RELEASE OF ARSENIC DURING THE CARBONISATION OF CCA-TREATED WOOD ON A LABORATORY AND PILOT SCALE

by

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The release of arsenic during pyrolysis of CCA(chromated copper arsenate)-treated wood starts at a temperature below 327 °C, but up to 600 °C only 30-40% of the arsenic initially present in the wood is volatilised. The changes of heating rate, wood moisture, degree of the comminution and methods of pyrolysis (fixed bed or mechanically pushed and loosened bulk of chips) do not substantially change the situation. The release of arsenic can be eliminated or strongly reduced by use of carbonisation catalysts. The ways and means of metals regeneration or practical use of this contaminated charcoal are still to be elucidated.

A substantial decrease of the As, Cr, and Cu content in charcoal from 2800-5550 ppm, 3700-14300 ppm, and 3500-8800 ppm, to 61 ppm, 1014 ppm, and 282 ppm, respectively, was achieved by carbonisation of the previously leached wood specimens. The leachability of CCA-salts from the wood treated with diluted sulphuric acid is good, and the amount of the leached-out metals exceeds 90-95%. Ultrasound treatment improves the leachability, although the effect is not high enough to achieve the full elimination of metals, especially chromium, to meet the concentration levels in charcoal set by legislation.

Key words: *chromated copper arsenate, CCA, wood preservatives, carbonisation, release of arsenic, leachability of chromated copper arsenate*

Introduction

Chromated copper arsenate (CCA) in pressure-treated wood to protect wood from rotting has been used since the 1940s. Since the 1970s, the main part of the wood used in construction, pole lines, residental settings *etc*. has been CCA treated one. Therefore, the problem of used-up impregnated wood is turning serious, because arsenic is a known human carcinogen. Chromium is toxic because one of Cr(VI) reduction products is the carcinogenic Cr(V), which lodges in any tissue to form cancerous growths. However, chromium and copper are present in ash and get into the atmosphere in much lesser amounts in comparison with arsenic. The high volatility of As_2O_3 makes it the most dangerous pollutant if CCA-treated wood is burnt. The life-cycle of CCA-treated wood is estimated to be about 20-50 years, depending on the method of treatment and conditions of service after which the wood is discarded as a waste.

The amount of the wood treated with CCA preservatives under pressure increases from year to year. The activities aimed at replacing of CCA-containing preservatives by alkaline copper quarternaries and copper-boron azoles in consumer use do not change the situation substantially. Correspondingly, the amount of used-up telegraph and electric transmission line poles available for recycling and disposal increases. The assessment of the potential for recycling used-up preservative-treated wood has demonstrated that the most viable recycling option for wood treated with arsenic is probably composite manufacturing, but problems of comminution emissions and adhesive compatibility still remain [1]. CCA recuperation from used-up treated wood by solvent extraction would allow the use of biodegradation or carbonisation processes. Nevertheless, the use of organic acids (acetic acid, formic acid, citric acid), forming complexes with copper and arsenic, and effectively leaching chromium from CCA-treated wood, is an expensive option due to the high price of solvents and wood crushing costs, since the useful wood particle sizes for extraction are 1-3 mm. At such sizes diffusion within the particle is not a limiting step of the leaching process [2-4]. Although technical papers and patents are reporting and recommending a great number of ideas as well as technical solutions and apparatuses for demolition wood decontamination, and the attractive recommendations for recuperating preservatives and impregnating substances promise clean residual wood chips or fibers and partial recovery of preservatives, all of them are complex and, therefore, are neglected by practitioners.

The investigations of CCA-treated wood – cement composites are reported to be successful, but it is evident that problems of comminution emissions and a high-energy consumption level will determine the low profitability of such a version [5]. If the preservative-treated wood has retained its physical and mechanical properties, it is recommended for use in producing, for example, palings, stakes, spacers, or lathes.

Practically all interfering noxious substances should be removed from the fuel. The limit values of demolition wood chips for arsenic, chromium, and copper are low, namely, 2, 30, and 20 mg/kg, respectively [6] and the control and test procedures are severe. These limits should be met by the extracted wood or charcoal made from CCA-treated wood if they are intended for use as fuels. The reduction of the As content in the charcoal during the pyrolysis of the CCA-treated wood and the investigation of the feasibility of CCA salts removal from CCA-treated wood and its charcoal were the aims of the present work.

Experimental

Materials

The feedstock used in the experiments was pine wood *(Pinus silvestris L.)* of used-up poles impregnated with CCA salt. The CCA-treated electric poles were obtained at a local "Latvenergo" branch in a township "Liči" near Riga. Four poles were chosen, their service time ranging from 20 to 30 years. Four sample logs from each pole were sawn out, the sawdust mean sample collected, and the specimen logs put in the storage room.

Untreated pine wood (pine-tree 5th age class) from the stock of the Laboratory of Xylogenesis of Latvian State Institute of Wood Chemistry (LSIWC) was used as a control specimen.

The feedstock for laboratory pyrolysis experiments in a fixed bed thermoreactor was prepared in cubical blocks measuring 2 × 2 × 2 cm and stored in airtight polyethylene bags. Chips measuring 30 × 15 × 5 mm were hacked by hand and used for experiments on a laboratory pilot scale thermoreactor fitted with a two-paddle stirrer. The apparatuses and procedures of pyrolysis are described elsevere [7]. The sapwood and heartwood samples for analysis were crushed in a laboratory mill to particles measuring 2 to 3 mm.

Analytical methods of wood and charcoal investigation

Determination of moisture was performed according to DIN 52183 by drying at 103 °C to a constant weight. The ash content of wood was determined according to ASTM Standard D-1102-84 at 560 °C. The ash content of charcoal, fixed carbon content and volatiles were determined according to the methods recommended by DIN 51749: ash at 710 15 °C, fixed carbon at 900 °C, 7 minutes in a closed crucible.

Quantitative determination of metals

Since the released arsenic is to be found in all products of the CCA-treated wood pyrolysis, our choice was the methods described in "Official Methods of Analysis of the Association of Official Analytical Chemists [8]. Preparation of solid samples (wood, charcoal, tar) was performed by the method of Kjeldahl digestion, while aqueous solutions of condensables were analysed directly. Since chromium is more strongly bound in charcoal than in CCA-treated wood, the well-known BSI method of leaching using a mixture of hydrogen peroxide and sulphuric acid does not ensure the complete solution of chromium [9]. Metals were brought into solutions by leaching of grinded wood and charcoal samples with a mixture of concentrated nitric and sulphuric acids as prescribed by [8].

The determination of arsenic content was performed by the photometric method employing silver diethyldithiocarbamate according to [10]. The intensity of the red colour developed by arsine, which is formed by reduction of trivalent arsenic, is measured at 520 nm. The content of chromium and copper was determined by atomic absorption spectroscopy (Shimadzu AA-6300).

Leaching of metals facilitated by ultrasound

Equipment: ultrasound water bath, frequency 35 kHz, "BANDELIN electronic", type RK 510.

Materials: air dry milled CCA-treated pole wood and charcoal average sample (particle measure 0.25 mm.

Leaching agent: 2.5, 5.0, and 10% aqueous sulphuric acid solution.

Procedure: portions of the crushed wood or charcoal samples, 20 g each, were placed into 500 ml round bottom flasks, and 200 ml of sulphuric acid solutions poured on. The flasks were closed with glass stoppers and immersed into a bath filled with distilled water, and the ultrasound generator switched on. Aliquots (0.5 ml) of the solution were taken at definite time intervals and concentration of As determined. The process was started at ambient temperature, but the temperature of the water bath rose gradually up to 55 °C during the experiment. After leaching, the acidic solution was filtered-off under vacuum, and the wood or charcoal washed twice with 200 ml of distilled water by treatment in the ultrasound bath for 1 h.

Results and discussion

It has been demonstrated by the thorough experiments conducted by Helsen and Van den Bulck that, during the carbonisation of CCA-treated wood, arsenic is released even at temperature 327 °C, which is considered to be the very starting temperature of the dramatic reduction of As(V) to As(III). They realised an even heating-up of wood by the flow of an inert heat carrier [12]. During our carbonisation tests set up on a pilot scale in a pushed on and loosened bulk of chips, the presence of arsenic in the condensate was detected at the medium bulk temperature 230 °C (fig. 1). At the maximum charcoal bulk temperature 322 °C, the amount of arsenic, being caught in condensables, was only by

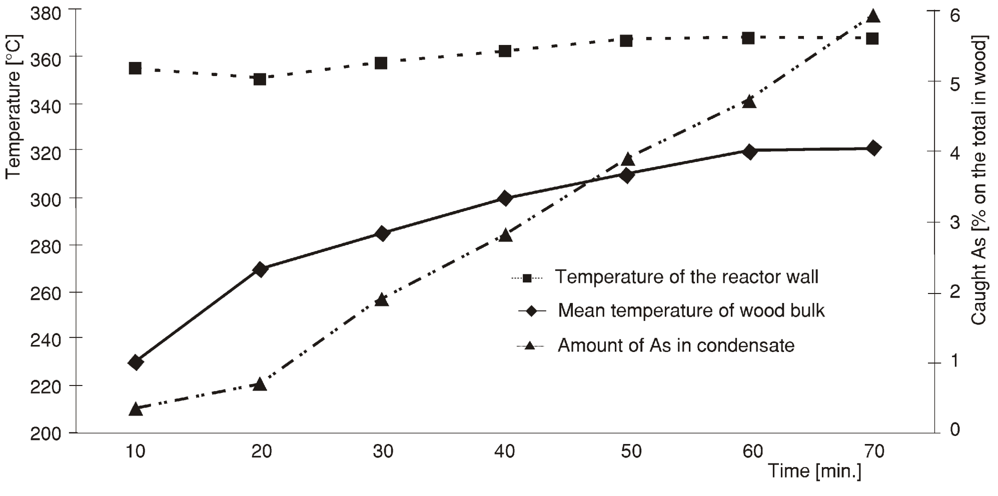

Figure 1. Increase of the As amount in the condensate during low-temperature pyrolysis of CCA-treated wood chips in the pushed on and loosened bulk in a pilot-scale reactor

40% less in comparison with the amount of arsenic in the condensate, captured at the mean bulk temperature 500 °C. The difference of the arsenic release in charcoal was more distinct, namely, 12 and 30% from the starting arsenic content in the CCA-treated wood samples, respectively. The release of arsenic at the mean wood bulk temperature below 327 °C was evidently due to the local superheating of the wood chips surface, directly contacting with the reactor's wall.

The increase of the maximum temperature of pyrolysis resulted in some increase of the arsenic release, but even at 700-800 °C, it did not exceed 40-42%. A more pronounced positive correlation between the temperature increase and arsenic release was demonstrated by sapwood samples containing a 1.5 times higher concentration of CCA salt (fig. 2).

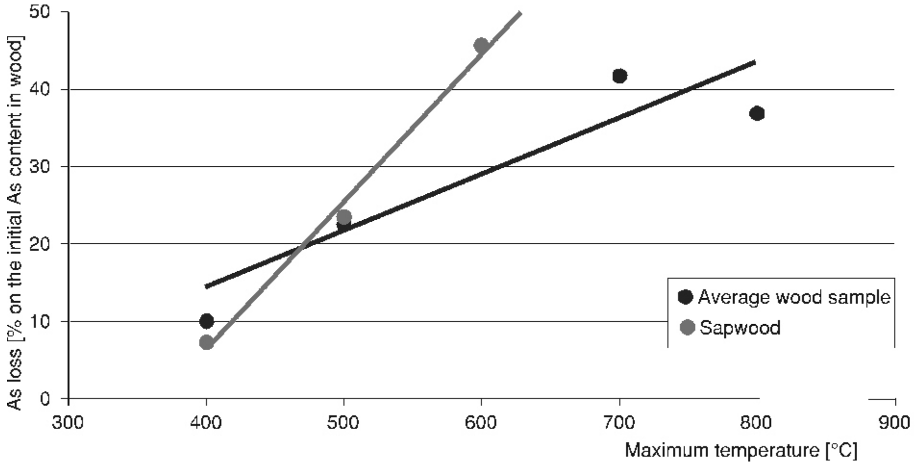

Figure 2. Release of the arsenic during slow pyrolysis in a fixed bed reactor

If the carbonisation of CCA-treated wood is a preparatory, partial decontamination process for co-firing of charcoal with the clean coal prepared by the "3R Clean Coal Plant" process [11], decontamination and carbonisation should be realised in a continuous flow externally heated rotary kiln, and wood granularity would be of special interest from the viewpoint of carbonisation, arsenic release, and also charcoal co-firing. We studied the impact of granularity and moisture content on the release of arsenic in a pilot-scale laboratory reactor with a stirrer, modelling an externally heated rotary kiln, at different maximum temperatures and heating rates. The results are summarised in tabs. 1, 2, and 3.

Unfortunately, it was demonstrated that it was impossible to get rid of arsenic by thermal treatment of CCA-treated wood. The obtained charcoal contained a lot of arsenic. Various temperatures, granularity, and moisture contents did not influence the amount of the lost arsenic during pyrolysis of CCA-treated chips or hogged chips. It was almost constant, namely, 28 to 32% of the initial arsenic content in wood. At increased heating rates, the release of arsenic and yield of charcoal was somewhat diminished (tab. 1).

Table 1. Release of arsenic and yield of charcoal during CCA-treated wood pyrolysis in a pushed on an loosened bulk at various heating rates (maximum temperature 400-500 °C)

Heating rate [°C/min.]	Charcoal yield [% o. d. wood]	Release of As [% on the initial As content basis in wood]
6.5	28.7	32.3
7.7	24.4	29.4
8.0	19.9	32.4
9.3	22.7	28.4
9.6	21.7	23.7

Table 2. Release of arsenic during pyrolysis of a CCA-treated wood in a pushed on and loosened bulk reactor

Characteristics	Units of measure	Chips [moisture % wet basis]			Crushed wood [moisture % wet basis]		
		9.7	14.5	27.6	10.3	10.6	31.6
Maximum temperature	°C	483	405	500	406	505	502
Mean heating rate	$°C\ min.^{-1}$	9.3	7.7	8.0	4.08	6.5	9.6
Charcoal yield	%, o. d. mass basis	22.7	24.4	19.9	26.8	28.7	21.7
Arsenic in wood	ppm	1255	1920	1052	1739	1178	1264
Arsenic in charcoal	ppm	3940	5555	3572	4680	2780	4443
Arsenic release	% on the total in wood	28.4	29.4	32.4	27.9	32.3	23.7

The above-mentioned studies of Helsen and Van den Bulck [12] have shown that, up to 327 °C, the arsenic release is negligible. We attempted to substantially decrease or to eliminate the arsenic release during carbonisation by using carbonisation catalysts to decrease the temperature of the active thermal destruction of wood. It has been

Table 3. CCA-treated wood charcoal characteristics (pilot-scale reactor with a stirrer, pushed on and loosened layer)

Characteristics	Units of measure	Chips measuring 20 × 20-30 ×3-5 mm				Crushed wood (hogged chips); particles measuring 0.4 to 2.0 mm comprise 80% on the total mass basis				
Process characteristics										
Wood moisture	% wet basis	14.5	32.2	9.7	27.6	10.3	10.3	35.0	31.6	10.6
Maximum temperature	°C	405	410	483	500	406	445	500	502	505
Mean heating rate	°C min.$^{-1}$	7.7	6.5	9.3	8.0	4.0	10.6	6.0	9.6	6.5
Duration of the process	min.	50	60	50	60	95	40	80	50	75
Yield of charcoal	% on the o. d. mass	23.3	29.4	22.7	19.9	26.8	23.5	30.0	21.7	25.6
Charcoal characteristics										
Ash	% on the o. d. char	6.1	2.4	4.7	4.6	2.8	3.4	–	3.3	3.8
Volatile matter	% on the o. d. char	24.4	25.8	18.1	16.3	22.6	19.3	–	15.7	17.1
Fixed carbon	% on the o. d. char	69.5	71.8	77.6	79.1	74.6	77.3	–	81.0	79.1
Arsenic	ppm	5555	6360	3940	2823	4680	4173	3079	4443	2780
Copper	ppm	8800	4180	7600	6170	3540	5120	5360	4980	3560
Chromium	ppm	14300	7270	13650	11100	1790	8300	6980	8400	3730
Combustion heat	MJ/kg	25.635	29.884	28.020	29.673	29.435	30.259	30.763	32.156	30.444

shown previously that, in the presence of sulphuric acid or ammonium salts of ortho-phosphoric acid, the temperature of the active destruction stage of wood is decreased by 100 to 150 °C, and, at the temperature 250-300 °C, the dehydration and carbonisation, in general, is completed due to the fast dehydration of the carbohydrate fraction of wood and accelerated formation of polycyclic aromatic structures of charcoal. The process characteristics and results of our experiments are demonstrated in tab. 4.

The charcoal yield is up to 60% on the o. d. wood mass basis, and the arsenic release is prevented during the process. As a result, the bulk volume and mass amount of the contaminated wastewood is substantially reduced, and is much more suitable for disposal, further decontamination or utilisation than the wastewood itself.

It was anticipated initially that, during the thermal destruction of wood treated with CCA salts, the fixed chromium lignin complexes will be disrupted, and the leaching of metals will be also facilitated. Unfortunately, probably due to reduction reactions, the leaching efficiency of metals even from fine grained charcoal particles (particles measuring less than 0.063 mm) was not high enough (tab. 5).

Table 4. Properties of CCA-treated wood charcoal obtained by catalytic low temperature pyrolysis

Characteristics	Units of measure	Catalyst	
		$H_2SO_4 + H_2O_2$	$(NH_4)_2HPO_4$
Process characteristics			
Catalyst concentration		7.25 + 3.1	3.2
Maximum temperature	°C	250	300
Mean heating rate	$°C\ min.^{-1}$	1.85	1.6
Duration of the process	min.	123	180
Yield of charcoal	% on the o. d. mass	59.3	60.6
Charcoal characteristics			
Ash	% on the o. d. char	3.0	6.4
Volatile matter	% on the o. d. char	44.1	41.5
Fixed carbon	% on the o. d. char	52.9	52.1
Arsenic	ppm	4123	4374
Copper	ppm	2170	3990
Chromium	ppm	3870	7570
Arsenic release	% on the total in wood	0	0

Table 5. Leaching of metals from CCA-treated wood charcoal with aqueous mineral acid solutions (temperature 50-60 °C; duration 2.5 h; with stirring)

Leaching agent	Concentration of metals [ppm]						Leaching efficiency [% on the initial concentration]		
	Before leaching			After leaching					
	As	Cu	Cr	As	Cu	Cr	As	Cu	Cr
65% HNO_3	2780	3980	5600	1116	1750	5280	59.8	56.0	5.7
11% H_2SO_4	9844	10300	13410	6825	7100	12810	30.7	31.1	4.5
9.4% H_3PO_4	9844	10300	13410	7314	6600	13340	25.7	35.9	0.5

The best results were achieved by 65% (concentrated) nitric acid, but were still unsatisfactory if the set object was clean charcoal.

The attempts to increase the leachability of charcoal by ultrasound treatment were not a success. A practically acceptable solvent, 5% sulphuric acid solution, was used to treat milled CCA-treated pole wood charcoal (granularity <0.2 mm) samples. The results are shown in tab. 6.

Table 6. Leaching of metals from charcoal facilitated by ultrasound

Duration of leaching [min.]	Leaching efficiency [% on the initial concentration]		
	Arsenic	Copper	Chromium
30	25.0	31.0	28.7
90	. . .	32.5	34.7
420	31.4	39.2	57.7

The effect of ultrasound is positive, but it is not high enough for full removal of metals from charcoal, containing CCA salts.

We tested also the idea suggested by some authors [2] regarding the oxidation of metallic Cr and Cu in charcoal to increase their solubility due to the formation of Cr and Cu oxides. Pulverised (measure <0.2 mm) charcoal was treated with a fifteen-fold (per weight) amount of hydrogen peroxide aqueous solution by aerating and stirring for 2.5 hours at various H_2O_2 concentrations (fig. 3). It can be seen that the increase in the concentration of hydrogen peroxide has some influence on leachability, but is still far from the practically necessary one.

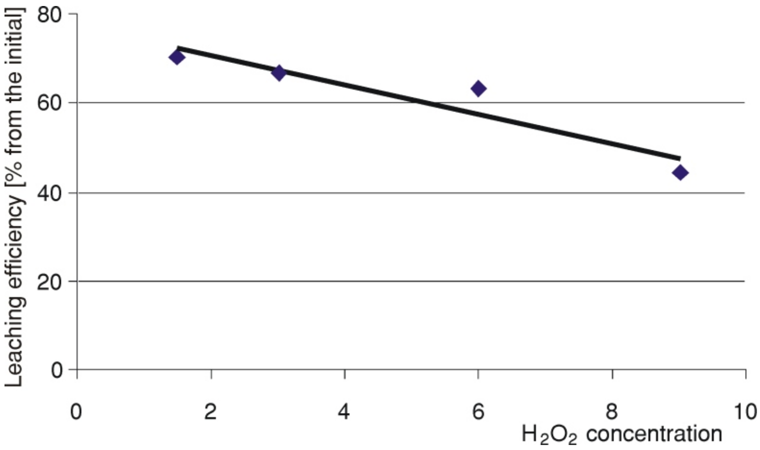

Figure 3. Impact of the oxidising agent concentration on the As leachability

Much better results of leaching with ultrasound were achieved by leaching a milled CCA-treated pole wood average sample (particles size <0.25 mm) with diluted sulphuric acid. The results are summarised in tab. 7.

Table 7. Ultrasound facilitated the CCA leaching efficiency (As, Cu, and Cr in wood)

Wood specimen pretreatment	Concentration of H_2SO_4 solution [%]	Arsenic			Copper			Chromium		
		Before [ppm]	After [ppm]	Leaching efficiency [% on initial conc.]	Before [ppm]	After [ppm]	Leaching efficiency [% on initial conc.]	Before [ppm]	After [ppm]	Leaching efficiency [% on initial conc.]
Untreated	5	1658	7.8	99.9	1242	17	98.6	1916	136	92.9
	10		6.9	99.9		19	98.5		122	93.6
Treated with H_2O_2	5	1370	6.5	99.6	1000	27	97.3	1408	151	89.3
	10		5.9	99.6		21	97.9		97	93.1

The results are good, and the method is suitable for regeneration of metals, before the waste disposal or its further processing. The oxidative pre-treatment by the fifteen-fold amount of 4.5 and 9.0 hydrogen peroxide solution during 2.5 hour stirring and aerating did not demonstrate any effect on the leachability of metals.

The carbonisation of the leached wood samples in a fixed bed reactor at 600 °C yielded 36.8% of charcoal (o. d. mass basis), which had an unexpected low arsenic content. The balance of metals is listed in tab. 8.

Table 8. Balance of Cr, Cu, and As of CCA-treated wood leaching and carbonisation products

Material	Concentration of CCA metals [ppm]		
	Arsenic	Copper	Chromium
CCA-treated ETL pole wood	1888	1103	2444
Wood after leaching	105	161	671
Charcoal	61	262	1014

The dramatically decreased arsenic amount in the charcoal suggests that the combined wood treatment with dilute sulphuric acid and ultrasound has favoured the formation of arsenic compounds, which are able to volatilise during pyrolysis at the temperatures up to 600 °C. Nevertheless, the concentrations of all metals still considerably exceed the permissible limits set for fuels by legislation.

Conclusions

The release of arsenic during pyrolysis of CCA-treated wood starts at the temperature even below 327 °C, and, up to 600 °C, only 30-40% of the arsenic initially present in the wood is lost. The variations in the pyrolysis conditions and methods do not substantially change this situation. The release of arsenic can be eliminated or strongly reduced by use of carbonisation catalysts. Unfortunately, this method has no practical value if the charcoal is intended for use as fuel, since the leaching-out of metals from the carbonised material is complicated and uneffective up to now. For all that the charcoal is more handy for deposition.

The leachability of salts from CCA-treated wood with diluted sulphuric acid is good and the amount of the leached-out metals exceeds 90-95%. Nevertheless, the residual concentrations of metals are still too high for clean fuel production. Ultrasound improves the leachability of metals from CCA-treated wood and charcoal. Still the effect is not high enough to achieve full elimination of metals, especially chromium, to meet the concentration levels set by legislation. Oxidative pre-treatment of charcoal does not sufficiently improve the leachability of metals. The efficiency does not exceed 10-20%. Ultrasound in this case only also slightly improves the efficiency. The leaching of CCA-treated wood with diluted sulphuric acid favoured by ultrasound is a viable method for regeneration of metals (Cu, Cr, As) and a pre-treatment before disposal or further processing.

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References

[1] Felton, C. C., De Groot, K. C., The Recycling Potential of Preservative-Treated Wood, *For. Prod. J. 46* (1996), 7/8, pp. 37-46

[2] Leichter, P., Method of Preservative Treated Wood Utilization (in German), European patent application EP 0298951, A1, Date of filing: 04.07.1998

[3] Cooper, P. A., Leaching of CCA from Treated Wood: pH Effects, *For. Prod. J. 41* (1991), 1, pp. 30-32
[4] Gasco, F., 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 Application EP 0774330, Date of filling: 15.11.1996
[5] Schmidt, R., Marsch, R., Balatinetz, J. J., Cooper, P. A., Increased Wood-Cement Compatibility of Chromate Treated Wood, *For. Prod. J. 44* (1994), 7/8, pp. 44-46
[6] ***, German Federal Government, Ordinance on the Management of Waste Wood, dated 15 August 2002, Annex 2
[7] Zandersons, J., Gravitis J., Kokorevics, A., Zhurinsh, A., Bikovens, O., Tardenaka, A., Spince, B., Studies of the Brazilian Sugarcane Bagasse Carbonization Process and Products Properties, *Biomass and Bioenergy, 17* (1999), 3, pp. 210-219
[8] ***, Official Methods of Analysis of the Association of Official Analytic Chemists, 15th edition. (Ed. K. Helvich), Publ. Ass. Offic. Anal. Chem., Arlington, VA, USA, 1990, pp. 50, 243-246
[9] Van der Broeck, K., Helsen, L., Vandecasteele, C., Van den Bulck, E., Determination and Characterisation of Copper, Chromium and Arsenic in Chromated Copper Arsenate (CCA) Treated Wood and Its Pyrolysis Residues by Inductively Plasma Mass Spectrometry, *Analyst 122* (1997), 7, pp. 695-700
[10] ***, Standard Methods for the Examination of Water and Wastewater, 19th ed. (Ed. A. D. Easton), Am. Publ. Health Assoc., Washington D. C., 1995, Method 3500-As C
[11] Someus, E. "3R" Solid Fuel Preventive Pre-Treatment Cleaning, Clean Fuels for Cost Efficient Clean Energy, www. terrenum.net/cleancoal, 2003
[12] Helsen, L., Van den Bulck, E., Low-Temperature Pyrolysis as a Possible Technique for the Disposal of CCA-Treated Wood Waste: Metal Behaviour, in: Progress in Thermochemical Biomass Conversion (Ed. A. V. Bridgwater), Blackwell Science Ltd., Oxford, London, 2001, Vol. 2, pp. 1417-1432

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