REVIEW OF THERMOCHEMICAL CONVERSION PROCESSES AS DISPOSAL TECHNOLOGIES FOR CHROMATED COPPER ARSENATE (CCA) TREATED WOOD WASTE

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ABSTRACT

Several alternative methods for the disposal of chromated copper arsenate (CCA) treated wood waste have been studied in the literature, and these methods are reviewed and compared in this paper. Extraction experiments have been carried out on CCA treated wood and evaluated as a method to recover the metal compounds into either fresh wood preservatives or other useful industrial materials. Recycling and recovery processes of the metals in the metallurgical industry have also been studied, but not yet all metal products are transformed to usable forms. A study about biorecycling of CCA treated wood through bioremediation and biodeterioration has been initiated. Numerous studies and experiments have been carried out on burning contaminated wood. Direct electrodialytic removal of the metals from CCA treated wood, as well as electrochemical cleaning processes for ash resulting from combustion of CCA treated wood, are under study. Pyrolysis processes (both slow and flash pyrolysis) have been investigated as a major process for the disposal of cellulosic wastes, also CCA treated wood waste.

The authors performed a lot of experimental and theoretical work to get more insight in the metal behaviour during the low-temperature pyrolysis of CCA treated wood waste. Experiments were carried out with CCA treated wood samples, as well as with arsenic model compounds and mixtures of arsenic oxides and reducing agents (glucose or activated carbon). The most important conclusion is that zero arsenic release during pyrolysis of CCA treated wood seems to be impossible since the reduction reaction ($As_2O_5 \rightarrow As_2O_3 + O_2$) can not be avoided in the reducing environment, created by the presence of wood, char and pyrolysis vapours. Once the trivalent arsenic oxide is formed, it is released. This release is driven by a vapour pressure controlled volatilisation process: the higher the temperature, the faster the release.

The insights gained through these studies are used to evaluate other thermochemical conversion processes (flash pyrolysis, gasification and combustion) with respect to their applicability to the disposal of CCA treated wood waste. This evaluation is compared with observations and calculations reported by other researchers in the literature. Finally, the most appropriate thermochemical disposal technology is identified.

***Keywords**: chromated copper arsenate (CCA), wood waste, disposal, thermochemical conversion*

INTRODUCTION

It is estimated that world-wide the wood preservation industry presently treats approximately 30 million cubic metres of wood each year, consuming some 500 000 tonnes of preservative chemicals. Approximately two-thirds of this volume is treated with chromated copper arsenate (CCA) [1]. CCA has been used to preserve wood from insects, fungi and water damage for many years, and is still used today (almost exclusively as oxides), albeit restricted to a limited number of industrial applications. Substantial amounts of CCA remain in the wood for many years and the disposal of scrap wood is a growing problem in Europe, the United States, North America and Japan. The quantities of discarded CCA treated wood will increase significantly in the future [2]. With respect to CCA treated wood at the end of its service life, the wood is classified as hazardous in some member states of the EU and subject to stringent requirements and classified as not hazardous in other member states and therefore subject to much less stringent requirements. Current legislation in the classification of waste is thus imprecise thereby creating a lack of consistency. For several wood products it has been concluded that the waste stage has a very significant impact on the Life Cycle Assessment results [3].

Future waste minimisation focuses on the use of alternative wood treatment preservatives that do not contain arsenic. However, these alternatives leach more copper than CCA treated wood. From a regulatory perspective, they pose a lower risk than CCA treated wood within the disposal sector and within terrestrial environments. Slightly higher risks are expected in aquatic environments due to the toxicity of copper to aquatic organisms [2]. A number of technical issues still have to be resolved with several potential alternative treatments, including corrosion effects,

weathering properties and fixation characteristics. Viable alternatives are available for CCA treated wood for the lower retention levels (4 - 6.4 kg/m^3).

Besides the use of alternative wood treatment preservatives other waste abatement, elimination or reduction methods could be [4]:

- substitution of CCA treated wood by other materials such as untreated cedar, teak, plastic lumber, concrete, steel, aluminium, brick, … for which complete and quantitative full life cycle assessments are needed,
- wood modification treatments (such as high temperature nitrogen or steam exposure or thermal oil submersion) for which research on durability and weathering performance is needed,
- optimisation of preservation treatment for specific end-use conditions (better quality control, selection of wood species),
- designing details that will minimise the potential for decay and thereby the overuse of preserved wood,
- service life enhancing technologies such as the use of stains and other surface protection coatings and water repellents,
- design to minimise waste during construction (reduction in off-cuts and other wastes from reprocessing).

Regardless of waste minimisation efforts, improved disposal-end management practices will play a key role in minimising the impacts of CCA treated wood upon disposal within the short term (25-40 y). The authors had the idea to give a critical overview of the different methods suggested in literature as solutions for the disposal of CCA treated wood waste. While reviewing the papers already published, an extensive review paper with a list of selected references, published by Cooper [5] in 2003, was found. Because a good review already exists, the aim of this paper is not to repeat this work. Therefore, in this paper the authors give a more detailed analysis of the thermal processes and try to identify the most appropriate thermochemical disposal technology for CCA treated wood waste. First, a short overview of the different methods under study is given, based on the material published by Cooper [4,5,6] and other researchers.

LITERATURE REVIEW: OPTIONS FOR MANAGING CCA TREATED WOOD WASTE

A first question that arises when looking for disposal-end management options for CCA treated wood waste is whether or not the CCA treated wood should be separated from mixed wood sources. In Florida, for example, construction and demolition (C&D) wood can contain up to 30 wt% CCA treated wood [2]. Sorting technologies have been studied [2,7,8,9,10,11,12,13,14] and will become a greater challenge as more alternative preservatives are introduced. Visual sorting based on the green colour is known to be not very effective, although it can potentially reduce the amount of CCA treated wood entering waste streams by 15-20%. Chemical stains (e.g. PAN indicator ($C_{15}H_{11}N_3O$) producing an orange colour if sprayed on untreated wood and a magenta colour if sprayed on CCA wood) were found to be effective for sorting small quantities (< few tonnes/y) of CCA treated wood. Both laser and X-ray systems were shown to be very promising technologies for sorting large quantities (> 8000 tonnes/y) of wood in a more automated way. The detection limit of XRF is found to be 3-5% CCA treated wood. Moskal and Hahn [8] designed, implemented and made a field evaluation of an online detector system using laser-induced breakdown spectroscopy (LIBS) for the analysis of CCA treated wood. Discrimination between CCA wood and untreated wood was based on the atomic emission signal of chromium. The accuracy of the LIBS-based analysis ranged from 92% to 100% for sorting the waste at a construction and demolition (C&D) debris recycling centre. The LIBS system did not prove reliable for the detection of severely rotted wood samples or samples that were completely soaked with water. Morak et al. [9] reported a very high spatial resolution for laser-induced plasma emission spectrometry (LIPS) and found that the influence of the humidity and the species of the wood on the results of the analysis is negligible.

The application of a permanent identification marking system similar to but more persistent than for grade stamping may become a requirement. Whether this be indelible stamp, bar code or embedded chip, it must be able to survive the service life exposure conditions to be of any use [6].

Industrial treated products, such as poles and railway ties, are easily recovered but CCA treated residential lumber presents a challenge to collection and transportation because of the increasing quantities and its widespread distribution. Eventually, it will be necessary to have a collection, transportation and processing infrastructure for this material. Since at European level the sale of arsenic-treated wood to consumer is banned and its use is restricted to a limited number of essential industrial applications, the collection and transportation of CCA treated residential lumber will be only a problem of the near future.

When looking for disposal-end management options for CCA treated wood waste, a hierarchy of options should be considered with some options being more acceptable than others. The acceptability can differ from location to location, e.g. in Europe a lot of treated wood waste is incinerated while in North America almost all treated wood waste is landfilled. However, a general order of preference can be defined:

1. waste abatement or elimination
2. waste reduction
3. waste reuse
4. waste refining for recycling
5. waste treatment and destruction
6. waste disposal

The first two points (abatement or elimination and reduction) have already been mentioned in the introduction, the existing and emerging technologies for managing CCA treated wood waste are summarised in Table 1, together with their barriers and prognosis with respect to implementation [4,5,6,15,16,17,18,19,20,21,22,23,24,25,26,27].

Table 1 Existing and Emerging Technologies for Managing CCA Treated Wood Waste

management option	barriers	prognosis
reuse	wood waste is bulky and inefficient to transport; contaminated sawdust may be generated	good for industrial products but of limited potential for residential treated products
• used as garden borders, posts, land piling, retaining walls, …	high contamination with nails and other fasteners; high cost to dismantle; low quality wood	
• remanufacture – fence components	high contamination with nails and other fasteners; high cost to dismantle; low quality wood	material would have to be refinished to even out differences in weathering discoloration
• salvage and reuse through waste exchange	high cost of handling sorting, transportation and storage	limited potential
refining for recycling		
• wood based composites	issue of using metal containing and contaminated wood and loss of ownership of treated wood (product should be identified as one containing treated wood); landfill disposal is only deferred, not avoided; CCA tends to interfere with the adhesives	the market is not in favour of using CCA wood in conventional wood composite manufacturing, questions about safety of workers and environmental problems
– wood-cement composites	CCA wood fibre cement products are unlikely to be used since pulping of treated wood releases the CCA components into the spent pulping liquor, unless it is mechanically pulped; slow process due to long	excellent potential for the development of new composite products; benefit from inclusion of decay resistant wood fibre; stabilisation of metals within a cement matrix; improvement in

	curing time of the composite; potential for hexavalent chromium release	bending strength and stiffness, internal bond strength, water absorption and thickness swelling performance
– wood-polymer composites	leaching, recyclability, decay resistance, emissions during processing and impacts on physical and mechanical properties should be evaluated	benefit from inclusion of decay resistant wood fibre; low cost and high strength to weight ratio
– thermosetting adhesives bonded composites, particleboard	it makes little sense to use CCA wood since the decay hazard is too low to justify it, except in the presence of termites; in that case the identification of the amount and distribution of CCA particles is required; an addition of 50% CCA wood does not significantly affect the board properties	unproven and unlikely to be a significant factor in the near term
– wet processed fibreboard and MDF	it makes little sense to use CCA wood since the decay hazard is too low to justify it; use of CCA wood would complicate the cleanup of process water	unproven and unlikely to be a significant factor in the near term
– exterior flakeboard products, oriented strand board (OSB)	OSB is made from high quality flakes; lumber products can not be flaked properly; the presence of CCA lowers all property values substantially; however, physical and mechanical properties were enhanced by spraying the flakes with a primer just before spraying and blending of the resin	unproven and unlikely to be a significant factor in the near term
• biodegradation by fungi	part of the contaminants left in the wood and loss in fibre quality; absence of end use for extracted wood and chemicals; problems with contamination of the system by other organisms	not economically feasible
• extraction of CCA components	not 100% effective and slow; recycling of CCA components is not proved; not cost-effective at this time; high cost of size reduction	some potential for treatment of minor amounts of treated wood such as that produced as a by-product of milling
– biological	almost complete extraction, only if combined with solvent extraction = dual remediation; several constraints that limit efficiency and cost-effectiveness	technically feasible but slow and expensive (high cost of the nutrient culture medium)
– chemical	huge amounts of chemicals are used; multistage extraction is required to ensure complete removal of CCA; technology to recover CCA chemicals is not disclosed (re-oxidation + elimination of extracting compounds), but mixing of recovered solution and fresh CCA solution is promising	more research and development is needed to improve, optimise and evaluate the process; effects of extraction on combustion characteristics of wood residue are not reported; extraction has negative effect on the properties of particleboard prepared from extracted wood; economic feasible for surface removed treated wood or sawdust by-products of a re-sawing operation to recycle CCA chemicals
– steam explosion	does not increase the extractability of	not economically feasible

	the chemical components if used as a pre-treatment prior to extraction; leave some residual material in the extracted wood (only 90% removal of CCA)	
– electro-dialytic	no field tests performed (pilot scale is now being tested); expected cost is high; after treatment the metals are distributed over the electrolyte solution, the membrane and as a precipitate on the electrode; total removal of metals not achieved, Cu/Cr/As ratio in the electrolyte differs from the ration in the fresh CCA solution	not yet economically feasible; difficult to compete with solvent extraction
• use for mulch, compost or animal bedding	more leaching due to increased surface area (less than 0.1% CCA wood causes a mulch to exceed risk-based direct exposure standard for arsenic); CCA chemical is dispersed into the environment; products will become untraceable	clear policies and regulations that prohibit inclusion of CCA wood in mulch should be developed
treatment and destruction		
• wood liquefaction	only initial lab-scale experiments; only 85% of the CCA is removed	much more research is needed to improve, optimise and evaluate the process
• thermal destruction	advantage of energy recovery and significant reduction of waste volume, but ash is considered as hazardous waste and arsenic compounds are volatile (modifications, controls and monitoring are needed to meet air quality standards); chipping or grinding is required increasing the energy consumption and cost	potential if the metals collected in the ash are dealt with and arsenic is trapped from the flue gas; most common method in Europe but strong resistance in Canada; more favourable climate for this option is expected in the future
– controlled environment incineration / combustion / cogeneration	cost of grinding dirty material; presence of arsenic in the emissions; collection of metals in the ash where it must be collected and dealt with (metal stabilisation or metal extraction through chemical or electrochemical processes or cyclone melting); general resistance in some countries to consider these options for disposal	some potential, but requires further development; lessens the dependence on fossil fuels; metal concentrations can be diluted by mixing with other waste streams (such as household waste) or fuels (such as coal)
– cement kilns	Portland cement standards have limitations on metal levels, chromium being the limiting element; cost of collection, transport, removal of metal contaminants, getting a permit	potential is limited to a fraction of wood generated; appropriate for milling residues and low retention residential wood
– controlled pyrolysis	arsenic is distributed over the three products (charcoal, bio-oil and pyrolysis gas); no time-temperature threshold found for zero arsenic volatilisation	besides elimination of dioxins and furans formation and possibly easier metal recovery, no additional advantages over the other thermal destruction methods
– high temperature gasification in a metallurgical furnace	high cost of pure oxygen; removal of pure metallic arsenic in the vapour not yet proven on a large scale; arsenic emissions during start-up and shutdown	pilot plant tests still have to be performed; more research is needed to evaluate the process

• energy and raw materials recovery by metallurgical processes	plant has to be well designed to scrub all volatile and particulate arsenic from the stacks; relatively low CCA concentrations in the lumber make CCA recycling economically infeasible; not yet all metal products are transformed to usable forms	excellent potential if infrastructure for collection and transportation of CCA wood waste is developed; further research is needed to examine the maximum amount of CCA wood that can be mixed with copper concentrates without interfering the process
landfill disposal	CCA chemical can leach from CCA wood (both unburned and as ash) in quantities that exceed regulatory thresholds; monofill results in the highest metal concentrations in the leachate compared to C&D debris landfill and MSW landfill; cost of landfilling (hazardous waste sites, lined landfills); shortage of landfill space	not a preferred option because it does not recover any value from the used product; may not be acceptable at individual landfill sites (by 2005 no organic wastes will be accepted at landfills in the EU)

As shown in Table 1 there are many technological options to manage waste of CCA treated wood, but all have their limitations and problems. Instead of importing (the major part from China and Mexico) considerable quantities of arsenic to Europe, it would be more reasonable to utilise the arsenic recovered in whatever way (recycling process at the wood preservation sites, in the metallurgical industry, arsenic containing solutions resulting from remediation processes, …). However, the metals must be converted to their proper valence state before reuse. Such additional processing adds to the cost of recycling which renders the current technologies not economically feasible at this time. The main restriction on commercial exploitation of reuse or recycling technology is the highly diffuse nature in which redundant treated timber enters the waste chain.

In the following sections the authors focus on thermochemical conversion processes as possible alternatives for the treatment of waste of CCA treated wood. Thermal utilisation of the wood waste offers the advantage of providing energy and concentrating wastes for recycling or disposal.

THERMOCHEMICAL CONVERSION PROCESSES: OBSERVATIONS

While the CCA preservative chemicals are relatively simple, inorganic reactions during the wood preservation process produce complicated inorganic compounds and complexes. The thermal decomposition behaviour of these inorganic compounds and complexes is unknown and difficult to determine. The reactions and thermal decomposition of a system containing a volatile compound, such as arsenic oxide, in a gas flow cannot be predicted solely based on equilibrium data. Therefore, in practical disposal of CCA treated wood by thermal decomposition, the reaction kinetics will likely determine the ultimate fate of arsenic in the system [28]. Thermogravimetric (TG) experiments with model compounds have been used to predict the thermal behaviour of the CCA treated wood system by Helsen et al [29] and Kercher and Nagle [28]. The main conclusions are listed below.

1. Volatile As_2O_3 loss occurs below practical wood pyrolysis and combustion temperatures (T_{onset} = 200°C), due to the high vapour pressure of As_2O_3.
2. Pure As_2O_5 does not reduce nor volatilise at temperatures lower than 600°C in air or nitrogen atmosphere. Oxygen content of the atmosphere shows no effect on volatile loss, which suggests a weight loss mechanism based on vapour pressure, not on the decomposition $As_2O_5 \rightarrow As_2O_3 + O_2$. A hydrogen containing atmosphere (5% H_2) causes As_2O_5 to volatilise at much lower temperatures (order of 425°C) which suggests that reducing gases from thermal

decomposition of wood (e.g. CO), which behave similar to hydrogen, likely would decompose As_2O_5 at lower temperatures.

3. The thermal decomposition of copper (II) oxide strongly depends on the oxygen content in the atmosphere (T_{onset} is 775°C versus 1050°C in respectively nitrogen and air), indicating that solid-state oxygen diffusion may be the limiting step. The onset of weight loss in a hydrogen/nitrogen mix is around 200°C, which is confirmed by the Ellingham diagram showing a driving force for the reduction of copper oxides by hydrogen (or carbon monoxide).
4. Chromium (III) oxide does not undergo any significant reactions during heating in inert or air atmosphere.
5. When a mixture of copper (II) oxide and arenic (V) oxide is heated, part of arsenic (V) oxide simply volatilises at slightly lower temperatures than in the pure As_2O_5 experiments; the remainder of arsenic (V) oxide reacts with copper (II) oxide to form mixed copper arsenates ($2CuO.As_2O_5$ and $Cu_3(AsO_4)_2$). The atmosphere exhibits a strong effect on the thermal decomposition of the copper arsenates; in air no weight loss is observed up to 900°C. During thermal decomposition of CCA treated wood the formation of copper arsenates may be a mechanism to limit arsenic loss up to 900°C.
6. When a mixture of chromium (III) oxide and arsenic (V) oxide is heated, free arsenic (V) oxide is volatilised; some As_2O_5 reacts with Cr_2O_3 to form chromium arsenate ($CrAsO_4$), which however does not exhibit any temperature range of zero weight loss.
7. In CCA treated wood, the thermal decomposition of the inorganic components can be influenced by interactions with wood and its decomposition products. Therefore the influence of the presence of glucose and activated carbon has been studied. The thermal decomposition of As_2O_5 is highly influenced by the presence of glucose, both in a nitrogen atmosphere and in a mixed nitrogen – oxygen atmosphere. The presence of glucose gives rise to a faster decomposition, the effect being more pronounced the higher the oxygen concentration in the purge gas is. The interaction of glucose and As_2O_5 is probably a combination of three effects: mutual acceleration of the decomposition reaction, oxidation-reduction reactions and the formation and decomposition of arsenate esters. Oxygen concentrations up to 10% are sufficient to accelerate the decomposition of both As_2O_5 and glucose, but insufficient to reverse the reaction $As_2O_5 \rightarrow As_2O_3 + O_2$. Also activated carbon influences the thermal behaviour of As_2O_5, by promoting arsenic volatilisation at temperatures higher than 300°C. Extrapolation of the behaviour of these model compounds to the real thermal decomposition of CCA treated wood indicates that the reduction of pentavalent arsenic to trivalent arsenic is favoured by the reducing environment, created by the presence of wood, char and pyrolysis vapours. Therefore, the most important conclusion is that zero arsenic release during thermal decomposition of CCA treated wood seems to be impossible since the reduction reaction ($As_2O_5 \rightarrow As_2O_3 + O_2$) can not be avoided in the reducing environment. Once the trivalent arsenic oxide is formed, it is released, obeying a temperature controlled solid-vapour equilibrium.
8. For a mixture of arsenic (V) oxide and yellow pine sawdust it was found that the products from inert pyrolysis of wood promote the volatilisation of As_2O_5. By heating at 5°C/min interaction between both compounds can be observed from 370°C, indicating that arsenic volatilisation occurs above 370°C. However, if the mixture is held for longer time periods at temperatures between 250°C - 370°C, it is observed that arsenic volatilisation occurs, the rate of arsenic volatile loss increasing with dwell temperature.
9. For a mixture of copper (II) oxide and yellow pine sawdust inert pyrolysis causes the reduction of copper (II) oxides at low temperatures (around 305°C).

These studies with model compounds may not take all effects into account, for example the formation of complexes and hydrates of arsenic (V) oxide during preservative fixation that may help to prevent arsenic loss below 400°C. Therefore thermal decomposition studies with real CCA impregnated wood samples are necessary. A lot of researchers have studied the pyrolysis, gasification or combustion / incineration of CCA treated wood and evaluated the fraction of arsenic, copper and chromium released to the atmosphere and retained in the solid residue. This

work has varied in scale from laboratory to industrial installations and has included 100 % CCA treated wood and mixtures with other waste timber sources or other industrial wastes. Both experimental and modelling work have contributed to new insights.

Percentages of arsenic volatilised have been reported to range between 8 and 95 % [16,30,31,32,33,34,35,36,37,38]. These percentages depend on temperature, residence time, extended period of ash heating, presence of chlorine and/or sulphur, oxygen partial pressure, air flow rate and the impregnation process. Amounts of copper and chromium volatilised are not well documented, but are found to be much lower than for arsenic. In all studies arsenic is identified as the problematic compound with respect to volatilisation. If working conditions can be determined for which arsenic losses are predicted to approach zero, extensive flue gas cleaning equipment (scrubbers and filters) is not required, resulting in a less expensive system. Therefore, a threshold temperature, below which the arsenic volatilisation is zero, has been looked for. Hata et al. [30] state that at 300°C already 20% of the total arsenic is volatilised, which is ascribed to part of the arsenic being unreacted (as As_2O_5 compound) after impregnation of the wood. The remainder of the arsenic has reacted during the impregnation process resulting in chromium arsenate ($Cr_2As_4O_{12}$) that decomposes only at temperatures higher than 700°C. Helsen et al. [16] conclude that metal (Cr, Cu and As) release seems to be "zero", but is inconclusive (because of the high experimental uncertainty) at a temperature of 300°C which is held for 20 minutes. Residence times of 40 minutes already result in non negligible arsenic releases. Furthermore, they show that the major part of arsenic in the solid pyrolysis residue (350°C, 20 minutes) is present in trivalent state [39]. Pasek and McIntyre [31] reported that arsenic volatilisation is predicted (through linear extrapolation) to approach zero under conditions of limited air flow and high combustion temperature in excess of 1100°C. No volatilisation of copper or chromium was observed. The residual ash is indigestible even under the strongest acidic conditions, which is thought to be due to the formation of transition metal arsenides at the higher combustion or calcination temperatures. The results from this work are contrary to other studies. Moreover, arsenic balances were far below 100%, which is suspected to be due to incomplete sampling and/or analysis of the metals released, a problem also appearing in several other studies [37,38,40,41,42,43]. These studies show that a threshold level (temperature-time) below which zero arsenic release is guaranteed will be very difficult or even impossible to reach in large industrial installations without flue gas cleaning.

The mechanism responsible for arsenic release during the thermal decomposition of CCA treated wood is not yet fully understood, although a lot of researchers have tried to identify the arsenic compounds released and to postulate some hypotheses. McMahon et al. [36] reported that negligible amounts of arsine (AsH_3) are formed during CCA wood combustion. Essentially all of the volatilised arsenic recovered was found in the condensed (particulate) form and consisted of both arsenites and arsenates. The volatile arsenic trioxide, however, could not be trapped efficiently. They stated that arsenic release is not so much a function of how the fuel is burned, but rather how long the residual ash is exposed to high temperature. Hirata et al. [40] stated that arsenic compounds are first reduced to As_2O_3 with heating, after which it is gasified according to the equilibrium $2As_2O_3 \leftrightarrow As_4O_6$ and generally accepted to be As_4O_6 for temperatures up to 1073°C. For minimising gaseous toxicants from arsenic, CCA treated wood must be burned at low temperatures with reduced air supply. Cornfield et al. [44] did not detect arsine or other metal compounds in volatile nonparticulate form. They suggested that the metals released are all present in particulate form. Helsen and Van den Bulck [45] concluded that the release of arsenic during pyrolysis of CCA treated wood is controlled by the reduction of pentavalent to trivalent arsenic, which is accelerated by the presence of reducing compounds originating from the pyrolysing wood. Once arsenic trioxide is formed, it will be released at temperatures as low as 200°C. In freshly treated wood arsenic is fixed in pentavalent state, but in weathered wood the arsenic may be partly reduced to the trivalent state. The only way to avoid or limit arsenic release (at low temperatures) is to control the reduction reaction. Once arsenic trioxide is formed, it is not easy to re-oxidise it. For example, during combustion with a high air/fuel ratio oxygen is present in the

flue gas, but arsenic trioxide does not get oxidised into arsenic pentoxide as the reaction is known to happen only under pressure [46].

Besides experimental studies modelling contributes to a deeper understanding of the metal behaviour during thermal decomposition of CCA treated wood. Sandelin and Backman [47] studied the high temperature equilibrium chemistry involved when CCA treated wood is burned by utilising an equilibrium model based upon minimising the Gibbs free energy of a hypothetical combustion system. They revealed that partial pressures of arsenic-containing compounds dominate in the temperature range from 500 to 1600°C. At temperatures between 500 and 1150°C, As_4O_6(g) is the dominating species, but at higher temperatures AsO(g) takes over. The following explanation was given: arsenic pentoxide is stable at low temperatures but "forms" gaseous As_4O_6 at about 580°C. They concluded that chromium and copper in impregnated wood are unlikely to volatilise at common combustion temperatures. At 1200°C only 0.05 % of the total chromium and 0.51 % of the copper was found in the gas phase. Arsenic was more volatile, existing 86.89 % in the gas phase at the same temperature. Supplementary calculations showed that magnesium, copper and chromium compounds may prevent arsenic from volatilising. In addition, reducing conditions within the char particle may affect the tendency of the metals to vaporise. Conclusions with respect to low-temperature chemistry were not given. Kitamura and Katayama [48] combined experimental studies and thermodynamic analyses and concluded that the higher retention of arsenic in charcoal (after pyrolysis in nitrogen atmosphere) compared to ash (after combustion in air) is due to absorption of arsenic in the charcoal. Thermodynamic calculations resulted in the identification of vaporised arsenic species in nitrogen and air atmosphere: As_4, As_2 and As_3 dominate up to 1100 K in nitrogen atmosphere, while AsO_2, AsO, As, As_4O_7 and As_4O_6 appear at temperatures above 1100 K in air. These results do not agree with the results published by Sandelin and Backman [47].

Since thermal processes inherently lead to volatilisation of arsenic, appropriate arsenic capturing devices have to be installed. These devices are said to be commercially available, but very few tests have been carried out on industrial scale for the specific case of thermal conversion of CCA treated wood that is characterised by the production of submicron aerosol fumes which are difficult to effectively collect. Even on lab-scale it is very difficult to obtain arsenic mass balances of 100%. The most important conclusions drawn from an extensive literature review are given elsewhere [49]. Syrjanen and Kangas [38] emphasised the need to change existing flue gas cleaning equipment when impregnated timber is burned. A venturi scrubber was found to be insufficient in combination with a grate boiler; the average arsenic concentration in the exhaust gas was 2.8 mg/Nm^3 [41]. Additional investments are needed for better cleaning systems, tuned in to the type of burner, gasifier or pyrolyser, and for measurements to control emissions. Industrial experience with other feedstocks can be helpful in the design of an appropriate arsenic capturing device. When incinerating arsenic containing waste an efficient filter (electrostatic filter) does not succeed in capturing all the arsenic. Around 5.4% of the arsenic originally present in the waste passes the electrostatic filter and is captured in the downstream wet scrubber (using lime and NaOH) by absorption and/or chemisorption [50]. Sorbent injection is a very attractive method to reduce arsenic emission during coal combustion [46,51,52,53]. Arsenic reacts, while still in the vapour state, at high combustion temperatures, with various sorbents to form larger particles which can be collected effectively by particulate collection devices. The sequestering action of the sorbents reduces the vapour form and/or fine particle form of the metal [51]. These sorbents can be fly ash, activated carbon or mineral material. Hydrated lime ($Ca(OH)_2$) and limestone ($CaCO_3$) are found to be very effective. While Ca is responsible for the reaction of As with these solids, it is the availability of active Ca sites at the surface of these solids that determines the rate of reaction [53]. At temperatures below 600°C tricalciumorthoarsenate ($Ca_3As_2O_8$) is formed, while temperatures between 700 and 900°C give rise to the formation of dicalciumpyroarsenate ($Ca_2As_2O_7$), which is unstable and therefore responsible for a decrease in As capture at higher temperature [46]. Sterling and Helble [53], however, reported a maximum capture of As with calciumoxide at 1000°C.

Besides the mechanism responsible for arsenic release and options available for arsenic capture, the characteristics of ash resulting from combustion of CCA treated wood and combustion of a mixture of untreated and CCA treated wood have been studied. It is concluded that the environmental impact of the ashes investigated (bottom ash, boiler ash, fly ash) is remarkable, none of them meeting the requirements for above-ground disposal [54,55]. Leachates concentrations according to the DIN 38414 part 4 leaching standard exceed the limits for arsenic and chromium. Moreover, chromium is present in the toxic hexavalent state [54]. Bottom ash from wood mixed with minimum 5% CCA treated wood is characterised as hazardous waste under US regulations [55]. To dispose the ash in an environmentally sound manner two options exist:

1. the elements enriched in the ash after the combustion process are recycled;
2. the ash is landfilled after pretreatment, e.g. solidification with cement, concrete, …

Different theories exist about the formation of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), but about the role of copper in the pathways all researchers are unanimous: copper is identified as a catalyst for PCDD/F formation [34,56,57,58,59,60,61]. Due to the presence of copper in CCA treated wood, the formation of toxic PCDD/Fs has to be taken into account [61]. Wunderli et al. [62] examined solid residues (bottom ash and fly ash) from wood (native and waste) combustion and concluded that wood burning is always accompanied by unwanted production of PCDD/F, the amount being dependent on the type of wood burned and the construction of the combustion system. Low carbon burnout and zones with low temperatures seem to support the formation of PCDD/F strongly [60,62]. Consequently, grate boiler fly ashes contain higher levels of PCDD/F than either bubbling or circulating fluidised bed boiler fly ashes [63]. One way to avoid the formation of PCDD/F in incinerators is by blocking the catalytically active sites of copper species by poisoning, for example through the addition of small amounts of sulfamide to the fuel [58]. Since PCDD/F formation is the combination of the elements C, H O and Cl under favourable conditions, another way is to ensure working conditions that eliminate one or more of the essential elements (C, H, O, Cl) or essential parameters (temperature 250-400°C), for example pyrolysis is performed in an oxygen-free environment or flue gases are immediately quenched to very low temperatures. In this aspect pyrolysis has an advantage over gasification and combustion.

BEST AVAILABLE THERMOCHEMICAL CONVERSION TECHNOLOGY

For an inert pyrolysis process to be a reasonable disposal method for CCA treated wood, volatile arsenic loss has to be controlled and the solid pyrolysis product must be suitable for recuperating the inorganic compounds. SEM-EDXA studies have shown [30,64], that during pyrolysis the metal compounds form agglomerates, which suggests that the metals can be easily recuperated from the charcoal in a dry way [65]. However, arsenic losses are already observed for temperatures as low as 275°C [28]. Lower temperatures give rise to very slow wood decomposition rates and thus extremely long reaction times. Therefore, in practice pyrolysis leads to non zero arsenic volatilisation. However, the amount of arsenic volatilised is much less compared to gasification or incineration and therefore the arsenic released may be easier captured by for example chemisorption. The use of flue gas cleaning equipment that captures all arsenic volatilised can thus not be eliminated. With respect to the formation of PCDD/Fs and maybe to recovery of the metals, pyrolysis could be a better option than gasification or combustion.

Flash pyrolysis, that aims at producing as much pyrolysis oil as possible, is not an option for CCA treated wood since a non negligible percentage of arsenic (between 5 and 18% [42]) is collected in the oil. The advantage of pyrolysis oil is that it can be stored, but substantial concentrations of arsenic make it useless.

Incineration of CCA treated wood can be coupled to a recycling process, provided that an extensive gas cleaning system is used to control air emissions. The arsenic containing solution,

collected in the scrubber, is recycled to the CCA solution production unit and the ash containing arsenic, copper and chromium is processed in a copper smelter [38,66] or recycled through chemical or electrochemical processes [67]. The arsenic trioxide dust collected in filters still poses problems with respect to occupational health. As far as occupational health is concerned the use of wet methods to capture arsenic is preferred. Incineration is thus an option for the disposal of CCA treated wood waste or mixed wood waste if three requirements are satisfied:

1. the arsenic and PCDD/F emissions are avoided by using an appropriate gas cleaning system and appropriate cooling trajectories for the flue gas,
2. the arsenic captured (scrubber solution and filter dust) can be recycled in a safe way,
3. an environmentally sound ash treatment technology is available.

A disadvantage of incineration is that it generates heat that has to be used immediately or converted to electricity (efficiency is relatively low), instead of producing a secondary fuel.

Co-incineration is often presented as the best solution for the treatment of wood waste. Advantages are:

- the attraction of co-incineration is the economy of scale; power stations are huge compared to incineration plants.
- low investment cost since the incineration plant already exists, only the gas cleaning equipment has to be extended or adjusted. In Norwegian waste incinerators, for example, the combination of bag filters with activated carbon and wet scrubbers is used [68].
- the installation can be designed and installed on a short term.
- the availability of CCA treated wood waste is not an issue since co-incineration is highly flexible with respect to the fuel used.
- if different waste streams are mixed, e.g. CCA treated wood waste and municipal solid waste (MSW), arsenic may be scavenged by the calcium present in the other waste stream.
- it is easier to comply with emission legislation due to the dilution effect.

However, it is not advisable to mix CCA treated wood with other fuels, such as coal, since CCA treated wood contains much more arsenic than coal. Consequently, the incineration process would deliver more bottom ash that has a higher concentration of water-soluble arsenic and the volatile arsenic has to be removed from a larger amount of flue gas [66]. Moreover in some countries (like Denmark) legislation prescribes that impregnated wood waste must be sorted out and treated separately. For these countries co-incineration is not an option. In other countries, like the Netherlands, a mixture of coal and up to 40% of wood waste (including CCA treated wood) can be used as input fuel for power plants, receiving green certificates [69]. In the European waste classification system, however, CCA treated wood waste is defined as dangerous waste and excluded form the biomass category for which green certificates can be handed out. Most European countries, except the Netherlands, follow this EU directive.

Gasification is characterised by higher energetic efficiencies (electricity generation efficiency is enhanced by burning a combustible gas in a gas turbine instead of fuelling a boiler) and lower environmental impact compared to incineration. If CCA treated wood is used as feedstock, appropriate gas cleaning equipment is still needed [43], but the amount of gas to be cleaned is lower than for incineration. During high temperature gasification the arsenic may be totally converted to metallic arsenic, which is much easier to capture than arsenic trioxide since metallic arsenic does not go through a liquid phase upon cooling and has a higher sublimation temperature than arsenic trioxide [15]. It is essential that the total amount of arsenic is released from the CCA treated wood and reduced to the metallic form. A cleaning system that captures all the arsenic is a very critical point in this gasification unit. Due to the high temperature (1100-1500°C) all organic compounds are cracked, eliminating the danger for PCDD/F formation. When a metallurgical furnace is used the chromium and copper can be caught in a slag, which can be applied as abrasive. The syngas (H_2 + CO, diluted by CO_2 + H_2O + N_2) can be used or sold as fuel and the pure metallic arsenic can be recycled in the CCA impregnation process. A disadvantage of the process is the high temperature needed, but the heat required can be recovered from the gas produced. This process has still to be proven at pilot scale.

The authors conclude that the best available thermochemical conversion technology for the treatment of CCA treated wood waste is:

- on the short term: co-incineration as long as CCA treated wood waste has not to be treated separately and dilution is allowed.
- on the long term a sustainable solution has to be found: preference is given to recycle as much material as possible but it has do be done in a cost-effective way. Dependent on the results of further research work one of the following methods will be identified as best available technology:
    1. low-temperature (380°C) pyrolysis in a moving bed [70];
    2. high temperature gasification (1100-1500°C) in a metallurgical furnace [15].

  Both technologies aim at recuperating the metals and the energy (as secondary fuels: combustible gas and charcoal or syngas) contained in the CCA treated wood waste, but both technologies still have to be proven.

The optimal scale of application is determined by a balance between the high investment cost of the reactor and flue gas cleaning equipment on one hand and the high transport cost to collect the waste timber on the other hand. The important issue is whether or not it is better to transport the wood waste over long distances to gain economy of scale for the operation of large thermal treatment plants.

ACKNOWLEDGEMENTS

L. Helsen is a post-doctoral research fellow of the Fund for Scientific Research of Flanders (Fonds voor Wetenschappelijk Onderzoek - Vlaanderen) (Belgium). The authors are grateful to the company ARCH Timber Protection Limited (UK) for the financial support of the research work.

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