Two possible pathways for the release of arsenic during pyrolysis of chromated copper arsenate (CCA)-treated wood

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Abstract

The behavior of arsenic during pyrolysis at temperatures between 135 and 500 °C has been widely studied. We examined the release of arsenic during the pyrolysis of chromated copper arsenate (CCA)-treated wood, and here we propose two models for the volatilization of arsenic: (a) a reacted arsenic compound, chromium arsenate, in CCA-treated wood was initially decomposed to arsenic pentoxide, which then appeared to be released at around 400–500 °C as a form of arsenic trioxide; and (b) an unreacted arsenic compound, arsenic pentoxide, in CCA-treated wood was released at much lower temperatures than reacted arsenic compound, as a form of arsenic trioxide. In order to restrain the release of arsenic during pyrolysis, it is possible to pyrolyze CCA-treated wood carefully at temperatures around 300–350 °C only if the wood contains little unreacted arsenic compound. Under these conditions, almost all toxic elements remain in the pyrolysis residue, and a weight reduction of the wood of approximately 50% can be obtained. On the other hand, the release of arsenic can be achieved easily using an unreacted arsenic compound under the same pyrolysis conditions. However, in the present study it was difficult to determine the accurate release point of arsenic in both cases due to the level of experimental uncertainty.
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1. Introduction

In recent decades, chromated copper arsenate (CCA)-treated wood has been widely used because of its high performance against rot and weathering over long periods of time. Currently, a large amount of CCA-treated wood has become waste material, and the disposal of these treated wood products poses a serious problem [2,5,18]. In Japan, it is estimated that 300,000 m^3 of CCA-treated wood will be removed from service annually and that this phenomenon will continue over at least 50 years.

In general, combustion is used to dispose of wood wastes or to recover energy from them. However, energy recovery is difficult to perform in the case of CCA-treated wood waste due to the toxic materials that are released during combustion. Dobbs and Grant [3] report that 59% of arsenic

is volatilized at a temperature of 1000 °C, and McMahon et al. [17] state that 13–27%, 22–44%, and 70–77% of arsenic is volatilized at temperatures of 400, 800, and 1000 °C, respectively. Hirata et al. [11] also report similar tendencies in the volatilization of arsenic during combustion. These data strongly suggest that the combustion of CCA-treated wood by normal combustion methods could produce environmental pollutants because toxic metals, particularly arsenic, are gasified at normal combustion temperatures and may easily be released into the atmosphere. Since the gasified arsenic is a highly mobile compound, it is difficult to capture with conventional cleaning equipment. The TBAH solution was only used in flue gas cleaning equipment in a lab-scale experiment [17], but it is too expensive for practical application. To date, no workable solutions have been proposed for this disposal problem, although it is essential that an appropriate disposal technology be developed soon.

Solvent extraction of CCA-treated wood has been considered to be a promising technique for purifying wastes and recovering CCA elements [1,14,15,28]. However, it has been

reported that efficient solvent extraction is prevented by the strong bonding between CCA elements and certain wood components, primarily chromium and lignin [20,21,26,27]. Thus, there are two possible methods for successfully conducting solvent extraction: mechanical or chemical pre-treating prior to solvent extraction, and the development of new solvents that can extract all CCA elements efficiently. Here we discuss the possibility of combining pyrolysis and solvent extraction, in other words, using pyrolysis as a thermochemical pre-treatment prior to solvent extraction. In the present work, the pyrolysis condition of CCA-treated wood is discussed, while the effect of pyrolysis on the extractabilities of CCA-treated wood have been reported elsewhere [13].

In the present study, we examined the behavior of arsenic during pyrolysis in order to study the volatilization of arsenic. To date, few researchers have reported on the pyrolysis of CCA-treated wood. Van den Broeck et al. [29], Helsen et al. [5,7], and Helsen and Van den Bulck [6,8,9] have conducted extensive studies on low temperature (300–450 °C) pyrolysis of CCA-treated wood. When applying pyrolysis to CCA-treated wood, the behavior of arsenic is of critical importance, particularly in terms of its volatilization. It is difficult to determine the volatile point of arsenic in CCA-treated wood [10] due to the experimental uncertainty, and so this point has not yet been well defined. Very few researchers have reported on the pre-pyrolysis range of CCA-treated wood at temperatures of less than 300 °C; however, we consider this range to be the most important in arsenic release [4]. In a significant study, Helsen and Van den Bulck [9] identifies the volatile point of arsenic in chromium arsenate/D-glucose composite as 327 °C based on thermogravimetric (TG) analysis using a model compound. Because there may be some differences in the behavior of arsenic between the model compound and real treated wood, we defined the purposes of this study as follows: (1) to study the release pathway of arsenic in CCA-treated wood as derived from different states of arsenic compound in the wood; (2) to model the release of arsenic in CCA-treated wood during pyrolysis; and (3) to determine the appropriate conditions for the pyrolysis of CCA-treated wood as a pre-treatment for solvent extraction such that the behavior of arsenic can be predicted and controlled.

2. Experiment

2.1. Sample preparation

The sample used in this experiment was western hemlock (*Tsuga heterohpylla*) treated with Type III CCA reagent (chromium as CrO_3, 45–51%; copper as CuO, 17–21%, arsenic as As_2O_5, 30–38%; [12]) supplied by Koshii Mokuzai Co., Osaka, Japan. After impregnation with the CCA solution, the treated wood was dried at room temperature for three weeks in accordance with commercial procedures [12]. The CCA-treated wood pieces were broken into chips and then milled to a powder with a particle size of smaller than 20 mesh and mixed sufficiently to minimize the non-uniform distribution of CCA salts in the sample (sample A). In addition to these treatments, post-heat treatment (drying at 60 °C for two weeks) was also conducted in order to complete the chemical reaction of the chemicals in the wood (sample B). We have confirmed that the arsenic concentrations and water contents were the same in samples A and B before pyrolysis, although the two samples were prepared by different fixation processes after impregnation.

2.2. Pyrolysis

One gram of CCA-treated wood was pyrolyzed in an N_2 atmosphere using an electric furnace (0.75 m height, 0.80 m width) equipped with a 100 ml volumetric pear-shaped glass flask reactor. The pyrolysis conditions varied in temperature from 135 to 500 °C and in time from 0 to 60 min. Heating rate and N_2 flow rates were adjusted to 3 °C/s and 12.5 ml/s, respectively. The duration of pyrolysis was defined as the duration between the time at which the sample reaches the desired temperature and its removal from the reactor before cooling. The samples were cooled to room temperature naturally. For example, a pyrolysis duration of 10 indicates that the sample was heated to the desired temperature, then pyrolyzed at the isothermal condition for 10 min (at the desired temperature). After a pyrolysis duration of 10 min, the reactor was removed from the furnace and cooled to room temperature naturally in an N_2 gas atmosphere.

2.3. Chemical analysis

After pyrolysis, the residual weight and changes in arsenic content in the samples (both wood powder and pyrolysis residues) were measured. The oven-dried samples were dissolved completely in nitric acid by being heated in a sand bath. After dissolution, the liquid specimen was analyzed quantitatively using a fluorescent X-ray analyzer, XRF (JOEL JSX-3220 Element Analyzer, JEOL Ltd., Tokyo, Japan). XRF analysis was repeated three times to check the repeatability and determine the accuracy of the analysis, and the mean values and corresponding standard deviations were taken.

3. Results and discussion

3.1. Weight reduction of CCA-treated wood

The weight reduction of CCA-treated wood during pyrolysis is tabulated in Table 1. Table 1 shows a greater reduction in the weight of the sample during pyrolysis, which was due to a higher pyrolysis temperature and longer duration. The weight reduction reached 50% under pyrolysis for 30 min at 300 °C, and the wood powder became dark brown

Table 1
Residual weight of CCA-treated wood after pyrolysis

Duration of pyrolysis (min)	Pyrolysis temperature (°C)							
	135	150	200	250	300	350	400	500
0	0.97[a]	0.97	1.01	0.97	0.92	0.67	0.56	0.34
10	0.99	0.97	0.88	0.71	0.57	0.40	0.35	0.30
30	0.95	0.97	0.90	0.76	0.50	0.39	0.35	0.22
60	1.00	1.00	0.92	0.63	0.43	0.40	0.32	0.23

[a] The weight of CCA-treated wood (g) after pyrolysis (the weight of each original sample was 1.00 g).

or black. Finally, a 77% weight reduction was obtained under pyrolysis for 60 min at 500 °C.

3.2. Changes in arsenic content

The changes in the arsenic content of samples A and B during pyrolysis determined by XRF analysis are shown in Tables 2 and 3, respectively. The arsenic concentration and its standard deviation in the original sample were determined to be 4.45 and 0.57 mg/g, respectively.

Table 2 shows that the arsenic in sample A decreased gradually with increasing pyrolysis temperature. Moreover, the effect of the duration of pyrolysis on arsenic release could be observed significantly in higher temperature zones, at temperatures around 400 and 500 °C. The difference in arsenic content in low temperature zones, upto 300 °C, was about 20%, and by the time the sample reached 500 °C it was around 50%. However, due to the high standard deviation of the arsenic content in the original sample, a determination of the release point of arsenic in sample A was inconclusive. Therefore, the attempt to determine the re-

lease point of arsenic in sample A has been unsuccessful since the present results are inconclusive. Approximately 20% or more of the arsenic had already been released at the time the sample reached 300 °C, and 50% had been released by 500 °C.

In sample B, on the other hand, a negligible amount of arsenic had been released at 300 °C. It is clear that samples A and B behaved quite differently in terms of arsenic volatilization. As was mentioned before, it was difficult to pinpoint the release point of arsenic in sample B. Helsen et al. [10] have also indicated that the high standard deviations in arsenic release made it impossible to draw conclusions regarding the "conditions under which the arsenic release was zero". The determination of arsenic release from CCA-treated wood delivers the highest contribution to these standard deviations. However, in the present experiment it was notable that there were two possible pathways for the release of arsenic as indicated by the different behavior of arsenic in samples A and B.

Fig. 1 shows the arsenic retention in the residue after the pyrolysis of sample B as a function of the duration of pyrolysis at different temperatures. The arsenic content in the pyrolysis residue was expressed as a percent ratio of the content in the original CCA-treated wood. The determination of the release of arsenic at 300, 350, and 400 °C (Fig. 1a–c) was inconclusive due to the experimental uncertainty, but the arsenic released was drastically incresed with longer pyrolysis at 500 °C, as shown in Fig. 1d. The behavior of arsenic in these temperature zones can be classified into two categories: at 300, 350 at 400 °C, the release of arsenic was negligible or insignificant; at 500 °C, drastic release of arsenic was observed.

Table 2
Changes in the arsenic content of sample A (dried at room temperature for three weeks)

Duration of pyrolysis (min)	Pyrolysis temperature (°C)							
	135	150	200	250	300	350	400	500
0	ND	ND	ND	ND	ND	ND	ND	ND
10	4.42[a] (0.16)[b]	4.44 (0.08)	4.44 (0.08)	4.13 (0.07)	3.27 (0.24)	3.23 (0.10)	2.74 (0.12)	2.52 (0.03)
30	4.54 (0.31)	3.68 (0.16)	4.14 (0.10)	4.07 (0.19)	3.27 (0.12)	3.14 (0.08)	2.61 (0.03)	2.21 (0.13)
60	5.06 (0.14)	4.47 (0.22)	4.18 (0.02)	3.99 (0.14)	3.18 (0.10)	2.70 (0.12)	2.48 (0.10)	2.08 (0.04)

ND: no data.

[a] The arsenic content in CCA-treated wood (mg) after pyrolysis (the arsenic content of each original sample was 4.45 ± 0.57 mg).

[b] Standard deviations on the metal analysis for 1 pyrolysis experiment.

Table 3
Changes in the arsenic content of sample B (dried at room temperature for three weeks and at 60 °C for two weeks)

Duration of pyrolysis (min)	Pyrolysis temperature (°C)							
	135	150	200	250	300	350	400	500
0	4.17[a] (0.41)[b]	4.99 (0.22)	4.51 (0.14)	4.00 (0.08)	3.98 (0.10)	4.56 (0.04)	4.23 (0.12)	3.64 (0.18)
10	4.40 (0.14)	5.06 (0.22)	4.75 (0.05)	4.16 (0.14)	4.14 (0.20)	4.07 (0.09)	3.66 (0.29)	2.78 (0.09)
30	4.51 (0.10)	3.95 (0.05)	5.01 (0.11)	4.97 (0.05)	4.79 (0.06)	4.25 (0.05)	4.03 (0.26)	1.86 (0.06)
60	4.76 (0.21)	4.00 (0.01)	4.11 (0.33)	4.74 (0.11)	4.61 (0.04)	4.30 (0.04)	4.13 (0.01)	1.37 (0.08)

[a] The arsenic content of CCA-treated wood (mg) after pyrolysis (the arsenic content of each original sample was 4.45 ± 0.57 mg).

[b] Standard deviations on the metal analysis for 1 pyrolysis experiment.
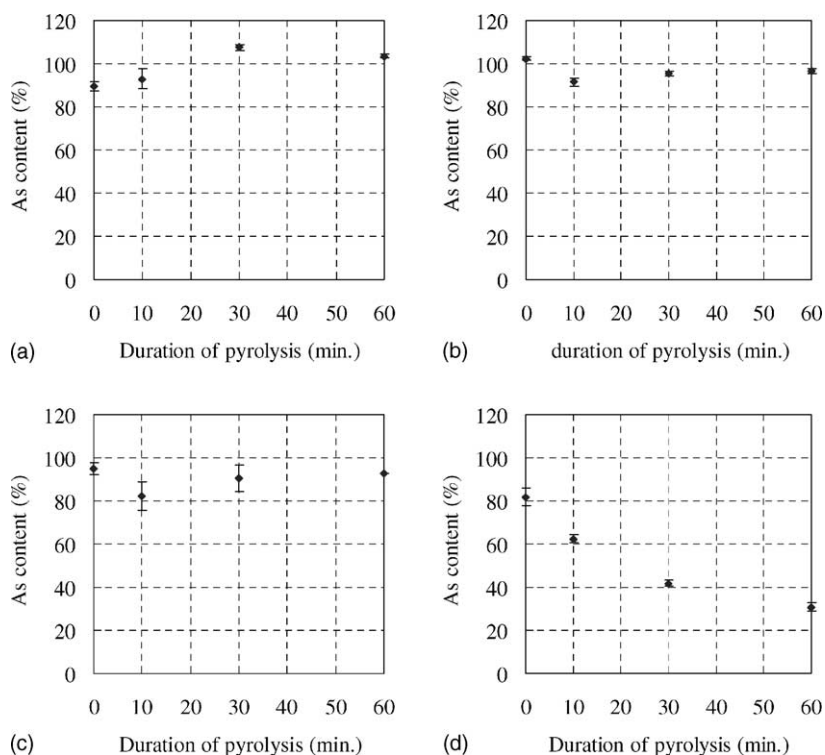
Fig. 1. Arsenic retention in the residue after pyrolysis of CCA-treated wood (sample B) as a function of the duration of the pyrolysis process: (a) at 300 °C; (b) at 350 °C; (c) at 400 °C; and (d) at 500 °C.

The original arsenic in liquid CCA reagent is arsenic pentoxide, which is reduced to arsenic trioxide and volatilized by heating. According to Helsen's TG analysis [8], a $CrAsO_4$/D-glucose model compound decomposed at 313 °C and formed arsenic pentoxide. In addition, Helsen et al. [10] indicated that the reduction reaction of arsenic pentoxide to arsenic trioxide did not occur under 500 °C according to TG analysis of pure arsenic pentoxide, and proposed that arsenic trioxide was already present, therefore arsenic would be released at temperatures below 500 °C. On the other hand, it was observed that the amount of arsenic released at 400 °C for 10 min from sample A was 39.6% in the experiment, which was more than could be released by the original arsenic trioxide. The thermochemical reaction in wood is highly complicated, and is affected by factors such as vapor pressure, reduction by carbons and oxidation. We therefore considered that the reduction of arsenic pentoxide to arsenic trioxide could occur, and some of that arsenic would be released at temperatures less than 500 °C.

Based on the study by Helsen and Van den Bulck [9], it was previously assumed that, during pyrolysis of CCA-treated wood, arsenic would be released at approximately 327 °C. However, in the present study, we found that very little arsenic was released at this temperature according to the results for sample B, which is assumed to be due to complete the formation of $CrAsO_4$ compound. The volatilization of arsenic from the wood carbons may be different from that of a simple $CrAsO_4$/D-glucose model compound. Thus, a part of the volatilized arsenic may be adsorbed on the wood carbon structure at temperatures below the boiling point of arsenic pentoxide at atmospheric pressure, 465 °C [19]. In our hypothesis, the arsenic release is significantly greater because it is volatilized explosively in quantities too great to be captured in the wood carbon structure when the pyrolysis temperature is over 465 °C. As a result, the arsenic content decreases drastically with longer pyrolysis times at 500 °C (Fig. 1d).

3.3. Two models of volatilization of arsenic during pyrolysis

During the fixation of CCA reagent in wood, the reduction of Cr^{6+} to Cr^{3+} is important [22–25]. The reduction state of Cr^{3+} reacts with As_2O_5, forming a slightly soluble $CrAsO_4$ salt. These reactions can be expressed as follows:

$$Cr^{6+} \rightarrow Cr^{3+}$$

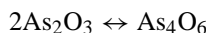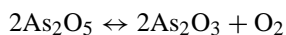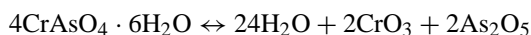$$Cr^{3+} + AsO_4^{3-} \rightarrow CrAsO_4$$
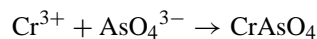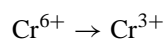
However, not all of the As_2O_5 reacts with Cr^{3+} during the conditioning process, and some can remain in the wood as unreacted reagents. In this experiment, unreacted reagents of As_2O_5, which might be present in sample A as free reagents, are expected to react with Cr^{3+}. The difference between samples A and B is considered to be the presence or the absence of these unreacted reagents.

Unreacted arsenic compound exists as a form of arsenic pentoxide, As_2O_5. Arsenic pentoxide is reduced to arsenic

trioxide, As_2O_3, by heating during pyrolysis. Kercher [16] reported that As_2O_3 starts to be released at 200 °C by TG analysis. This is consistent with the behavior of the arsenic in sample A. Therefore, the release of arsenic from sample A was considered to derive from As_2O_5, which first has to be reduced to As_2O_3 before being released.

In contrast, the reacted arsenic compound exists as a form of chromium arsenate, $CrAsO_4$. Chromium arsenate initially decomposes to arsenic pentoxide, which is reduced to arsenic trioxide by pyrolysis. Arsenic trioxide is gasified as a form of As_4O_6. Helsen and Van den Bulck [9] observed decomposition and gasification at 313 and 327 °C, respectively. The release of arsenic in sample B in the present study is consistent with the behavior of arsenic derived from $CrAsO_4$ decomposition. Based on these data, we assume that there may be two types of arsenic release reaction during pyrolysis:

(a) The first possible pathway is caused by reacted arsenic compound, $CrAsO_4$, which appears to be released at around 400–500 °C, and can be expressed by the following reactions [9]:

$$4CrAsO_4 \cdot 6H_2O \leftrightarrow 24H_2O + 2CrO_3 + 2As_2O_5$$

$$2As_2O_5 \leftrightarrow 2As_2O_3 + O_2$$

$$2As_2O_3 \leftrightarrow As_4O_6$$

(b) The second possible pathway is caused by unreacted arsenic compound, As_2O_5, in CCA-treated wood, which appears to be released at a much lower temperature than chromium arsenate, possibly 200 °C. This pathway can be expressed by the following reactions:

$$2As_2O_5 \leftrightarrow 2As_2O_3 + 2O_2$$

$$2As_2O_3 \leftrightarrow As_4O_6$$
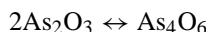
The behavior of arsenic during pyrolysis, and particularly the different states of arsenic compounds, have not previously been clarified. The volatility point of arsenic has been difficult to pinpoint due to the different states of arsenic, and to the presence or absence of unreacted compound prior to pyrolysis. Based on the behavior of arsenic in sample B in the present study, particularly as it related to the formation of $CrAsO_4$ salt, the release of arsenic in CCA-treated wood appeared to start at a temperature of around 400–500 °C, although the release point could not be determined accurately due to experimental uncertainty. However, it is possible to restrain As via the pyrolysis of CCA-treated wood if the wood contains little unreacted arsenic, and if the wood is carefully pyrolyzed at temperatures around 300–350 °C. Under these conditions, almost all of the elements remain in the pyrolysis residue. In practice, CCA-treated wood waste after long-term weathering may contain only a small amount of unreacted arsenic compound, because the free arsenic compound may have already been washed or leached out from the treated wood. In contrast, if there is a significant amount of unreacted arsenic compound, we should handle it carefully.

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