂O₂ concentration. During oxidation reactions Cr^{VI} in the reaction products was measured quantitatively using the diphenylcarbazide method (ASTM D1687-86, 1987) by UV-VIS spectrophotometer at a wavelength of 540 nm.

To evaluate the feasibility of reusing the recovered CCA solution for wood treatment, the rejuvenated CCA solution was mixed with fresh CCA-C solution at a ratio of 1:3 and 1:2. The CCA-C concentration was adjusted to 1.0 % in all cases. The compatibility of rejuvenated CCA was compared with fresh CCA-C solution by monitoring the concentration of Cr^{VI} and the pH of the solutions for more than 2 months. The three sets of mixed CCA-C solution were used to vacuum treat 19mm red pine wood cubes (20 minutes at 20 kPa absolute pressure). The cubes were incubated at saturated humidity and a temperature of 60°C until fixation was complete. The fixation process was followed over this period by removing CCA treated blocks periodically from the incubator and squeezing them in a press at approximately 60 MPa to express treating solution from the wood void space. The expressed solution was analyzed for unfixed Cr^{VI} quantitatively using the diphenylcarbazide method and the percentage fixation calculated. When chromium reduction was complete in the wood blocks, they were subjected to a standard leaching test following the AWWA E-11 (1996) standard. The leachate was analyzed for Cr (total), Cu and As by Inductively Coupled Plasma Emission Spectrometer (ICP-ES) and the percentage of CCA components leached from the wood over the two week leaching cycle compared for the different treating solutions.

2.2 Extraction of sludges

Attempts to use hydrogen peroxide to extract and rejuvenate CCA components from sludges were not successful because of interactions with other sludge components such as waxes and other additives and dirt contaminants. Based on our observation (Taylor *et al.* 1999) that sodium hypochlorite was effective at oxidizing and extracting chromium from wood, we evaluated the effects of solution concentration, extraction time and temperature on efficiency of extraction and oxidation of chromium. This treatment was effective for the removal of chromium, and to a lesser extent arsenic, but did not remove copper effectively. We selected phosphoric acid as a secondary treatment since it is effective at extracting copper and other CCA components from treated wood (Figure 2) and is known to be compatible and relatively effective in copper/chrome preservatives (Tillott and Coggins 1981). The effects of the above processing variables were also evaluated to optimize this treatment. The hypochlorite extraction oxidized most of the chromium removed during the extraction. This resulted

in a solution ready for reuse. The phosphoric acid extract, on the other hand, had to be treated with an oxidizing agent and sodium hypochlorite was used for this. The efficiency of extraction under different extraction conditions and oxidation of chromium and compatibility of rejuvenated CCA solution were evaluated as above. Three types of industrial generated sludge were treated in this way.

3 Results and Discussion

3.1 Treated wood

The efficiency of extraction with H_2O_2 increased greatly with increased temperature (Figure 4), increased concentration (Figure 5) and increased extraction time (Figure 6). Copper was always the easiest element to remove and arsenic the most difficult. Of the conditions evaluated, the most efficient extraction was for conditions of 6 hours of extraction at a constant temperature of $50^\circ C$ and aqueous H_2O_2 concentration of 2.5%. Use of a more concentrated solution at a higher temperature should be even more efficient. Treating parameters were selected for a scaled up trial that were thought to best minimize processing costs. In the present studies, extraction temperature, time and H_2O_2 concentration were selected as $50^\circ C$, 6 hours and 10% respectively. A lower extraction temperature was chosen to avoid unwanted reactions of hydrogen peroxide with wood components that would consume more chemicals and produce organic byproducts since these byproducts would further consume H_2O_2 during the oxidation step of the process. Longer extraction and higher hydrogen peroxide concentration were selected to attempt to extract CCA elements completely from the sawdust.

In the treated sawdust the concentrations of Cu, Cr and As as elements were 0.27, 0.67 and 0.45% respectively (Table 1). After extraction with 10% H_2O_2 at $50^\circ C$ for 6 hours the amounts of CCA components extracted were determined by Inductively Coupled Plasma Emission Spectrometer (ICP-ES) to be approximately 95% Cu, 94% Cr and 97.5% As (Table 1).

The Cr^{III} oxidation obtained experimentally as a function of temperature, time, H_2O_2 concentration and the number of stages are shown in Figures 7 to 10. At a fixed reaction period of one hour and aqueous H_2O_2 concentration of 2.5%, the percentage of Cr^{III} increased exponentially with increasing oxidation temperature (Figure 7). A threshold oxidation temperature of more than $80^\circ C$ was observed, below which no oxidation occurred. A maximum conversion of Cr^{III} to Cr^{VI} of 21% occurred at a reaction temperature of $140^\circ C$ with 2.5% H_2O_2 and a reaction time of one hour. In subsequent studies we selected $100^\circ C$ as the optimized oxidation temperature to simplify the process and avoid the need to operate in a pressurized vessel.

The effect of time on the percentage of chromium oxidation was studied at two moderately high temperatures of 90 and $100^\circ C$ with 2.5% H_2O_2 (Figure 8). At reaction times of 30 minutes or less, there was essentially no oxidation of the trivalent chromium. The percentage of Cr^{III} oxidation in the first stage reached a maximum value of 8.5 at $90^\circ C$ and 11.6% at $100^\circ C$ in one hour of oxidation. Longer reaction periods

did not show appreciable improvements on the efficiency of oxidation at either temperature. In fact at 100°C, the efficiency dropped at longer times. This yield loss could be due to the formation of chromium polymers via condensation reactions of Cr^{VI} anions in acid media (Funahashi *et al.* 1978). Based on these observations, we selected an oxidation duration of 1 hour for the first oxidation stage to gain maximum conversion.

There was no apparent improvement in chromium oxidation with increased H₂O₂ concentration above 2.5% (Figure 9). This concentration was selected for additional studies.

To try to improve on the percentage of chromium oxidation, the effect of multi stage oxidation was studied at two different reaction temperatures of 90 and 100°C using 2.5% aqueous H₂O₂ solution. Concentrated H₂O₂ (20%) solution was added to the extracted CCA solution until the concentration reached 2.5%. Results show that with increasing number of oxidation stages the cumulative percentage of oxidation was increased and reached a maximum value of 56% (at 100°C) after 5 consecutive oxidation stages (Fig 10). Additional oxidation stages did not increase the percentage of oxidation, probably because the equilibrium conversion stage at that experimental condition was reached. The effect of temperatures on multi stage oxidation appeared to be insignificant over the temperature range (90-100°C) studied.

For multi stage oxidation studies, we selected oxidation temperature and hydrogen peroxide concentration as 100°C and 2.5% respectively (similar to that of the first stage oxidation). The oxidation duration was the only parameter optimized for 2nd, 3rd and 4th stages. After completion of the first stage oxidation the second stage begins with the addition of a dose of concentrated (20%) H₂O₂ solution into the reacting system to bring H₂O₂ concentration in the reaction mixture to a level of 2.5%. In our optimization studies we have calculated the cumulative percentage of oxidation. So at zero time of the second stage, the percentage of oxidation is that obtained after the completion of the first stage oxidation. In second stage we observed that the percentage of oxidation increased with time as was expected and reached a maximum value in 30 minutes, after that it dropped a few percentage points and remained unchanged over the reaction duration studied. In the second stage, the cumulative percentage of oxidation increased from 11.6 to 31.2% when the oxidation duration was increased from 0 to 30 minutes respectively, and remained almost unchanged to a value of 28% even at the end of 2 hours of oxidation. A small variation of the percentage of oxidation over time could be due to experimental errors. Therefore we selected the optimum duration for the second stage oxidation as 30 minutes. A similar experimental approach was used to optimize the third and fourth oxidation stages. With increasing oxidation time, the cumulative percentage of oxidation in the third stage increased linearly then leveled off in 15 minutes at approximately 51%. In the fourth stage, similar oxidation behavior was observed. At the end of 30 minutes the cumulative percentage of oxidation reached a maximum value of 58%. There was a sharp drop in % oxidation at about 5 minutes to 23% oxidation; this apparently resulted from the sudden addition of 20% hydrogen

peroxide. After addition of the H_2O_2 , Cr^{VI} was reduced temporarily then gradually converted back to Cr^{VI} .

The cumulative percentages of oxidation obtained for the different stages are shown in Fig. 13. The results show that the percentage of oxidation increased sharply up to 3 stages then leveled off at the fourth stage. This behaviour could be due to reaching the conversion equilibrium at the experimental conditions studied.

For the evaluation of the recovered solution for its suitability for treating new wood, several liters of rejuvenated (oxidized leachate) CCA solution were prepared using three conversion stages and the optimized process parameters. The 1% solutions with different amounts of recovered solution and mixed with fresh CCA-C solution had similar initial Cr^{VI} concentrations as the control solution. Over the more than two month monitoring period, the Cr^{VI} concentrations did not change appreciably, indicating that the recovered solution is compatible with fresh CCA solution and did not result in destabilization of the solution. Similarly, the pH's of the solutions were identical over the test period, another indication that addition of the recovered solution did not destabilize the CCA solution.

There were no significant differences in the rates of chromium fixation at $60^\circ C$ (rate of conversion from Cr^{III} to Cr^{VI}) among the fresh CCA solution and the mixtures of recovered solution and fresh solution (Figure 11). Similarly there were no significant differences in the average concentration of CCA components in the leachate of water extracted samples for the different solutions (Figure 12). These results confirm that CCA treating solution amended with recycled CCA recovered from CCA treated wood is not impaired in any way and can be used for commercial treatment of wood.

Economic feasibility

The chemical and energy cost components of the total variable cost of CCA extraction and re-oxidation with hydrogen peroxide are approximately \$310 per tonne of wood. It is evident that the treatment might have application only for surface removed (e.g. planed) treated wood, or sawdust byproducts of a re-sawing operation. If the system could be used to economically extract whole wood samples, as evaluated for other systems by Kamdem *et al.* (1998) it would be more practical.

Assumptions: (1) Value of recovered CCA is \$6.60/dry kg (oxides basis); (2) Heat Energy cost is \$0.042/kWh; (3) Cost of 50% H_2O_2 is \$1.33/kg; (4) Disposal cost for extracted waste is \$90/T; (5) wood is reused not landfilled.

3.2 *Sludge recycling*

The characteristics of five industrial sludges collected for the study are summarized in Table 2. It is clear that the composition depends on the source of the sludge. Some samples had CCA components in approximate proportion to that in the treating solutions, while others were predominantly chromium arsenates, as had been observed by Michel (1995).

Over the temperature range evaluated, there was little effect of temperature on efficiency of extraction of CCA components with sodium hypochlorite, as estimated by the X-ray fluorescence analysis of the residual sludge (Figure 13). In all cases, more than 90% chromium was removed. Estimates of chromium oxidation based on chromium analysis by the diphenylcarbazide method suggest that an even higher proportion of chromium was extracted, all as oxidized chromium. Arsenic was also significantly extracted (about 80%) but copper was not (about 10%). Similarly, extraction/reaction time between 0.5 to 3 hours had little effect on Cr, As and Cu extraction (Figure 14). Efficiency of chromium oxidation increased with ratio of hypochlorite to sludge (Figure 15). For laboratory evaluation of the first extraction/oxidation stage, sludge was treated with 5.25% hypochlorite at 100°C for 2 hours with a hypochlorite to sludge ratio of 150. It is evident from Figures 13-15 that the extraction process may be further optimized.

For the second stage extraction with phosphoric acid, the copper could be removed almost completely by 2 hours extraction at 100°C with 2.5% H_3PO_4 (Figure 16). This treatment also removed most of the residual chromium and arsenic. The residual chromium in this extract could be partially oxidized by treatment with 5.25% sodium hypochlorite. This conversion was optimized (25-30%) at a leachate to oxidant ratio of 10, which resulted in a pH of about 2 in the mixture (Figure 17).

The recovered solutions, when mixed with fresh treating solution are still stable after 7 months. Tests are underway to evaluate the impacts of the recycled solution on CCA fixation rates and leaching of CCA components.

Economic Feasibility

When the variable costs for the extracting chemicals and energy are considered assuming that the extractants can be purchased at the lowest costs available (e.g. hypochlorite for pulp bleach), the savings on reduced disposal costs and value of recovered chemical exceed the chemical and energy variable costs using the assumptions shown in Table 3. We have not considered the capital costs and the other operating costs. Other considerations are the benefits of reducing hazardous landfills with this material and the potential for using multiple stage extractions that could more efficiently use the extracting chemicals.

5 Summary and Conclusions

Most of the CCA components can be extracted from treated wood particles by 10% aqueous hydrogen peroxide at a relatively low temperature of 50°C in 6 hours. The solution, containing extracted chromium(III) can be oxidized with dilute aqueous hydrogen peroxide at elevated temperature (>80°C) and low pH. The percentage of oxidation in the present studies was maximized to a cumulative value of 51% in three stages at reaction temperature of 100°C in 105 minutes.

The oxidized leachate (rejuvenated CCA) was compatible with freshly prepared CCA-C solution even at high ratios of recovered solution to fresh CCA-C (1:1).

The mixture of rejuvenated/fresh CCA-C solution behaves similarly to that of fresh CCA-C solution in compatibility, fixation and leaching tests.

Treating plant sludges were not efficiently extracted with hydrogen peroxide, but most of the CCA components could be removed with sequential extraction with sodium hypochlorite and phosphoric acid. The hypochlorite simultaneously extracted and oxidized the chromium and removed much of the arsenic and only a small amount of copper. A second extraction with phosphoric acid removed most of the copper and remaining chromium and arsenic. This extract could be further treated with sodium hypochlorite to oxidize enough of the chromium to allow both solutions to be mixed with CCA working solution for treatment of wood. Preliminary tests show that this mix is also stable in solution and does not affect the fixation and leaching stability of the working solution.

References

1. Amacher, M.C. and D.A. Baker. 1982. Redox Reactions Involving Chromium, Plutonium, and Manganese in Soils. Final Report, DE-ASO8-77DPO4515. Inst. For Res. on Land and Water Resour., Penn. State Univ.
2. Ardon, M. 1965. Oxygen: Elementary Forms and Hydrogen Peroxide. W.A. Benjamin, Inc. New York. p. 87.
3. ASTM D1687-86. 1987. Annual book of ASTM standards. Standard test method for chromium in water. Vol. 11.01. Philadelphia, PA.
4. AWWA E11-86. 1996. American Wood Preservers' Association Standards. Woodstock, Maryland, pp.316-317.
5. Bartlett, R. and B. James. 1979. Behaviour of chromium in soils. III. Oxidation. *Journal of Environmental Quality*. 8, 31-35.
6. Bernardin, G. 1995. St. Lawrence Cement. Proceedings of the CITW Life Cycle Assessment Workshop. June 20-21. Canadian Institute of Treated Wood, Ottawa, Ont.
7. Blesa, M.A., P.J. Morando and A.E. Regazzoni. 1994. Chemical dissolution of metal oxides. CRC Press Inc. USA.
8. Burgstaller, W. and F. Schinner. 1993. Leaching of metal with fungi. *Journal of Biotechnology*, 27, 91-116.

9. Cooper, P.A. 1993. Disposal of preservative treated wood-the issues. *In: Environmental Considerations in the Manufacture, Use and Disposal of Preservative-Treated Wood*. Forest Product Society, Madison, Wisconsin, USA. Pp. 85-90.
10. Cooper, P.A., Y.T. Ung, C. Huang and X. Wang. 1998. Cement bonded boards using CCA-treated wood removed from service. *In: Inorganic bonded wood and fiber composite materials*, vol. 6, pp. 330-348.
11. Franco, G. 1997. Process to Recover Poles or Other Elements of Impregnated Wood and the Respective Impregnation Substances in Solution Form, and to Regenerate Said Solution. European Patent, EP 0 774 330 A1.
12. Funahashi, S., F. Uchida, and M. Tanaka. 1978. Reactions of hydrogen peroxide metal complexes. 3. Thermodynamic and kinetic studies on the formation, dissociation, and decomposition of peroxochromium(VI) complexes in acid media. *Inorganic Chemistry*, 17(10), 2784-2789.
13. Hirata, T., Inoue, M. and Y. Fukui. 1993. Pyrolysis and combustion toxicity of wood Treated with CCA. *Wood Science and Technology*, 27, 35-47.
14. Honda, A., Kanjo, Y., Kimoto, A., Koshii, K. and S. Kashiwazaki. 1991. Recovery of copper, chromium and arsenic compounds from the waste preservative-treated wood. International Research Group on Wood Preservation, Document IRG/WP/3651.
15. Huang, C. and P.A. Cooper. 1999. Wood cement composites using spent CCA treated wood. International Research Group on Wood Preservation, Document IRG/WP 99-50126.
16. James, B.R. and R.J. Bartlett. 1983. Behaviour of chromium in soils. VI. Interactions between oxidation-reduction and organic complexation. *Journal of Environmental Quality* 12, 173-176.
17. Kamdem, D.P., W. Ma, J. Zhang and J. Zyskowski. 1998. Recovery of copper chromium and arsenic from old CCA treated commodities. IRG/WP 98-50118.
18. Kazi, K.M.F. and P.A. Cooper. 1998. Solvent extraction of CCA-C from out-of-service wood. International Research Group on Wood Preservation, Document IRG/WP 98-50107.
19. McMahon, C.K., P.B. Bush and E.A. Woolson. 1986. How much arsenic is released when CCA treated wood is burned? *Forest Products Journal*. 36(11/12), 45-50.
20. Michell, A.J. 1995. FTIR studies of sludges from copper-chrome-arsenate wood preservative formulations. *Holzforschung*. 49(3):217-221.
21. Nurmi, A.J. 1996. Disposal of CCA treated waste wood by combustion: An industrial scale trial. International Research Group on Wood Preservation, Document IRG/WP 96-50068.
22. Pal, S.C. and M.T.H. Tarafder. 1996. Kinetics and mechanism of oxidation of two new chromium(III) complexes by hydrogen peroxide. *Indian Journal of Chemistry*, 35A, 960-963.
23. Pasek, E.A. and C.R. McIntyre. 1993. Treatment and recycle of CCA hazardous waste. International Research Group on Wood Preservation, Document IRG/WP 93-50007.

24. Piper, C.S. 1950. Soil and plant analysis. Interscience Publishers, Inc., New York
25. Schroeder, D.C. and G.F. Lee. 1975. Potential transformations of chromium in natural waters. *Water Air Soil Pollution* 4, 355-365.
26. Smith, R.L. and R.J. Shiau. 1997. Steam processing of treated waste wood for CCA removal. Chapter 4. In: Final Report to SRBEP of the Tennessee Valley Association.
27. Solo-Gabriale, V. Calitu, M. Kormienko and T. Townsend. 1999. Disposal of CCA-treated wood. An evaluation of existing and alternative management options. State University System of Florida. Florida Center for Solid and Hazardous Waste Management. Report No. 99-XX Draft.
28. Stephan, I. and R.D. Peek. 1992. Biological detoxification of wood treated with salt preservatives. International Research Group on Wood Preservation, Document IRG/WP 3717-92.
29. Taylor, A., P.A. Cooper, Y.T. Ung. 1999. Effects of deck washes and brighteners on the leaching of CCA components. IRG/WP 99-50128.
30. Tillott, R.H. and C.R. Coggins. 1981. Non-arsenical waterborne preservatives – A review of performance and properties. *Rec. Ann, BWPA Convention*. 32-46.
31. Vick, C.B., R.L. Geimer and J.E. Wood, Jr. 1996. Flakeboards from recycled CCA-treated southern pine lumber. *Forest Products Journal*, 46(11/12): 89-91.

Table 1: Summary of extraction efficiency from CCA treated wood. 10% H₂O₂ at 50°C for 6 hours.

CCA Component	Sample	Initial concentration in sawdust (%)	Concentration after extraction (%)	Percent extracted	Average
Cu	1	0.269	0.011	96.0	94.8
	2	0.269	0.017	93.6	
Cr	1	0.674	0.032	95.3	94.0
	2	0.674	0.050	92.6	
As	1	0.415	0.004	99.2	97.5
	2	0.415	0.019	95.9	

Table 2: Characteristics of Five Industrial Sludges Evaluated

Sludge Description	CCA Component % Concentration (Oxides)			
	Copper	Chromium	Arsenic	Total
Fine textured green material from in line filter (Aged)	11.9	23.5	40.5	75.9
Fine textured green material from in line filter (Relatively fresh: 1 year old)	3.6	39.6	50.8	94
Fine textured green material from in line filter (Fresh)	18.9	19.3	19.2	57.4
Dark waxy material containing wax	0.8	10.4	7.1	18.3
Sump pits containing sand	6.5	14.3	11.2	32

Table 3: Economic Analysis of CCA Recovery from Sludge (all values for 1 Tonne sludge) – chemical and energy costs only

[CCA] –Oxides in Sludge (%)	NaOCl (\$)	H ₃ PO ₄ (\$)	Heat Energy (\$)	Total Cost (\$)	Value of recovered CCA (\$)	Saved Disposal Cost (\$)	Net Gain (\$)
10	412	190	76	678	660	919	901
20	825	380	152	1357	1,320	928	891
70	2888	1330	532	4750	4,620	973	843

Assumptions: (1) Value of recovered CCA is \$6.60/dry kg (oxides basis); (2) Heat Energy cost is \$0.042/kWh; (3) Cost of 5.25% NaOCl is \$0.0275/kg (rate for in plant manufacture of NaOCl, e.g., for pulp mills); (4) Cost of phosphoric acid is \$ 1.00/kg; (5) Disposal cost for all sludge waste is \$1000/T and for extracted waste is \$90/T.

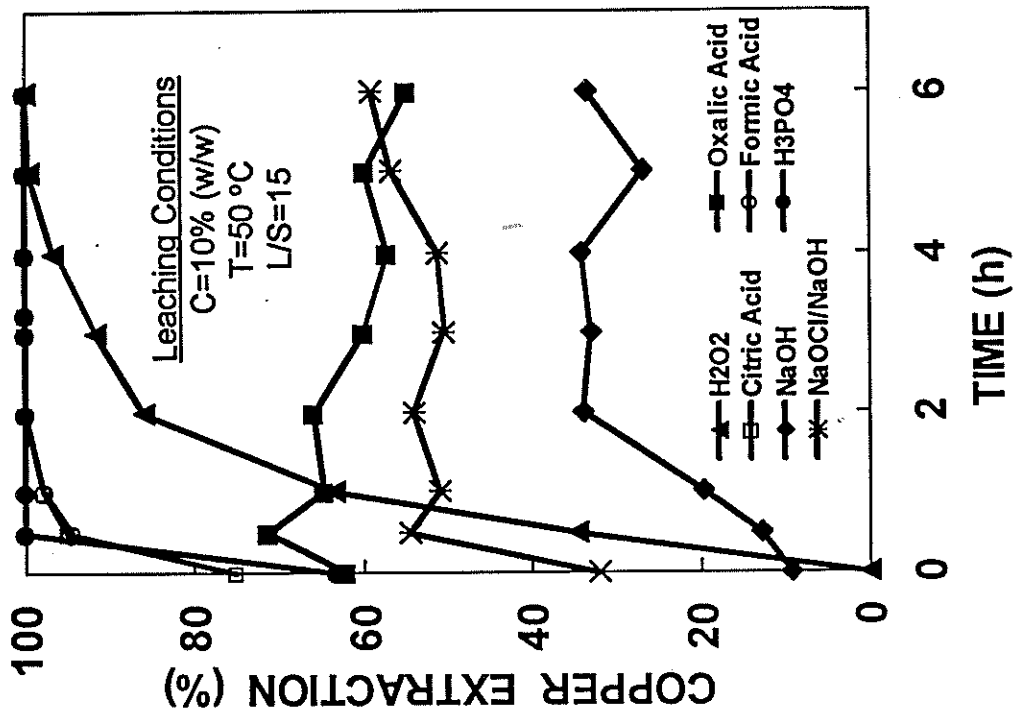


Figure 2. Rate of copper extraction at 50 °C when 10% (w/w) solution of different leaching agents were used.

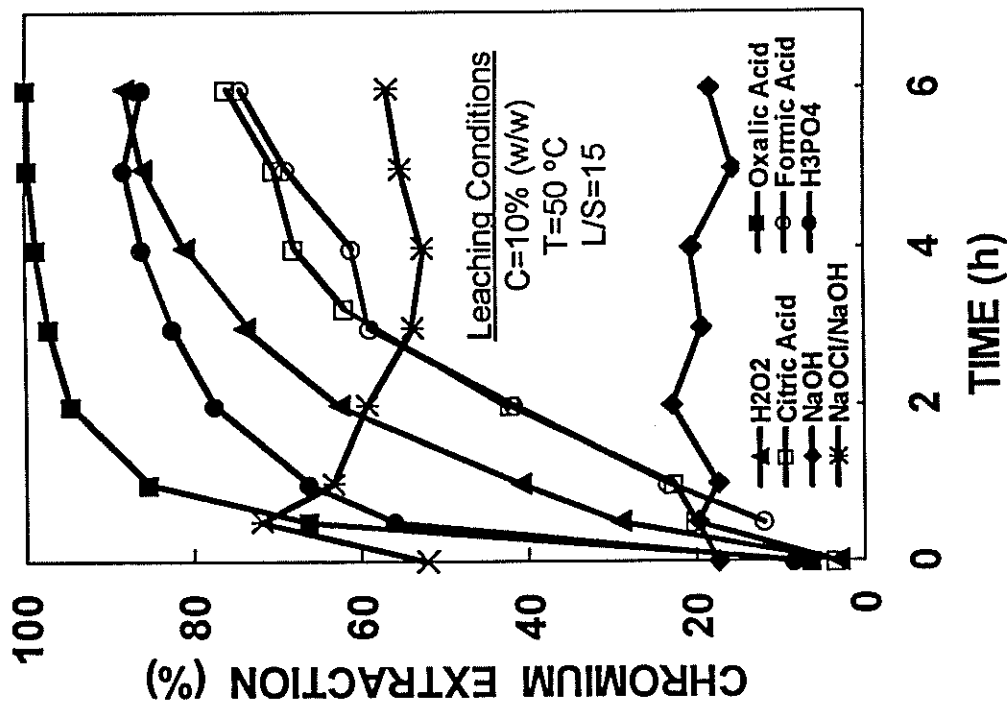


Figure 1. Rate of chromium extraction at 50 °C when 10% (w/w) solution of different leaching agents were used.

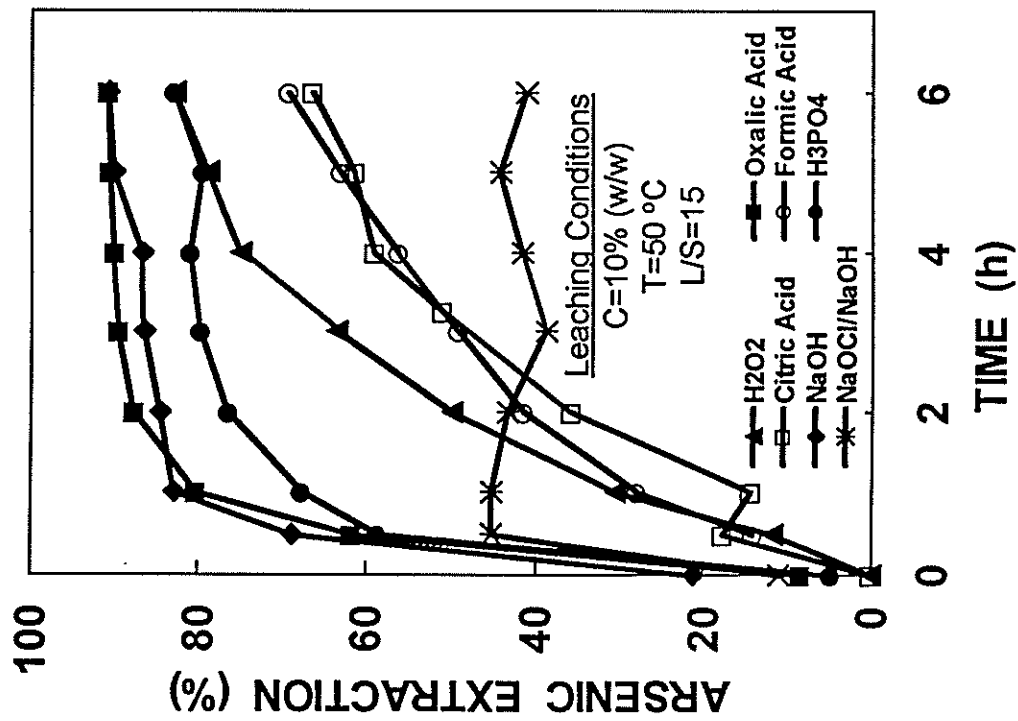


Figure 3. Rate of Arsenic extraction at 50 °C when 10% (w/w) solution of different leaching agents were used.

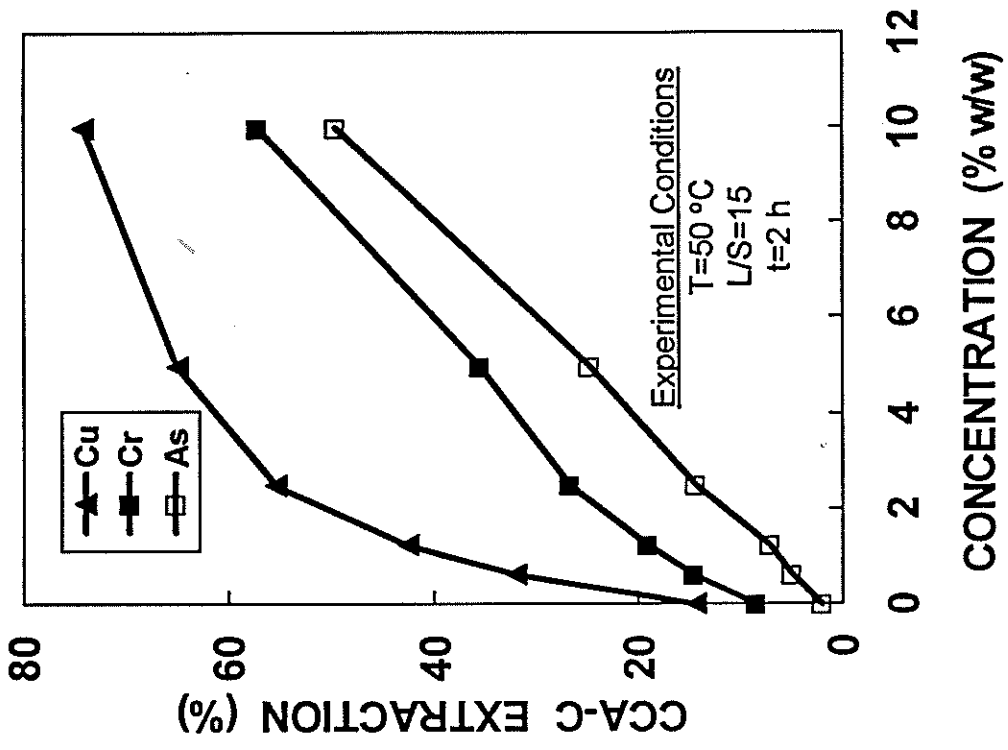


Figure 5. Effect of H_2O_2 concentration on CCA-C extraction from wood at $50\text{ }^{\circ}\text{C}$ for 2 hours ($L/S=15$)

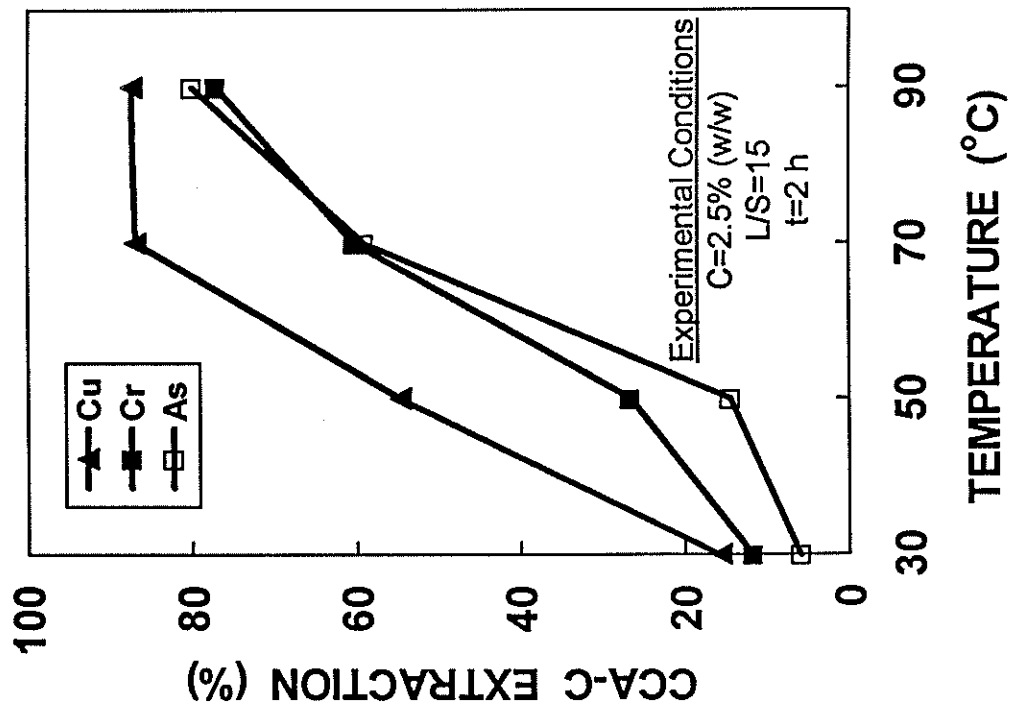


Figure 4. Effect of temperature on CCA-C extraction from wood with $2.5\% \text{ H}_2\text{O}_2$ for 2 hours ($L/S=15$)

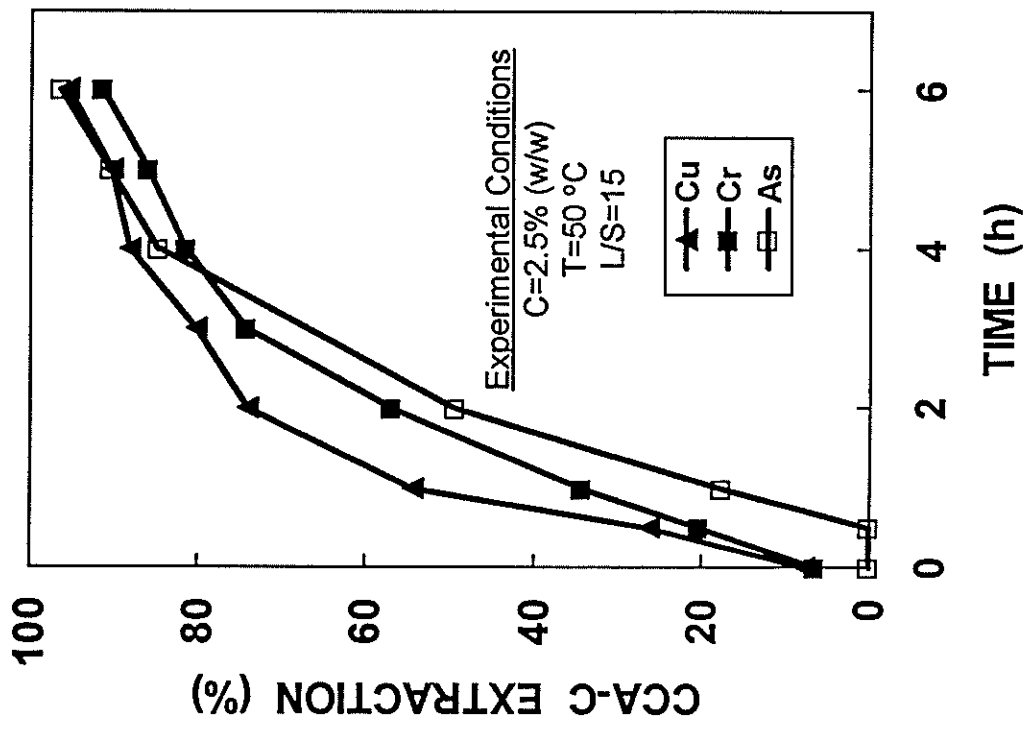


Figure 6. Effect of time on CCA-C extraction from wood with 2.5% H₂O₂ at 50 °C (L/S=15)

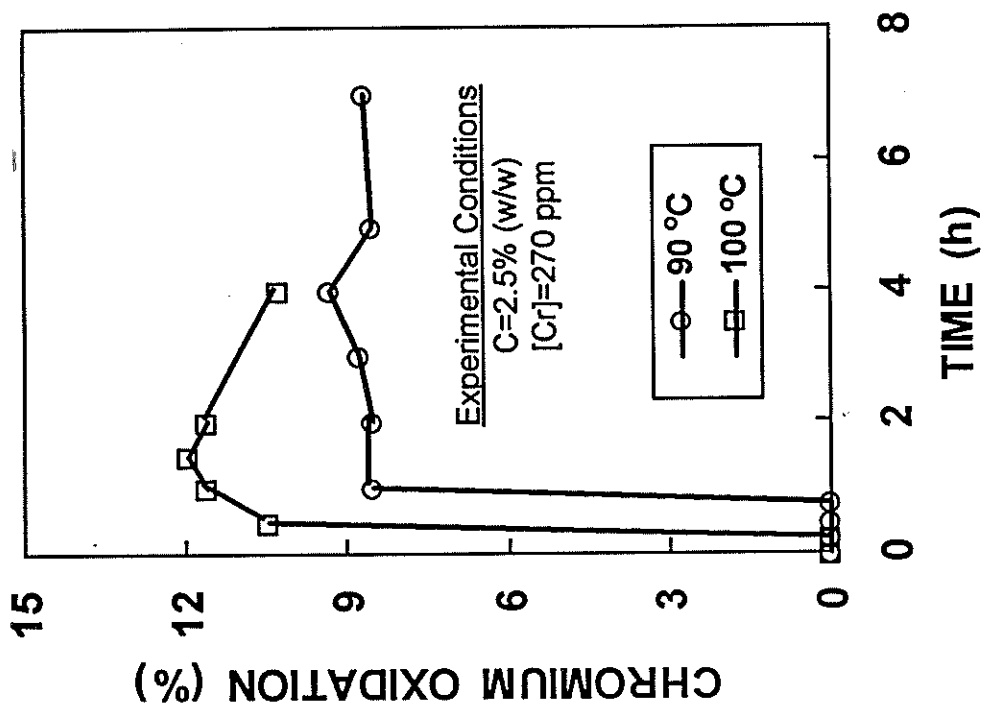


Figure 8. Effect of time on oxidation of extracted chromium with 2.5% H₂O₂ at two different temperatures of 90 and 100 °C. Total [Cr] =270 ppm

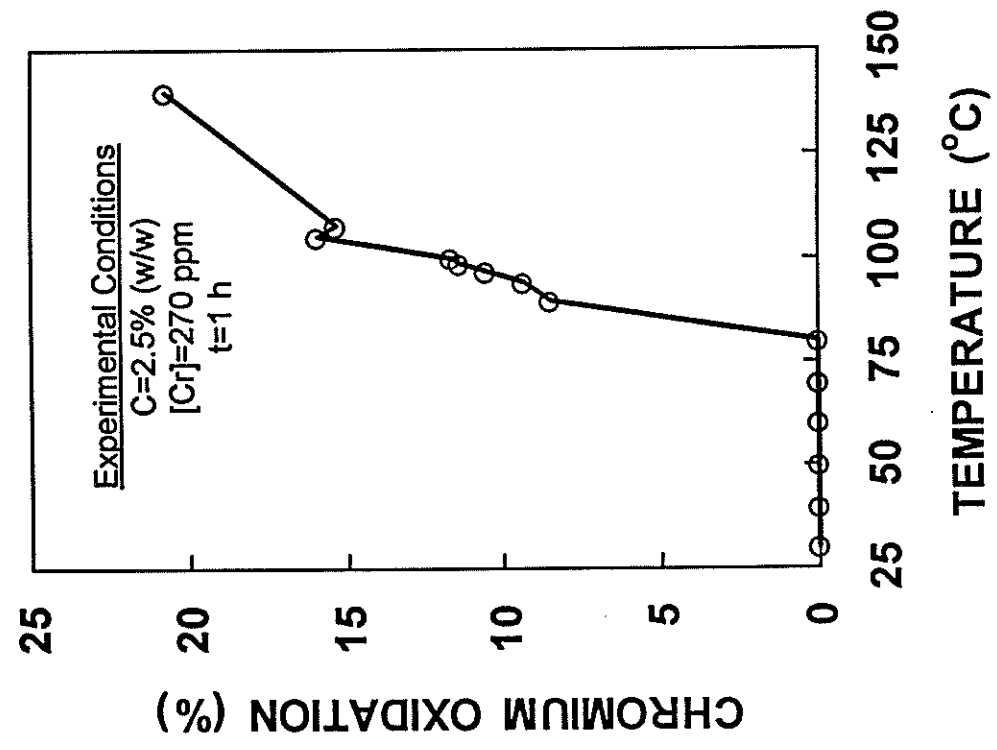


Figure 7. Effect of temperature on oxidation of extracted chromium with 2.5% H₂O₂ (1 hour reaction). Total [Cr] =270 ppm

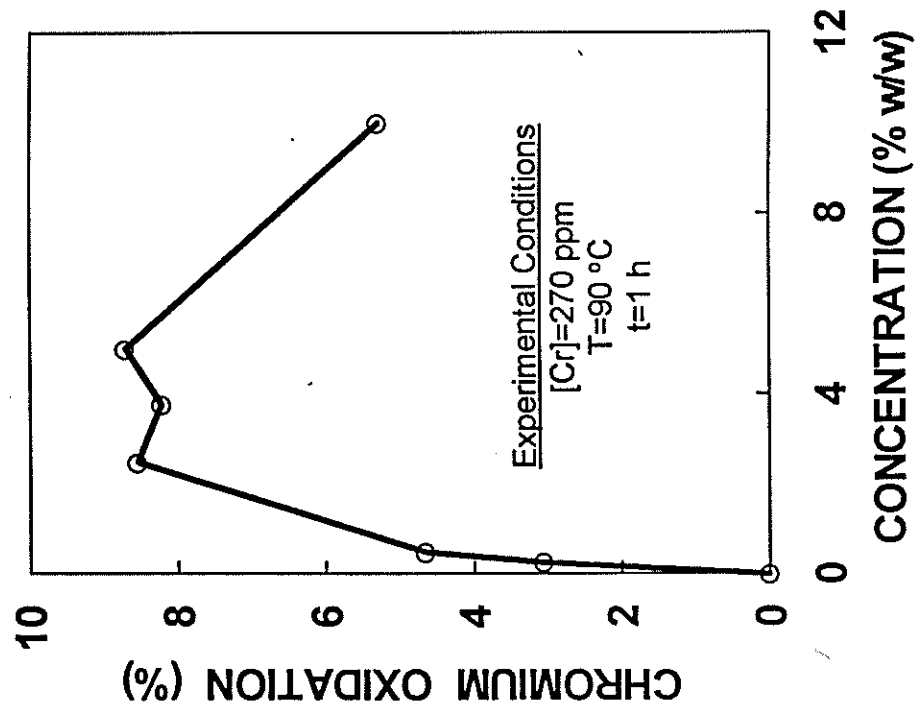


Figure 9. Effect of H₂O₂ concentration on oxidation of extracted chromium at 90 °C for 1 hour. Total [Cr] =270 ppm

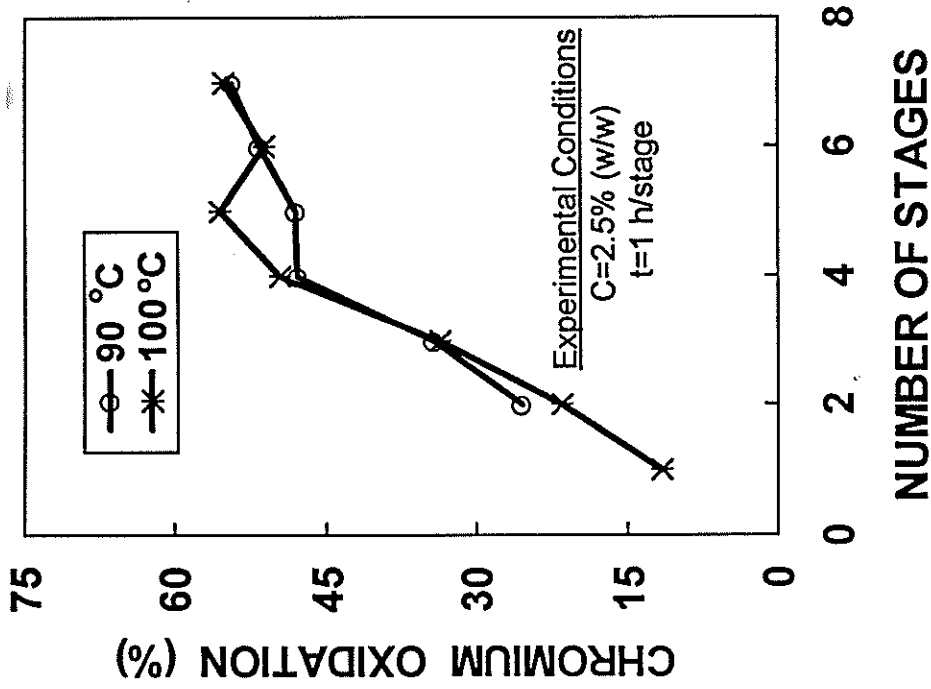


Figure 10. Effect of number of reaction stages on oxidation of extracted chromium at two different temperatures of 90 and 100 °C with 2.5% H₂O₂ for 1 hour in each stage

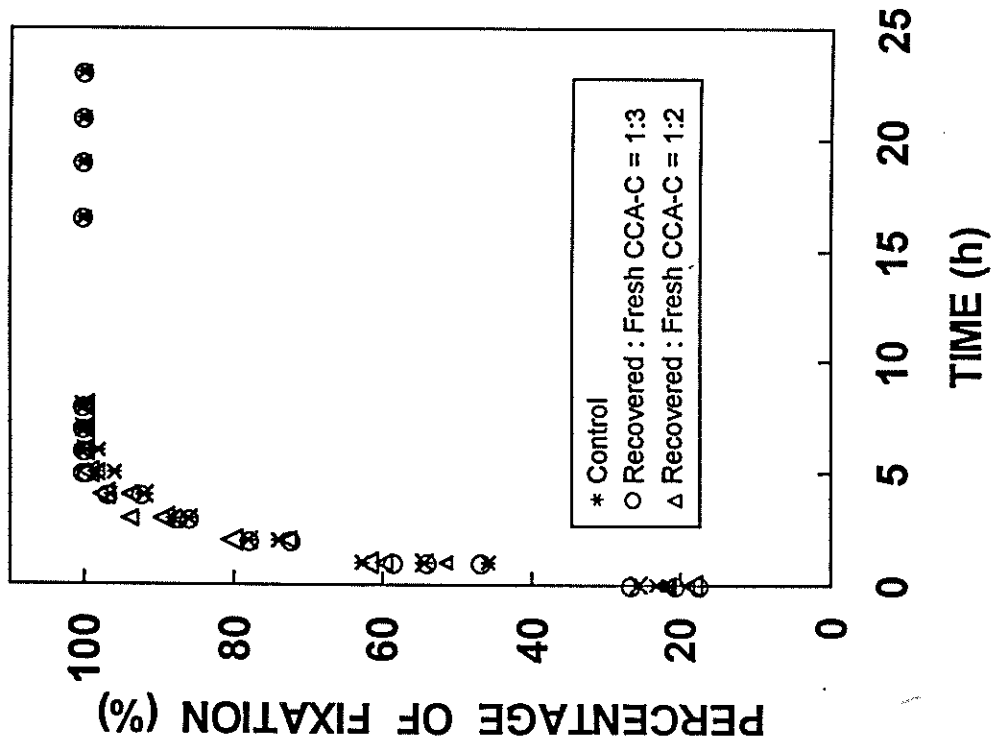


Figure 11. Comparison of fixation rates of fresh CCA and solution containing recovered CCA. Fixation was done at 60 °C.

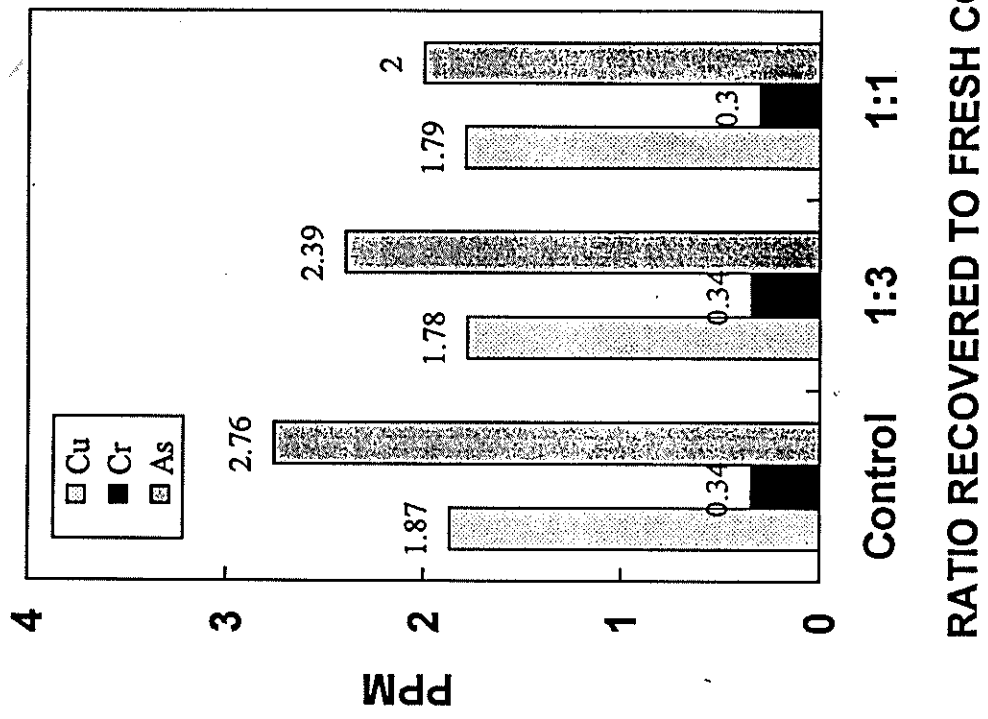


Figure 12. Comparison of leaching results (AWPA E11-87) of blocks treated with fresh CCA and with solutions containing recovered CCA.

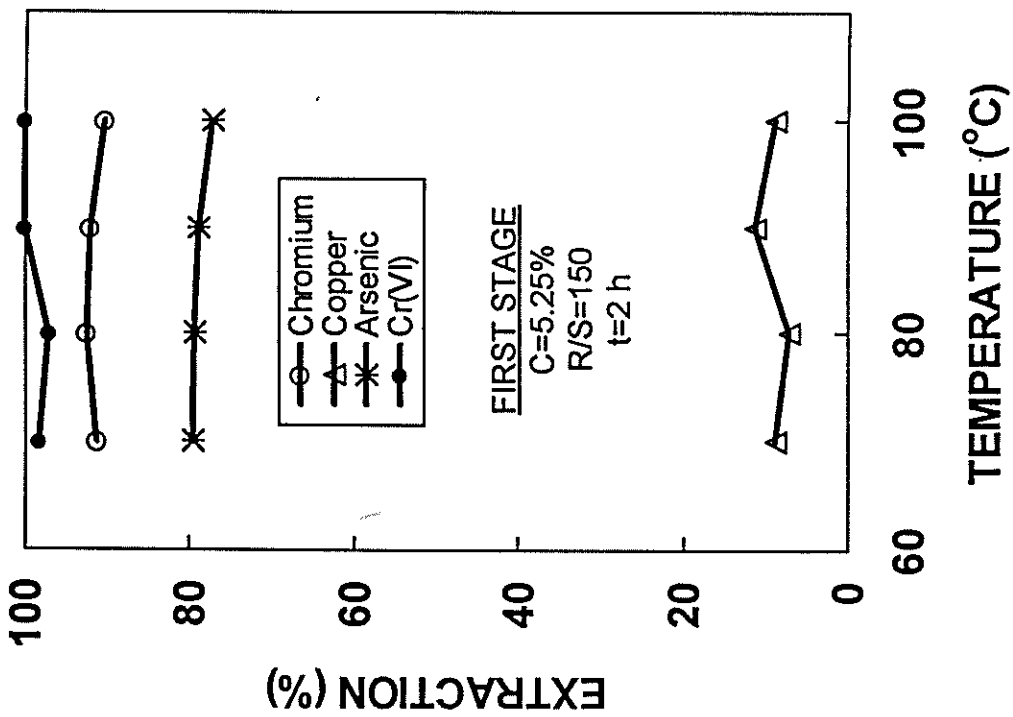


Figure 13. Effect of temperature on first stage extraction and oxidation of CCA sludge using 5.25% NaOCl for 2 hours. The ratio of reagent to oven dry sludge was used as 150:1.

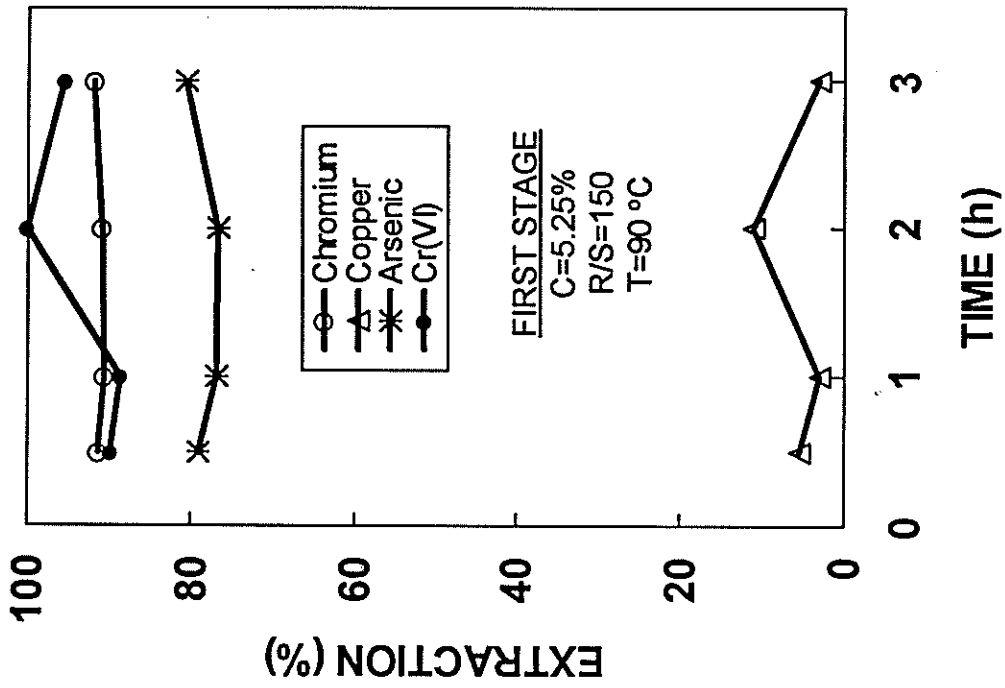


Figure 14. Effect of time on first stage extraction and oxidation of CCA sludge using 5.25% NaOCl at 90 °C. The ratio of reagent to oven dry sludge was used as 150:1.

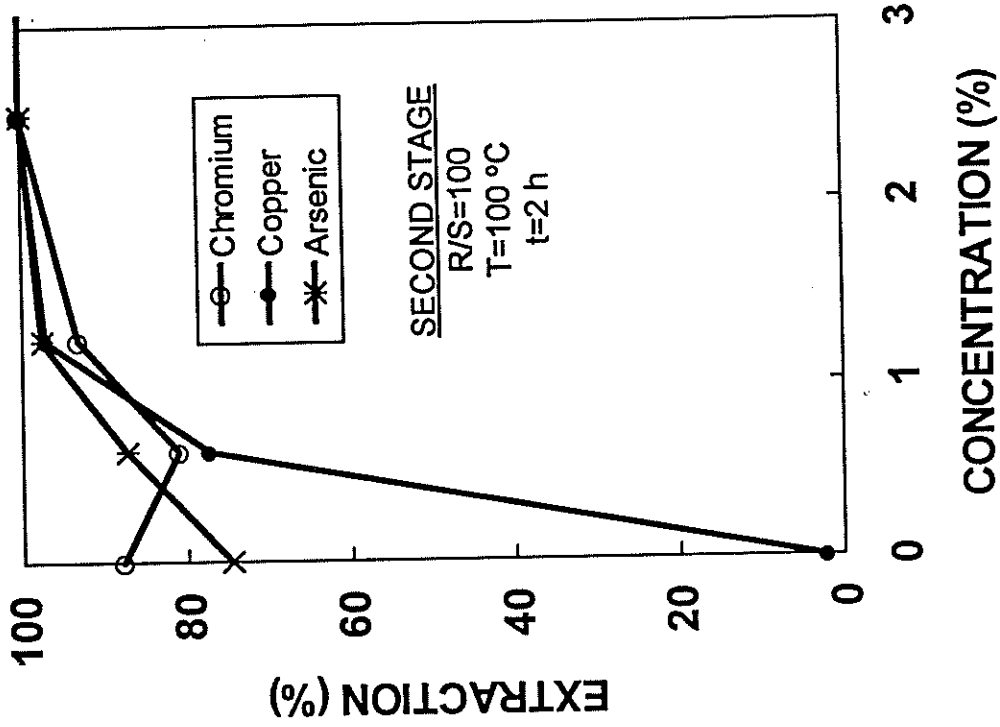


Figure 16. Effect of H_3PO_4 concentration on second stage extraction of CCA sludge at 100 °C for 2 hours with a liquid solid ratio of 100.

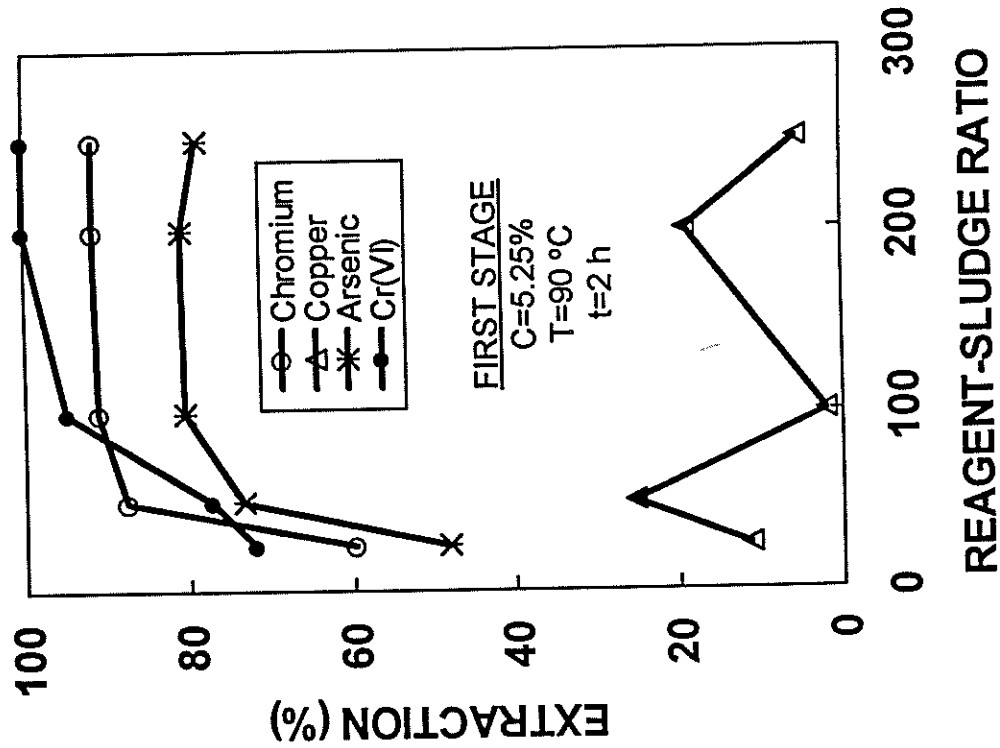


Figure 15. Effect of reagent to sludge ratio on first stage extraction and oxidation of CCA sludge using 5.25% NaOCl at 90 °C for 2 hours.

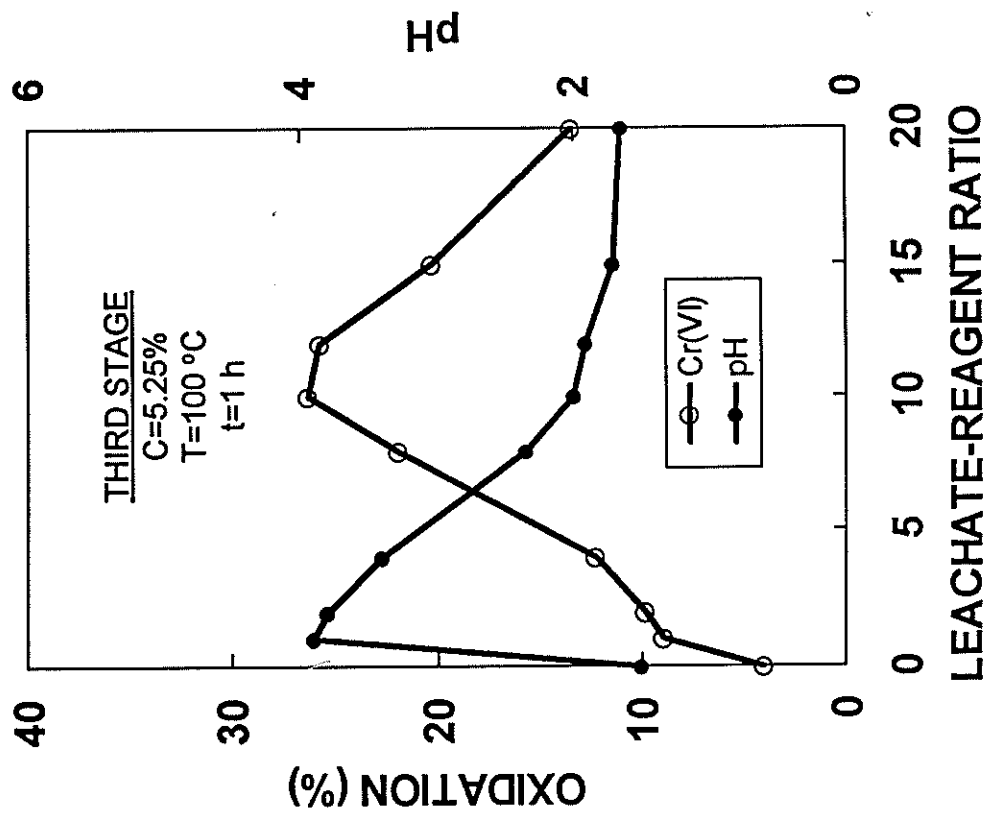


Figure 17. Effect of leachate-reagent ratios on percentage of oxidation and product pH. Oxidation was carried out at temperature of 100 °C for 1 hour.