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removal of arsenate with pyroligneous liquor**

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## 【Original article】

## Carbonization of timbers treated with copper chromium arsenate and removal of arsenate with pyroligneous liquor

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Abstract: In order to develop a reusing method of the wood treated with copper chromium arsenate, arsenic content in the charcoals obtained from the wood treated with CCA was analyzed. Arsenic content in the charcoals differed between the charcoals obtained below 400°C and above 500°C. The charcoals obtained below 400°C retained over 70% of the arsenic, whereas those obtained above 500°C showed lower arsenic retentions. Heating rates did not affect arsenic content.

About 25% of arsenic in the charcoals obtained at 400°C was leached with pyroligneous liquor, but pyroligneous liquor could not remove all of the arsenic in the charcoals. The leachability of solvent might be influenced by leaching temperature and the state of arsenic in the charcoals.

Key words: preservative treated wood, carbonization, charcoal, pyroligneous liquor, leaching

## CCA処理木材の炭化と木酢液によるヒ素の除去

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概要：CCA 処理木材の有効利用をはかるため、炭化と抽出を組み合わせたヒ素の除去法を検討した。炭化温度がヒ素の保持率に与える影響を検討するため、異なる炭化温度で調製した木炭中に含まれるヒ素の含有量を調べたところ、炭化温度 400°C 以下で得られた木炭では炭化前のヒ素量の 70% 以上が保持されていた。一方、500°C 以上で炭化した炭では、炭化前のヒ素の 50% 以上が木炭外に放出されていた。400°C で炭化して得られた炭を木酢液で抽出したところ、木炭中に保持されていたヒ素の 25% 程度が流出することが確認された。ヒ素の抽出量は抽出温度に比例したが、全てのヒ素を抽出することはできなかった。抽出温度と木炭内のヒ素の酸化状態が、ヒ素の抽出に影響しているのではないかと考えられる。

キーワード：CCA 処理木材、炭化、木炭、木酢液、抽出

## 1. Introduction

Chromated copper arsenate (CCA) treated timbers have been used for various wooden equipment for outdoor use <sup>1),2)</sup>. When CCA treated wood is recycled or disposed of, CCA may leach and cause serious damage to the environment and human health <sup>3)</sup>. Hence, to remove

CCA from treated wood, many trials, such as burning inside a kiln equipped with a heavy metal trap, reclamation of crashed treated wood and leaching of heavy metal with solvent, have been performed <sup>4)</sup>. Ashes obtained from treated woods are prepared so that heavy metals will not leach and are used for landfill. However

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burning releases gases that contain arsenic compounds simultaneously with ashes, and so requires a removal equipment of those toxic exhausts. Ashes with a high arsenic content causes another problem of how to render the ashes harmless. The disposal of crushed treated wood into landfill risks contaminating the soil and ground water with high concentrations of organic matter and heavy metals that are released by the degradation of CCA woods. Although leaching techniques of CCA with solvents is still under development, leaching method is possible to achieve complete removal of CCA from CCA wood <sup>4)</sup>. Furthermore, CCA will be recovered easily from the solution obtained by leaching rather than from solid CCA wood.

For the disposal of CCA wood and recovery of CCA from it, it is important to reduce the material volume and to concentrate CCA in it. Carbonization is one of possible solutions. However, carbonization of CCA treated material poses the risk of releasing arsenic during carbonization. The mobility of arsenic changes by temperature, and whether it is released or retained depends on the carbonization temperature <sup>5)</sup>. When carbonization is performed, pyroligneous liquor is obtained from the material besides charcoal.

So, if arsenic can be completely removed from charcoal by leaching with pyroligneous liquor, then safe charcoal and arsenic liquid that can easily be reused will be available by carbonizing CCA wood.

Hence, in this study, carbonization of CCA wood at various temperature and leaching with pyroligneous liquor were performed.

## 2. Materials and Methods

### Materials

Wood (90 x 90 x 2000 mm) of *Tsuga heterophylla* Sarg. treated with type 2 CCA by incising method was used in this experiment. Type 2 CCA which is regulated in JIS K 1554 contains 33 - 38% of CrO<sub>3</sub>, 18 - 22% of CuO and

42- 48% of As<sub>2</sub>O<sub>5</sub>. After injection of CCA, wood was kept in room temperature for minimum 3 months. To use high CCA content part of the wood for this experiment, surface of wood was collected up to 1.5cm depth. The collected wood was milled into chips. The chip size are less than 2mm in diameter with Wiley mill. The arsenic content in the chip was 0.65mg/g. Moisture content of the chip was 8.5% and no moisture control were performed in advance of charcoal making.

For charcoal leaching test, quality guaranteed commercial product of pyroligneous liquor (Mokusaku kikou, Taiko Tec inc.) was applied to equalize the quality of extractant. The pyroligneous liquor was produced as follows. At first, tar and low boiling point compounds in the condensed smoke were removed by repeated distillation under reduced pressure. After that, the liquor at 100-120 °C of boiling point was collected by the following distillation. And the liquor was used in this experiment as pyroligneous liquor. It contains over 7% of acetic acid, over 0.15% of guaiacol, 0.06% of 4-methylguaiacol and less than 92% of water and pH ranges about 2.2.

### CCA content change at different carbonization conditions

Figure 1 shows the carbonization apparatus. About 30 - 40 g of wood powder was put into a glass retort and the retort was set into an electric kiln. When carbonization was performed, two parameters of carbonization, maximum carbonization temperature and heating rate were changed. Combination of five carbonization temperatures (300, 400, 500, 600 and 700°C) and three heating rates (3, 5 and 10 °C/min) were applied. After the maximum carbonization temperature was obtained, the retort was kept at the maximum temperature for 1 hour and then cooled to room temperature. After cooling down, the charcoal in the retort was collected and amount of arsenic was analyzed

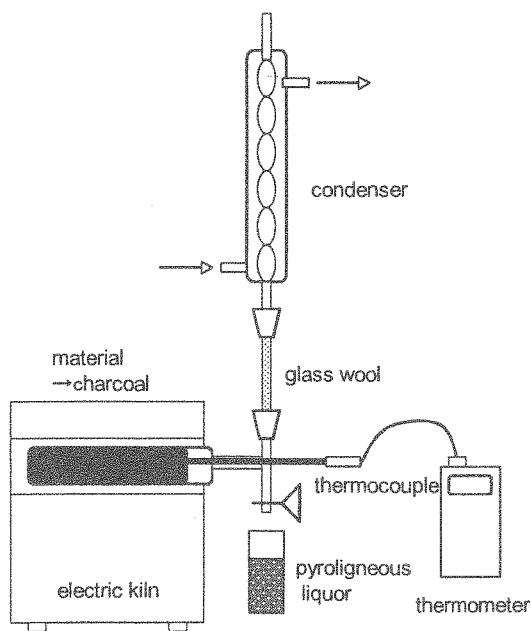


Figure 1 Carbonization apparatus

with atomic absorption spectrophotometer (AA-6800, Shimadzu). Smoke generated during carbonization was cooled in a condenser and collected in a reservoir. Arsenic contained in the condensed smoke was also analyzed with atomic absorption spectrophotometer.

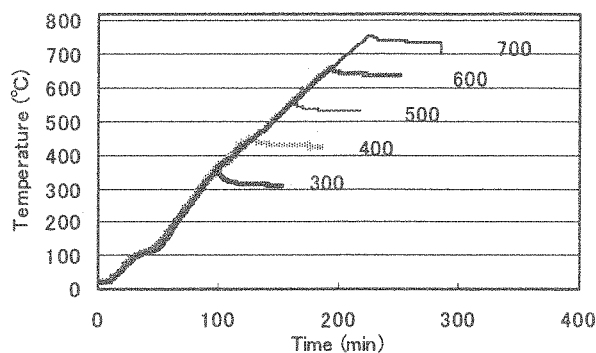
### Charcoal leaching with pyroligneous liquor

Charcoal obtained at 400°C and heating rate of 10°C/min was subjected to pyroligneous liquor leaching. Five gram of the charcoal and 100ml of pyroligneous liquor were mixed in a 200-ml conical flask. The flask was sealed with film and soaked in a water bath for 1 hour. Leaching was performed at four temperatures, 40, 60, 80 and 100°C. After leaching, charcoal and pyroligneous liquor were separated by filtration with a piece of filter paper. Charcoal was stored in the oven which was kept at 105°C for 1 day. After drying up of the charcoal, the arsenic content in the charcoal was analyzed with atomic absorption spectrophotometer.

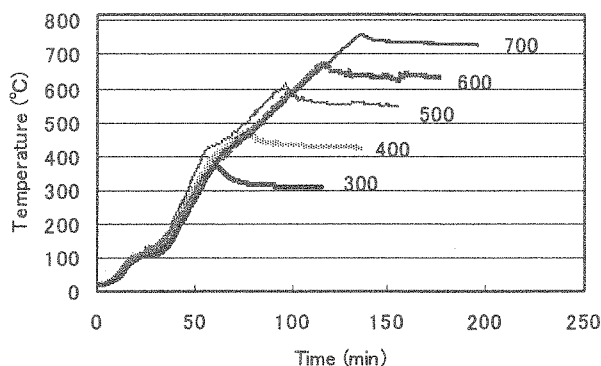
## 3. Results and discussion

### CCA content change at different carbonization conditions

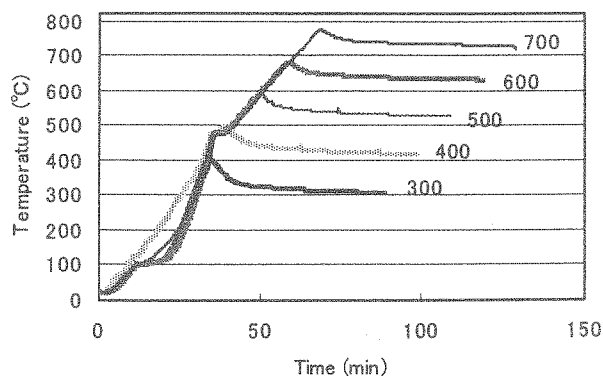
Figures 2a) to 2c) show the inside temperature changes during carbonization. Due to the mechanism of the heater provided in the electric kiln, the inside temperatures exceeded the set temperature.



a) Heating rate 3°C/min



b) Heating rate 5°C/min



c) Heating rate 10°C/min

Figure 2 Inside kiln temperature changes during carbonization

Table 1 Arsenic content in the charcoals obtained from various carbonization temperatures and heating rate

Sample	Yield		As content		Trapped As (%) to As content in CCA treated wood			Loss As (%)
	Charcoal	Pyrolygneous liquor	Charcoal	Pyrolygneous liquor	Charcoal	Pyrolygneous liquor	Total	
	(%)	(%)	(mg/g)	(mg/L)	(%)	(%)	(%)	
<b>300°C</b>								
3°C/min	59.0	26.2	0.9	124	78.8	5.0	83.8	16.2
5°C/min	60.5	34.1	0.8	147	72.1	7.7	79.8	20.2
10°C/min	38.8	37.0	1.3	170	76.2	9.7	85.8	14.2
<b>400°C</b>								
3°C/min	42.4	42.9	1.3	152	82.4	10.0	92.4	7.6
5°C/min	39.8	47.2	1.2	162	76.1	11.8	87.9	12.1
10°C/min	32.9	40.8	1.5	166	74.7	10.4	85.1	14.9
<b>500°C</b>								
3°C/min	35.9	53.3	0.9	143	52.1	11.7	63.8	36.2
5°C/min	32.9	46.5	1.0	166	48.7	11.9	60.5	39.5
10°C/min	31.7	41.7	1.2	173	58.9	11.1	70.0	30.0
<b>600°C</b>								
3°C/min	33.3	48.7	0.9	146	45.8	10.9	56.7	43.3
5°C/min	31.5	43.4	1.1	155	52.7	10.4	63.1	36.9
10°C/min	29.0	37.0	1.1	165	47.1	9.4	56.5	43.5
<b>700°C</b>								
3°C/min	31.4	49.1	1.0	150	47.3	11.3	58.7	41.3
5°C/min	28.6	47.0	1.2	156	54.2	11.3	65.4	34.6
10°C/min	28.6	41.4	1.3	173	55.5	11.0	66.5	33.5

Table 1 shows the arsenic content in each charcoal. Charcoal groups obtained at under 400°C and at over 500°C showed different tendencies of arsenic contents. As for charcoals obtained at 300 and 400°C, charcoals retained over 70% of arsenic that was contained in the CCA. Charcoal obtained at heating rate of 3°C/min and at 400°C of the setting temperature showed the highest arsenic retention and over 80% of arsenic was retained in the charcoal after carbonization. Contrary to the charcoals obtained at 300 and 400°C, the charcoals obtained at over 500°C showed lower arsenic retention; arsenic content in the charcoals was only 45 to 55 % after carbonization. Kakitani *et al.* reported that 20 % of arsenic was released at 300°C and 50% was released at 500°C<sup>5)</sup>.

Generally, arsenic is injected in the form of As<sub>2</sub>O<sub>5</sub> into wood material. Pure As<sub>2</sub>O<sub>5</sub> is reported to be a stable compound against heat. When pure As<sub>2</sub>O<sub>5</sub> is independently heated, volatilization of As<sub>2</sub>O<sub>5</sub> never starts under 600°C<sup>6)</sup>. However, the stability of As<sub>2</sub>O<sub>5</sub> is easily decreased by the addition of other compound. Chromium and copper, which are two other elements besides arsenic, affect the volatilization of arsenic. When copper (II) oxide is present with As<sub>2</sub>O<sub>5</sub>, the temperature of volatilization of As<sub>2</sub>O<sub>5</sub> is slightly lower than that of pure As<sub>2</sub>O<sub>5</sub> as a report says<sup>6)</sup>. As for the rest of As<sub>2</sub>O<sub>5</sub>, it reacts with copper oxide to form mixed copper arsenates (2CuO · As<sub>2</sub>O<sub>5</sub> and Cu<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>)<sup>6)</sup>. These compounds are stable under 900°C. As for chromium, chromium (III) oxide causes similar effect as copper (II) oxide; part of the

As<sub>2</sub>O<sub>5</sub> is volatilized and the rest reacts with chromium (III) oxide to form chromium arsenate (CrAsO<sub>4</sub>).

Besides the CCA compound, other compound generated during carbonization affect volatilization and decomposition of As<sub>2</sub>O<sub>5</sub>. In the presence of water, gas exhausted from wood material during carbonization contains about 12 to 15 % of hydrogen <sup>7)</sup>. A report says that in the presence of 5% hydrogen, As<sub>2</sub>O<sub>5</sub> volatilization occurs at 425°C which is lower than that of volatilization of pure As<sub>2</sub>O<sub>5</sub> <sup>6)</sup>.

It is known that reducing agents decrease the temperature of degradation of As<sub>2</sub>O<sub>5</sub>. Glucose and activated carbon are reported to speed up the thermal decomposition of As<sub>2</sub>O<sub>5</sub> <sup>8)</sup>. Besides the decomposition of As<sub>2</sub>O<sub>5</sub>, activated carbon reduces arsenate to arsenite. Arsenate is reported to volatilize at 200°C <sup>8)</sup>. This reaction was reported to occur in a reducing environment. Although both glucose and activated carbon are not generated during carbonization, the charcoal that is generated from material can act as a reducing agent inside the kiln. For example, it was also reported that heating a mixture of arsenate and wood promotes the volatilization of As<sub>2</sub>O<sub>5</sub> <sup>6)</sup>. Compounds generated during pyrolysis are reported to promote the volatilization of As<sub>2</sub>O<sub>5</sub>. Hence, the same mechanism may contribute to arsenic release from CCA wood in this experiment.

The heating rate did not affect on the retention of arsenic in this experiment. Although the proportion of arsenic in the charcoals to arsenic in raw material was widely affected with changes of the carbonization temperature, those under the same carbonization temperature showed similar results despite of the different heating rate (Table 1). Furthermore the proportion of trapped arsenic to arsenic in raw material showed independent tendency among the sample series at each carbonization temperature. For example, the sample series at 400°C retained less arsenic with increase of heating rate. However, those at 700°C showed

opposite results.

The amounts of arsenic retained in the pyroligneous liquors are similar to each other, although the loss of arsenic increased as carbonization temperature increased. These results indicate that arsenic capturing ability of the trap was limited.

#### Charcoal after leaching with pyroligneous liquor

Table 2 shows the arsenic content in the charcoal (carbonization temp. 400°C, heating rate 10°C/min) after leaching with pyroligneous liquor. Each sample is named by the leaching temperature.

Leaching of arsenic was observed for all samples. As leaching temperature become higher, leachability of the solvent gradually increased. The sample extracted at 100°C showed the maximum leaching ability, and 26.5% of arsenic was extracted with the pyroligneous liquor. Though the leaching ability in this experiment were not so high, arsenic collection will be performed easier from the leachate rather than from solid, CCA wood.

Although no reports on the leaching of charcoals obtained from CCA wood could be found, there are many previous reports on the leaching or leaching tests of powder of CCA wood. In these papers, factors such as pH <sup>9)</sup>, ability to form a complex with metal <sup>9)</sup> and leaching temperature <sup>4), 10)</sup> were reported to be effective for leaching arsenic from CCA wood.

Although the leaching rate by using distilled water as a control were not determined in this report, it seems that pyroligneous liquor shows higher leaching rate than distilled water, because Stock *et al.* showed that lower pH solution showed higher metal leachability by using four different pH solutions; deionized water (solution pH ranges 6 - 7), synthetic landfill leachate (solution pH of 4.2 ± 0.05), synthetic rain water (solution pH of 4.93 ± 0.05) and sea water (pH = 8.5). Since solution pH of the pyroligneous liquor used in this experiment is low (pH = 2.2), pH might affect arsenic leachability. Metal

Table 2 Arsenic content in the charcoals after leaching with pyroligneous liquor

	Charcoal extraction residue				
	40°C	60°C	80°C	100°C	
Concentration of retained arsenic (mg/g)	1.32	1.12	1.14	1.02	0.97
Leaching rate (%)	–	15.4	13.9	22.5	26.5

leachability increased as pH decreased. Because water, acetic acid is the main constituent of the pyroligneous liquor used in this experiment. Acetic acid is reported to form a complex with copper<sup>9)</sup>, however no report on the formation of complex with arsenic was found. As for leaching temperature, temperature increase is reported to promote the leachability of solvent. Hence, temperature might have a major effect on the leachability of solvent.

Besides the conditions of the media, the oxidation state of arsenic might affect leachability in this experiment. The initial oxidation state of arsenic mixed in CCA at the injection into materials is pentavalent. However, it is gradually reduced to trivalent while the injected wood is in use<sup>11)</sup>. In addition, carbonization will reduce arsenate to arsenite<sup>8)</sup>. Arsenite is reported to be a more soluble and more mobile species than arsenate and it does not bind strongly to the wood<sup>12)</sup>. Hata *et al.* also reported that 20% of total arsenic is lost by 300°C<sup>6)</sup>. Since the materials used for this experiment were carbonized before leaching, some of the arsenic retained in the wood might have changed into trivalent form and thus affected the leaching of arsenic. Although arsenite is more toxic than arsenate, its higher solubility and mobility assist its removal from CCA treated materials. Further studies on controlling the form of arsenic in the charcoal are required to improve the removal of arsenic from CCA treated material.

#### 4. Conclusion

Maximum temperature which achieved during carbonization widely affects an arsenic retention in a material. Charcoals obtained below 500°C retained 72 –

82% of arsenic, however those obtained above 500°C exhausted about 50% of arsenic into gas or pyroligneous liquor. Arsenic retention in a raw material was less influenced by heating rate. Arsenic retained in the charcoal was extracted with pyroligneous liquor and leachability of arsenic was promoted as extraction temperature increase.

Many factors, for example, temperature, the other compounds in CCA mixture and compounds generated during carbonization, easily affect the oxidation state of arsenic. The oxidation state of arsenic also affects its mobility. It is important to study controlling arsenic oxidation state in charcoal to develop to arsenic removal method from CCA wood.

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