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D. Bartak, and A. Reddy, Department of Chemistry, University of Northern Iowa,

A. Darchen and A. Robert, ENSCR, Rennes France

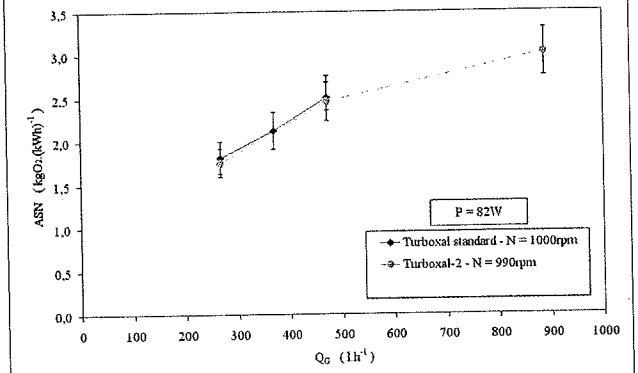

Figure 5. Comparaison des Turboxal et Turboxal 2. Apport spécifique net.

du gaz dans l'eau sont supérieurs en conditions réelles. Il en va de même pour le rendement des mobiles, qui augmente. C'est ainsi que seules les tendances sont à retenir lorsque l'on travaille sur des maquettes.

5. CONCLUSION

Le Turboxal 2 est un appareil qui répond parfaitement aux objectifs de l'étude : repousser le point d'engorgement en conservant des performances en transfert équivalentes à celles de l'ancien système. On peut aussi signaler la simplification du système (deux mobiles d'agitation au lieu de trois) ce qui réduit le coût de fabrication.
L'extrapolation a plus que confirmé les tendances observées sur la maquette Turboxal 2, puisque les débits d'oxygène injectés, mais aussi le rendement de transfert ont été largement augmentés. Cette extrapolation a donné naissance au Turboxal de deuxième génération T300 V2. ●

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MÉTAUX LOURDS

Electrochemical process for the recycling of chromium, copper and arsenic containing solutions. Application to the remediation of CCA wood

Véronique Alonzo*, André Darchen*, Charles-Péguy Nanseu, Emmanuel Ngameni**, Duane Bartak***, Archana Reddy*****

** Laboratoire d'électrochimie, ENS de Chimie de Rennes, avenue du Général-Leclerc, 35700 Rennes (France), e-mail: Andre.Darchen@ensc-rennes.fr*

*** Laboratoire de chimie analytique, Université de Yaoundé-1, BP 812, Yaoundé (Cameroun)*

**** Department of Chemistry, University of Northern Iowa, Cedar Falls, IA (USA)*

1. INTRODUCTION

Wood is an interesting renewal material but it must be treated in order to be protected against dry rot, fungi, termites and other pests when used in outdoor wood products (Connell, 1991). The main efficient preservative used is a mixture of three heavy metals: copper, chromium and arsenic known as CCA, which give the treated wood a greenish appearance. The levels of Cu, Cr and As in CCA-treated wood are relatively high. For example, the average concentration of arsenic is in the range of 1-10 g of arsenic per kg of wood. Thus, the use of CCA-treated wood is a time bomb waiting to drop in the environment because of the disposal of CCA-treated wood products when they come out of service (Cooper, 1993). At the end of its life CCA-treated wood cannot be burnt because arsenic would be dispersed by ashes, and in particular in the fumes as As_4O_6 which is difficult to capture and very toxic. Now CCA is banned in wood treatment. However, there are vast quantities of CCA-treated wood in the word that are in use and will need remediation.

Owing to the global occurrence of CCA-treated wood we carried out a collaborative research network within three countries to address this problem. This research was financially supported by the French MEN, MAE (through the French Embassy in Cameroun) and the Recycling and Reuse Technology Transfer Center of Cedar Falls, IA. In CCA-treated wood since a long time, As and Cr elements are founded with oxidation states As(III) and Cr(III). So, in this paper we consider only the behavior of these species. When this is not the case, it is possible to use chemical reagents to reduce As(V) and Cr(VI).

2. SCHEMATIC PROCESS

The goal of a recycling process conceived for reuse of wood implicates the extraction of Cu, Cr and As and consequently their transfer from the wood into a solution. Some recent studies have been performed in the same purpose (Kartal, 2003; Takeshita et al., 2000). Such process is presented in the scheme of Figure 1. The main steps are: (i) the washing of CCA wood leading to cleaned wood and (ii) a CCA solution to be recycled. In this recycling it is possible to concentrate the washing solution thanks to membrane separation and to extract the CCA elements by electrochemical means. After detoxification of the washing solution the water may be recycled. The overall process consumes reagents and electrical energy and may afford a concentrated CCA solid as a waste.

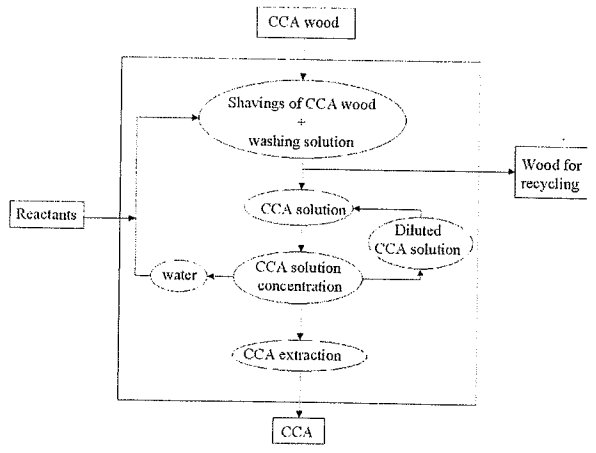

Figure 1. Scheme of the recycling process.

3. WASHING OF CCA WOOD AND ANALYSIS

We have tested several extracting media including EDTA salt, oxalic acid, citric acid, ascorbic acid and we measured pH effects on the extracting efficiency. All analysis were carried out using the British standard method BSI and the ASTM method. From our data it appears that dilute sulfuric acid or oxalic acid are the best means of extracting the CCA metals

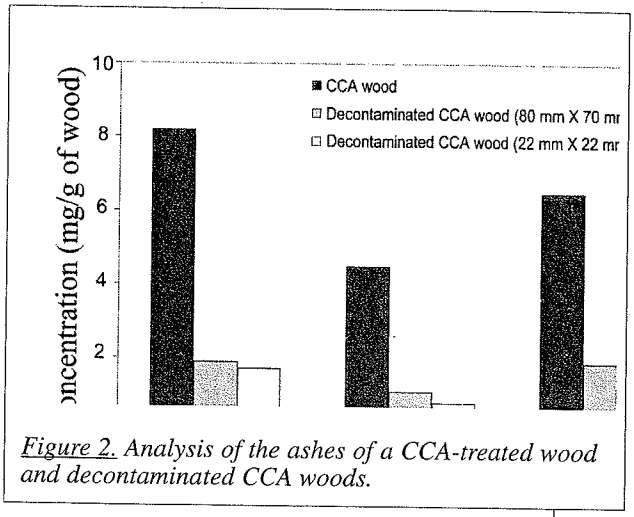

Figure 2. Analysis of the ashes of a CCA-treated wood and decontaminated CCA woods.

from wood (A. Reddy). Figure 2 shows extracting results obtained by analysis of ashes (C.P. Nanseu, 2004). The efficiency is controlled by diffusion inside pieces of wood.

4. ARSENIC EXTRACTION FROM THE WASHING SOLUTION

The recycling of copper and chromium has been already studied in electronic industries and in metal surface treatment. Copper may be extracted as metal deposited on a cathode. Cr(III) may precipitate as insoluble hydroxide. Arsenic is the main problem of extraction and recycling of the washing solution. In CCA-treated wood the arsenic is considered to be the most toxic element. Moreover, arsenic compounds are soluble in water whatever the pH of the solution, so the extraction of arsenic from the washing solution must be the key step in the overall process. The metal removal (either As alone, or Cu, Cr and As) from the CCA solution needs to be

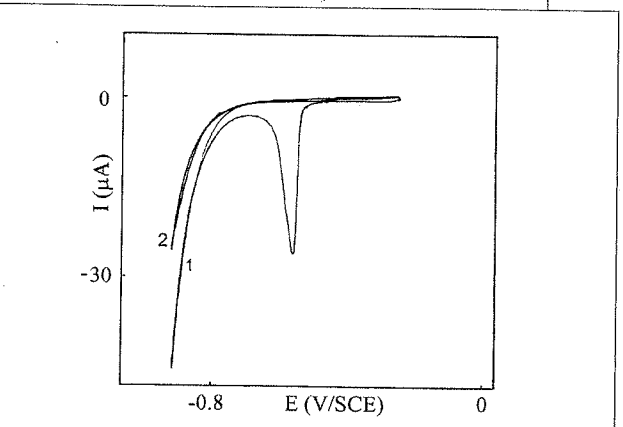

Figure 3. Voltammogram of 10-^{3}M As(III) in 0.1M HCl on stationary copper electrode. Scanning potential rate: 50 mV/s.

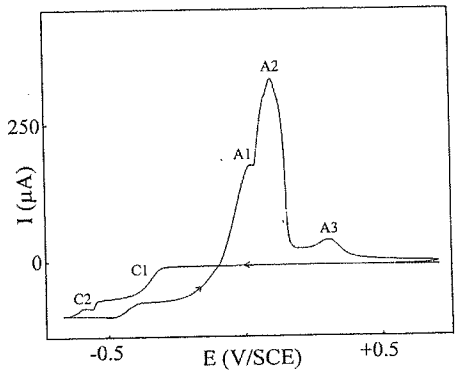

Figure 4. Voltammogram of 10-³M As(III) and 10-³M Cu(II) in 0.1M H2SO4 on a rotating vitreous carbon electrode (1 000 rpm). Scanning potential rate: 50 mV/s.

carried out in order to allow the recycling of the chemical compounds of the washing solution. This point has been investigated following two methods.
(i) An indirect electrochemical reduction utilizing cementation with zinc powder.
(ii) A direct electrolytic reduction. The optimization of this reduction has been investigated by cyclic voltammetry.
Despite its high standard potential (E° $HAsO_2$/As = +0.248 V/NHE) As(III) is difficult to reduce to As (J. Van Muylder et al., 1963). Moreover, at lower potential (- 0.608 V/NHE) As may be reduced to arsine gas AsH_3 which is very toxic. At a copper microelectrode, the voltammetric behavior of a As(III) solution was characteristic of a surface controlled reaction. The voltammetric curve (Figure 3) shows a symmetrical current peak during the first potential scanning. The reduction product of As(III) inhibits the reduction, whatever the pH of the solution was. Assuming the formation of As(0) the integrated current gives a 0.2-0.3 nm layer.

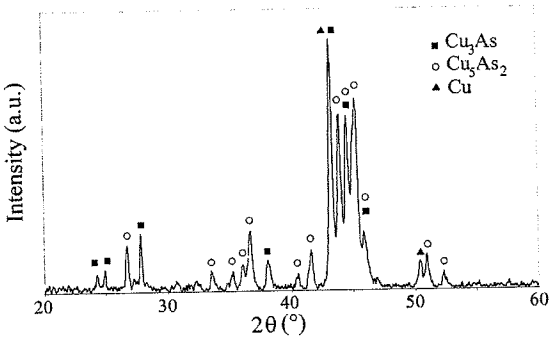

Figure 5. Powder X-ray diffraction pattern of cathodic deposit obtained after controlled current electrolysis of acetic buffer solution containing 0.1M As(III) and 0.1M Cu(II).

As proved by the voltammetric curve at a rotating carbon electrode (Figure 4) in the presence of Cu(II) the reduction of As(III) occurs with a constant current at negative potentials (wave C2) after copper deposition (wave C1). The concomitant formation of copper allows the reduction of As(III) and the reduction products are solid compounds which are oxidized during the reverse potential scanning (waves A1-A3). The electrochemical data were in agreement with the following equation:

$$HAsO_2 + 3\ Cu^{2+} + 3\ H^+ + 9\ e^- \rightarrow Cu_3As + 2\ H_2O$$

The chemical nature of the reduction products was established by X-ray diffraction. The compounds isolated after a controlled current electrolysis were a mixture of copper arsenides Cu_3As and Cu_5As_2, and copper (Figure 5). The electrolysis carried out in an undivided cell with a graphite cathode and a copper anode led to the formation of a black deposit without AsH_3 emission.

5. PERPECTIVES AND CONCLUSION

This work has shown that arsenic could be extracted from solutions by electrochemical co-deposition with copper. The cupric cation needed for this reaction arose from the copper anode. No toxic gas was detected during electrolysis. The main experiments needed by a process dedicated to the remediation of CCA-treated wood have been investigated. From our data we believe that an aqueous washing with recycling the solution by electrolysis may be a viable process. ●

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