

Formation of metal agglomerates during carbonisation of chromated copper arsenate (CCA) treated wood waste: Comparison between a lab scale and an industrial plant

Lieve Helsen^{a,*}, Amélie Hacala^b

^a *Katholieke Universiteit Leuven, Department of Mechanical Engineering, Division of Applied Mechanics and Energy Conversion, Celestijnenlaan 300A, B-3001 Leuven (Heverlee), Belgium*

^b *Company Thermya, 1 rue Nicolas Appert, 33140 Villenave d'Ornon, France*

Received 2 March 2006; received in revised form 4 April 2006; accepted 11 April 2006

Available online 2 May 2006

Abstract

This paper compares the results obtained by scanning electron microscopy coupled to X-ray analysis (SEM-EDXA) of the solid product after carbonisation of treated wood waste in a lab scale and in an industrial installation. These setups (lab scale and industrial) are characterized by different operating conditions of the carbonisation process. Moreover, the wood waste input to the processes differs significantly. From this study, it is clear that some similarities but also some differences exist between the lab scale study and the study with the industrial Chartherm plant. In both reactors, a metal (and mineral) agglomeration process takes place, even in the case of untreated wood. The agglomerates initially present in the wood input may serve as a seed for the metal agglomeration process during “chartherisation”. The industrial setup leads to a broader range of agglomerates’ size (0.1–50 μm) and composition (all possible combinations of Cu, Cr, As and wood minerals). Some agglomerates contain the three metals but the major part is a combination of wood minerals and one or two of the three preservative metals, while all agglomerates analysed in the lab scale product contain the three metals. The separate influence of wood input characteristics and process conditions cannot be derived from these experiments, but the observations suggest that the higher the CCA retention in the wood input is, the easier is the metal agglomeration process during chartherisation of CCA treated wood waste. From the analyses performed in this study it seems that copper behaves differently in the sense that it agglomerates easily, but the resulting particles are small (<1 μm).

© 2006 Elsevier B.V. All rights reserved.

Keywords: Chromated copper arsenate (CCA) impregnated wood waste; Carbonisation; Agglomeration; Lab scale; Industrial

1. Introduction

Thermal carbonisation seems to be a promising technology for material and energy recuperation out of chromated copper arsenate (CCA) treated wood waste, which is classified as a hazardous waste stream [1]. Material recuperation is based on the formation of clusters or agglomerates, consisting of metals and minerals, during the carbonisation of CCA treated wood [2]. The formation of agglomerates, containing the heavy metals Cr, Cu and As (originating from the CCA impregnation solution fixed into the wood), is the subject of the research work presented in this paper.

Earlier scanning electron microscopy coupled to energy dispersive X-ray (SEM-EDX) analyses, performed by Helsen and Van den Bulck [3], have shown the formation of metal (Cr, Cu and As) agglomerates in the solid product resulting from low-temperature (350 °C) pyrolysis of CCA treated wood. In that study, pyrolysis was performed in a lab scale batch fixed bed reactor, and the wood samples were impregnated specially for these experiments.

Recently, the authors have performed SEM-EDX analyses on the solid product (called Carmath) produced in an industrial carbonisation process (called Chartherm). The carbonisation process as well as the wood input used differs significantly from the lab scale conditions. Nevertheless, some similarities were observed during the SEM-EDX study. However, the difference in reactor operating conditions and wood input has also led to deviating observations. Both, similarities and differences, will be described and discussed in this paper. The insights gained in

* Corresponding author. Tel.: +32 16 32 25 05; fax: 32 16 32 29 85.

E-mail addresses: lieve.helsen@mech.kuleuven.be (L. Helsen), hacala@thermya.com (A. Hacala).

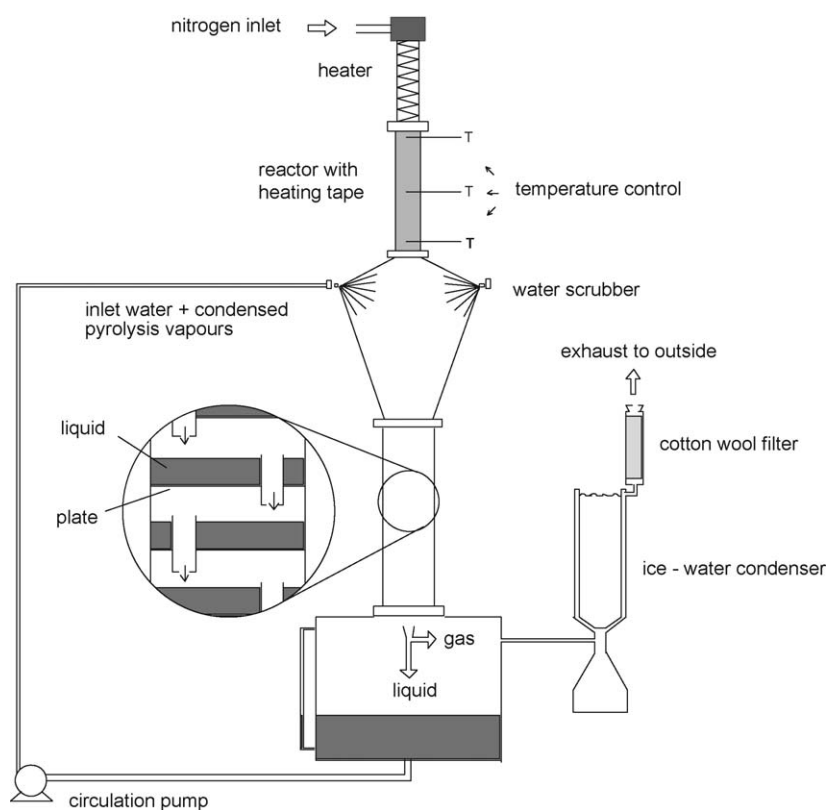


Fig. 1. Schematic presentation of the lab scale batch fixed bed pyrolysis reactor.

this study enable to identify scaling up problems and to improve the process design.

The paper is organized as follows. First, the materials and methods used in previous lab scale experiments and recent industrial experiments are presented (Section 2). Second, the results

for both setups are summarised (Section 3). In Section 4, a comparison is made between the lab scale and the industrial results, and between observations made in the presents study and results found in literature. Finally, the most important conclusions are summarized in Section 5.

Table 1
Characteristics of both carbonisation setups (lab scale and industrial)

Characteristic	Lab scale setup	Industrial setup
Reactor dimension	Diameter = 0.05 m Height = 0.20 m	Diameter = 2.50 m Height = 3.25 m
Operation	Batch operation Fixed bed reactor	Continuous operation: wood supplied at top, charcoal collected at bottom Moving bed reactor
Reactor temperature	$T_{\text{top}} = T_{\text{bottom}} = 350\text{ }^{\circ}\text{C}$	$T_{\text{top}} = 65\text{ }^{\circ}\text{C}$ $T_{\text{bottom}} = 320\text{ }^{\circ}\text{C}$
Reactor pressure (overpressure)	$p_{\text{top}} \cong p_{\text{bottom}} = 10,000\text{ Pa}$	$p_{\text{top}} \cong 0\text{ Pa}$ $p_{\text{bottom}} \cong 60\text{--}70\text{ Pa}$
Residence time of wood	Peeling: 20 min Sapwood: 100 min	8 h in column 5 min in hot zone
Hot gas	Nitrogen, $0.8\text{ N m}^3/\text{h}$ Flowing downward	Combustion gas, flowrate not known Flowing upward
Gas cleaning	Water scrubber Condenser Filter	Wood column Water bath Post combustor
Principle	Low-temperature pyrolysis with uniform temperature over wood column	Distillation column (with controlled temperature and pressure gradient over wood column) where the wood column is acting as condenser and filter, while being carbonized at the bottom

2. Materials and methods

2.1. Lab scale pyrolysis process

Details of the lab scale study (CCA wood sample preparation, pyrolysis process, SEM-EDX analysis, . . .) can be found elsewhere [3]. Section 2.1 is limited to the presentation of the most important conditions.

2.1.1. Wood samples

Two batches of CCA treated wood (*Pinus sylvestris*) samples were prepared for these experiments: peeling wood chips (originating from peeling a stem after it was barked and dried) and sapwood samples (originating from crushed poles). In the case of the peeling wood chips the impregnation process was chosen such that the resulting treated samples would simulate the worst case: peeling wood chips with high porosity were used and the impregnation with CCA salts was carried out twice for class 4 impregnation (wood may be in contact with groundwater and sweet water, requiring a salt retention of 9 kg CCA solution per m³ of wood) in order to obtain a high retention level (higher than the levels found in CCA treated wood waste, thus simulating a limiting case for industrial scale processes and problems). The exact CCA retention of these double-treated samples is not known, but determination of the metal content using ICP-MS results in average concentrations of 1.19% for Cr, 0.43% for Cu and 1.05% for As [4]. The corresponding retention for each metal is estimated to be: 2 kg m⁻³ for Cu, 10 kg m⁻³ for Cr and 5.5 kg m⁻³ for As. The sapwood samples were only treated once for class 4 impregnation (which means that the CCA retention is 9 kg m⁻³), simulating the CCA treated wood waste as it arises if no leaching takes place while in service.

2.1.2. Thermochemical conversion process

Fig. 1 presents a scheme of the lab scale batch fixed bed pyrolysis reactor. The most important characteristics of this setup are listed in Table 1.

2.1.3. Micro-analysis

The specimens were examined in a Philips XL30 FEG scanning electron microscope with an attachment from Edax International Inc. for energy dispersive X-ray analysis (SEM-EDXA). The samples, placed on an aluminium support, were coated with a carbon layer by vacuum evaporation. Random analyses were made of different structures, such as cell walls, bordered pit membranes, ray cells, etc. in order to study the anatomical structure. Furthermore the distribution of the metals (Cr, Cu and As) was examined.

2.2. Industrial Chartherm process

2.2.1. Wood samples

The wood samples used in this study result from crushing waste electricity and telephone poles. These poles are non-homogeneous in terms of age, state of repair and type of industrial treatment. Some have been treated by immersion, others by the Boucherie process, still others autoclaved according to the

Rüping, Estrade or Bethell method. The type of wood preservative used has also undergone continual changes: pentachlorophenol, creosote, metal salts, copper sulphate up to the mid 1970s; CFK (copper, chromium, fluorine), CCB (copper, chromium, boron) and above all CCA (copper, chromium, arsenic) since then.

Today the wood input to the Chartherm process is expected to be a mixture of poles (pine and spruce wood), some of them have been treated with CCA, others with CCB, others with CFK, others with copper sulphate, others with creosote (sometimes the below-ground part of a CCA pole is treated a second time with creosote). These poles are ground by a crushing and splitting process, resulting in a mixture of wood chips with different compositions and sizes [2]. A typical range of wood chips is presented in Fig. 2a.

XRF analysis of the wood chips shows that the major fraction has been treated with Cu-based preservatives, only a smaller fraction has been treated with CCA. The relative distribution between the three metals is, respectively, 70% Cu, 19% Cr and 11% As, while the average concentrations are as small as 0.18% Cu, 0.049% Cr, 0.028% As. Analysis of chips from CCA treated



Fig. 2. (a) Typical range of wood species, (b) typical range of Carmath species.

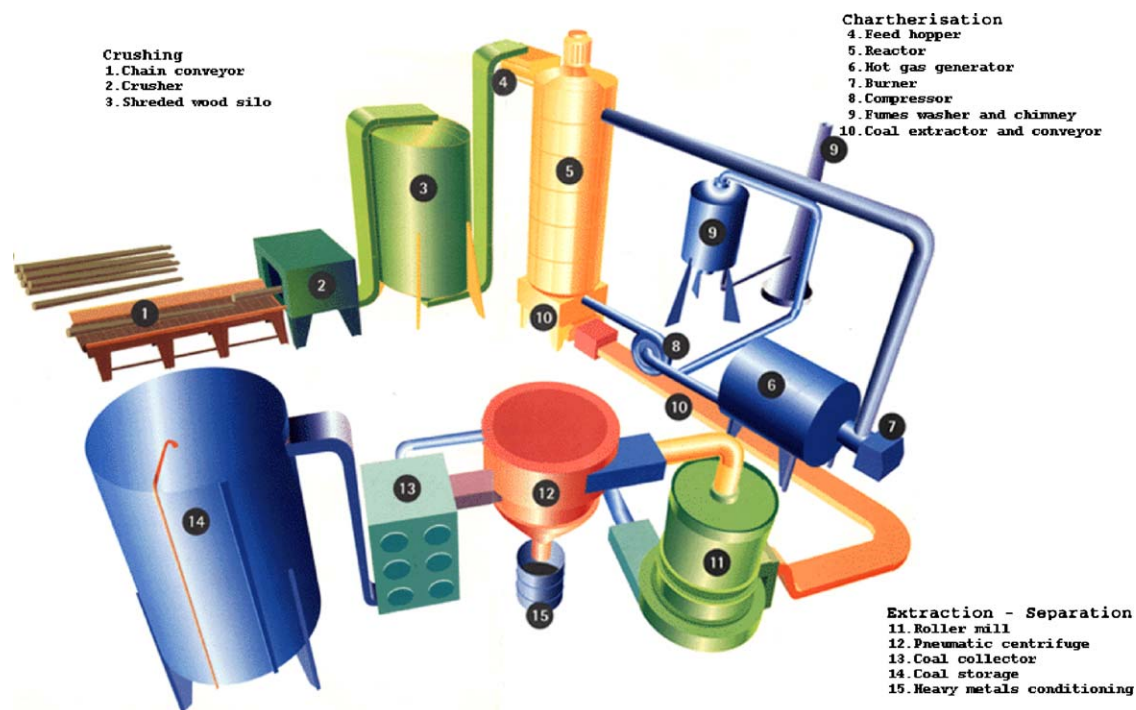


Fig. 3. Schematic presentation of the industrial Chartherm plant.

poles (classified by visual inspection) results in the following concentrations: 0.24% Cu, 0.62% Cr and 0.38% As. The outer surface of the poles gives rise to wood chips with higher metal concentrations: 0.48% Cu, 1.81% Cr and 1.20% As. Applying the same XRF analysis to double-treated CCA wood chips (which were treated after crushing) delivers the following concentrations: 0.56% Cu, 2.41% Cr and 1.38% As, which is up to 50 times the average concentration of the mixed wood chips used as input to the Chartherm process.

2.2.2. Thermochemical conversion process

The Chartherm process, which has been developed by the company Thermya on an industrial scale (capacity of 1500 kg h^{-1} wood waste), is based on the following principle. The process consists of three stages: (1) grinding, (2) chartherisation (thermochemical conversion) and (3) separation. During chartherisation the crushed wood is heated in a reaction column by subjecting it to a current of hot gases. The wood is carbonised, releasing volatile combustible vapours and producing a coal-type residue that entraps the metals and minerals. The combustible vapours are burnt in a gas burner that supplies energy to the system. The charcoal product (Carmath, see Fig. 2b), which is extracted from the bottom of the column, is cooled, compressed to powder and fed to the subsequent separation stage. Centrifugal separation results in a clean carbon product on the one hand and a powder containing the metals, other minerals and some carbon on the other hand [2]. A schematic presentation of the Chartherm process is given in Fig. 3. The most important characteristics of the reaction column are listed in Table 1. It should be emphasized that the Chartherm process is not a real low-temperature pyrolysis process. The chartherisation resembles rather a distillation process. The wood at the bottom of the

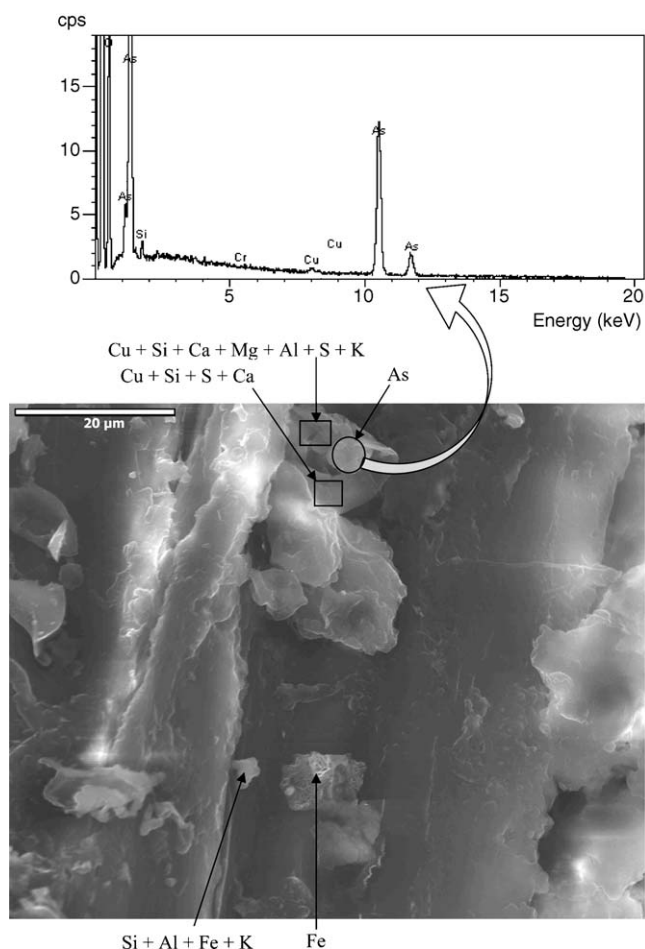


Fig. 4. Detail of CCA treated wood: SEM-EDX analysis of the spots indicated on the photograph.

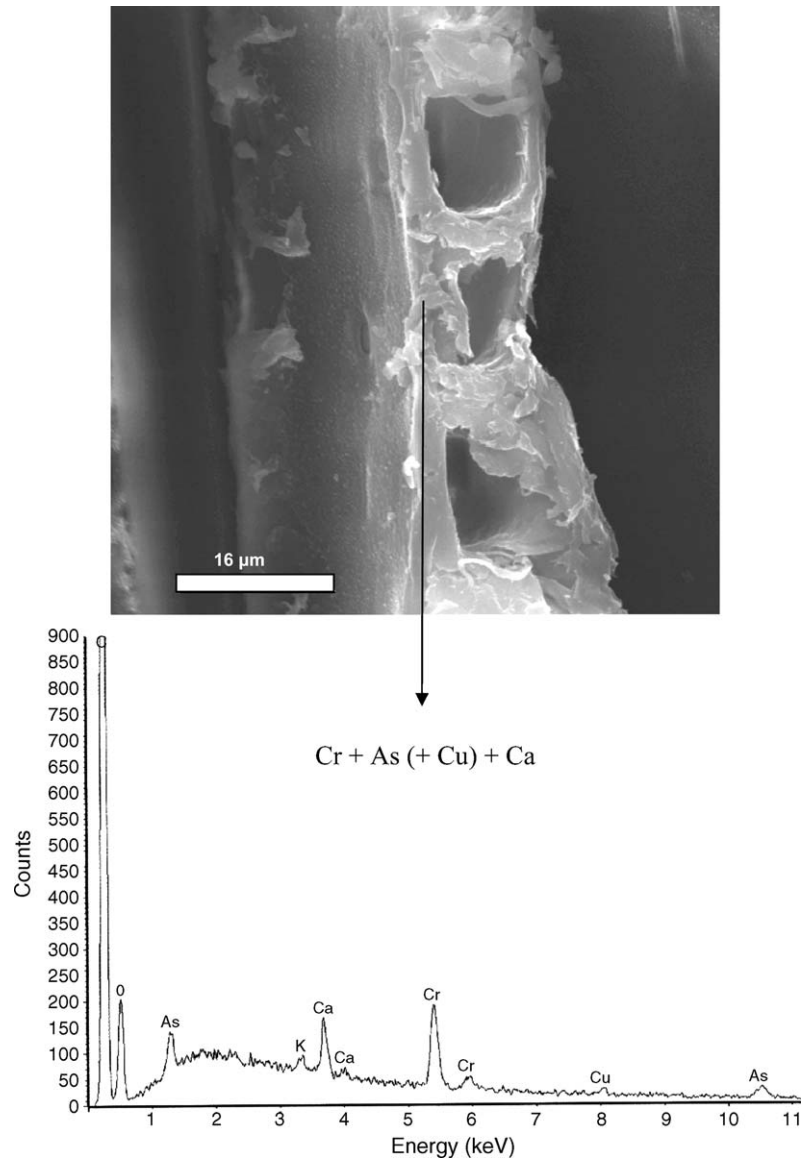


Fig. 5. Detail of CCA treated wood: SEM-EDX analysis of a spot (agglomerate) containing Cr, As and Ca.

column is subjected to a well defined elevated pressure and temperature, transforming it to a coal-type product. The pressure as well as the temperature decreases stepwise with the height of the wood column. The vapours, released by thermal decomposition of the wood, flow upward where part of them is condensed due to the cooling effect of the wood column. These condensed compounds are cracked when they arrive again in the hot zone at the bottom of the column, and so on. The process is thus characterized by a sequence of evaporation, cooling, condensation, heating, cracking, ... where the wood column acts both as a condenser and as a filter.

2.2.3. Micro-analysis

Due to the low availability of the SEM-EDX analysis apparatus the experimental campaign has been split in two series: (1) SEM-EDX analyses performed at the Centre de Ressources en Microscopie Electronique et Analyse (CREMEM, Bordeaux,

France) and (2) SEM-EDX analyses performed at the Centre de Microscopie Electronique (Orleans, France).

The first series of measurements used a JEOL JSM 840A scanning electron microscope with an attachment from Voyageur de Noran for energy dispersive X-ray analysis. The samples, placed on an aluminium support, were coated with a carbon layer by vacuum evaporation. An operating voltage of 25 kV was applied. The total measuring time was 180 s for each location with 15–25% dead time. Specimen count emission for each element per analysis was corrected for background radiation using the PROZA correction method.

The second series of measurements used a Hitachi S4500 scanning electron microscope with an attachment from Oxford link isis for energy dispersive X-ray analysis. The samples, placed on an aluminium support, were coated with a carbon layer by vacuum evaporation. An operating voltage of 25 kV was applied. The total measuring time depended on the analysis

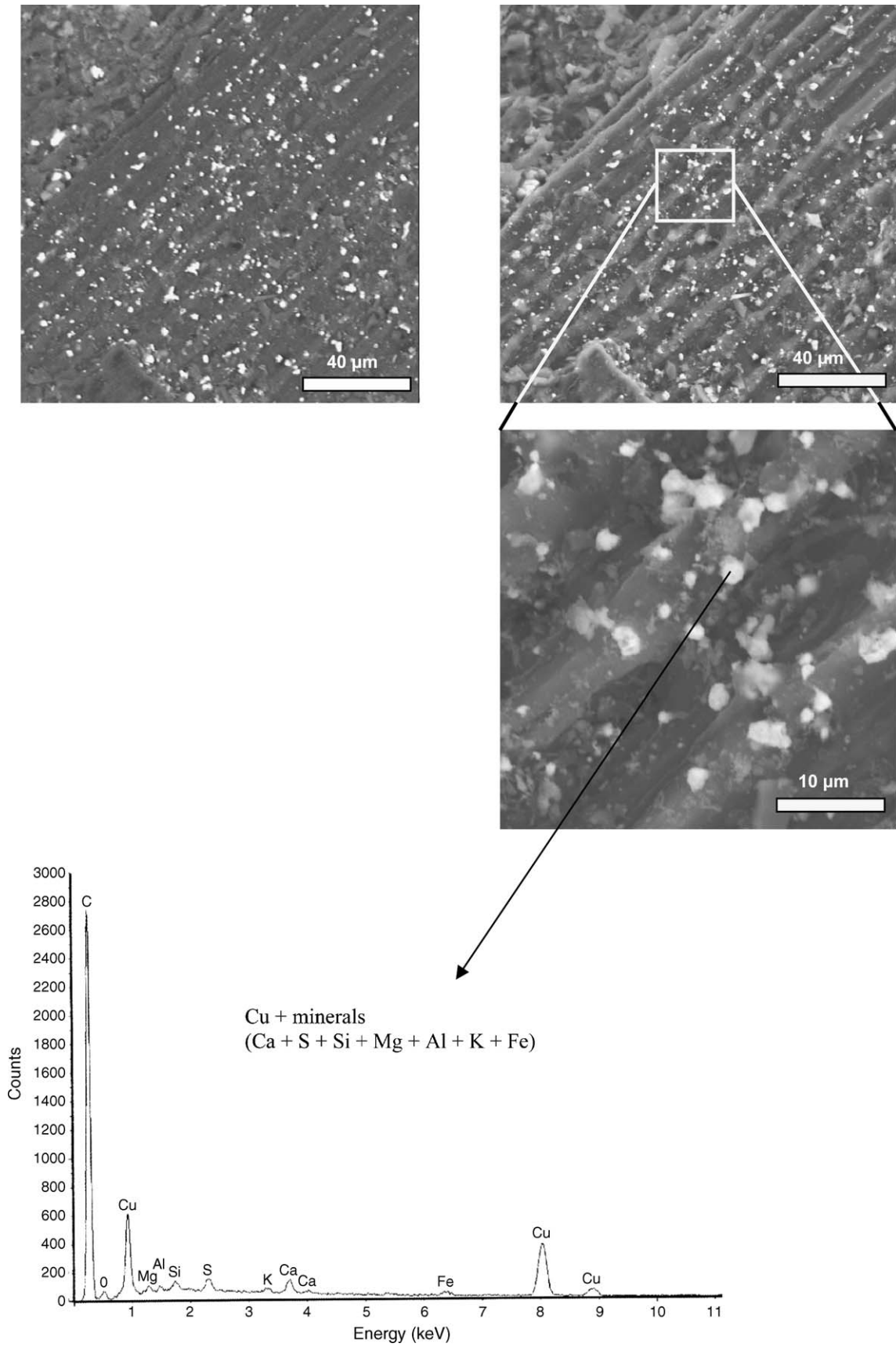


Fig. 6. Detail of Carmath resulting from Cu treated wood: SEM-EDX analysis shows many Cu agglomerates (*left*: image by backscattered electrons, *right*: image by secondary electrons).

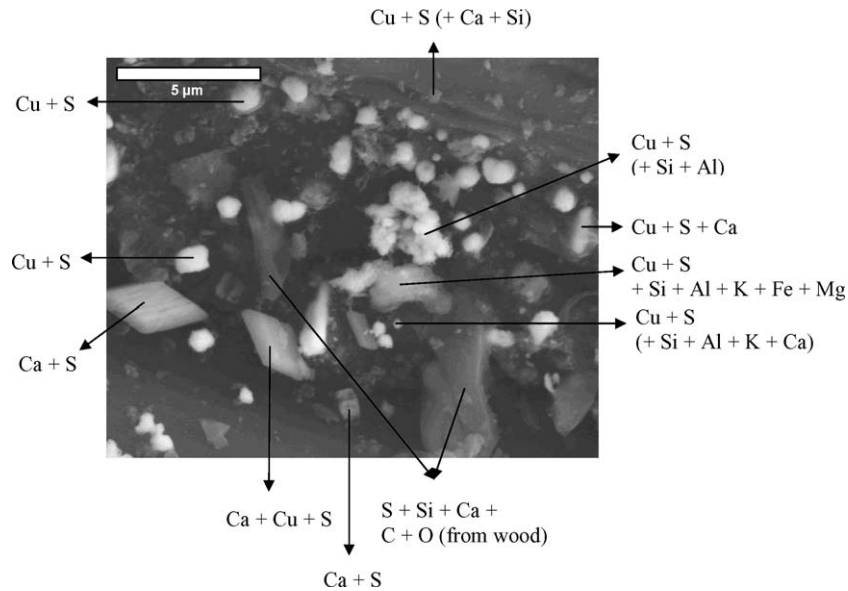


Fig. 7. Detail of Carmath resulting from Cu treated wood: SEM-EDX analysis shows many Cu agglomerates and crystals consisting of Ca and S.

point. Specimen count emission for each element per analysis was corrected for background radiation using the ZAF correction method.

Qualitative analysis was performed by creating pictures by secondary electrons, by backscattered electrons or by cartography. Semi-quantitative results about the metal distribution were

obtained through the coupling with energy dispersive X-ray analysis. Quantification of results using this technique is unreliable due to various difficulties (e.g. detection of the total X-ray intensities of elements present in the cell and production of a reliable matrix for control determinations).

3. Results

3.1. Lab scale pyrolysis process

Details of the results of the lab scale study can be found elsewhere [3]. Section 3.1 is limited to the presentation of a summary of the most important observations enabling a comparison with the industrial setup.

3.1.1. Peeling samples

The CCA treated peeling had a similar structure to the untreated sample, but more precipitates and clusters of irregular shape and size were observed. CCA analyses carried out at random locations in the CCA treated peeling revealed that the three metals (Cr, Cu and As) were present in each of the microscopic volumes of wood examined, although in different ratios and ratios which differ from the original treating solution composition. This may indicate a selective fixation of the metal compounds by the different wood components. Examination of the pyrolysis product showed that the structure of the pyrolysis product was similar to that of the CCA treated wood, although some differences were observed: vestures and warty layers were present, a result of the decomposition of cellulose and hemicellulose during pyrolysis, leaving lignin in the solid product to produce a char-like material. Again, Cr, Cu and As were found in all volumes (randomly chosen) examined, but the variance in ratio was less. The high initial metal concentration may explain the abundance of Cr, Cu and As in the pyrolysis product.

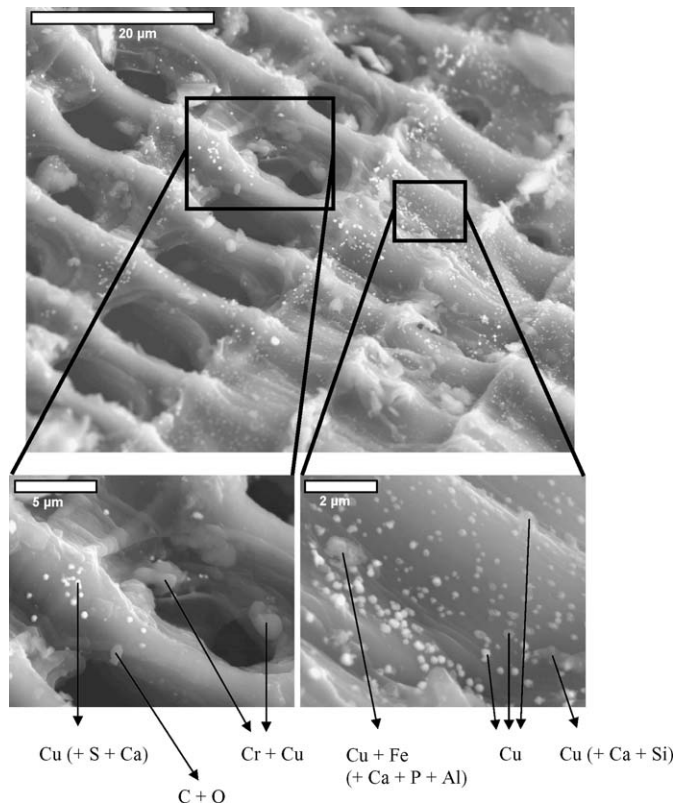


Fig. 8. Detail of Carmath resulting from Cu/Cr treated wood: SEM-EDX analysis shows many agglomerates consisting of Cu (and minerals) or Cu and Cr.

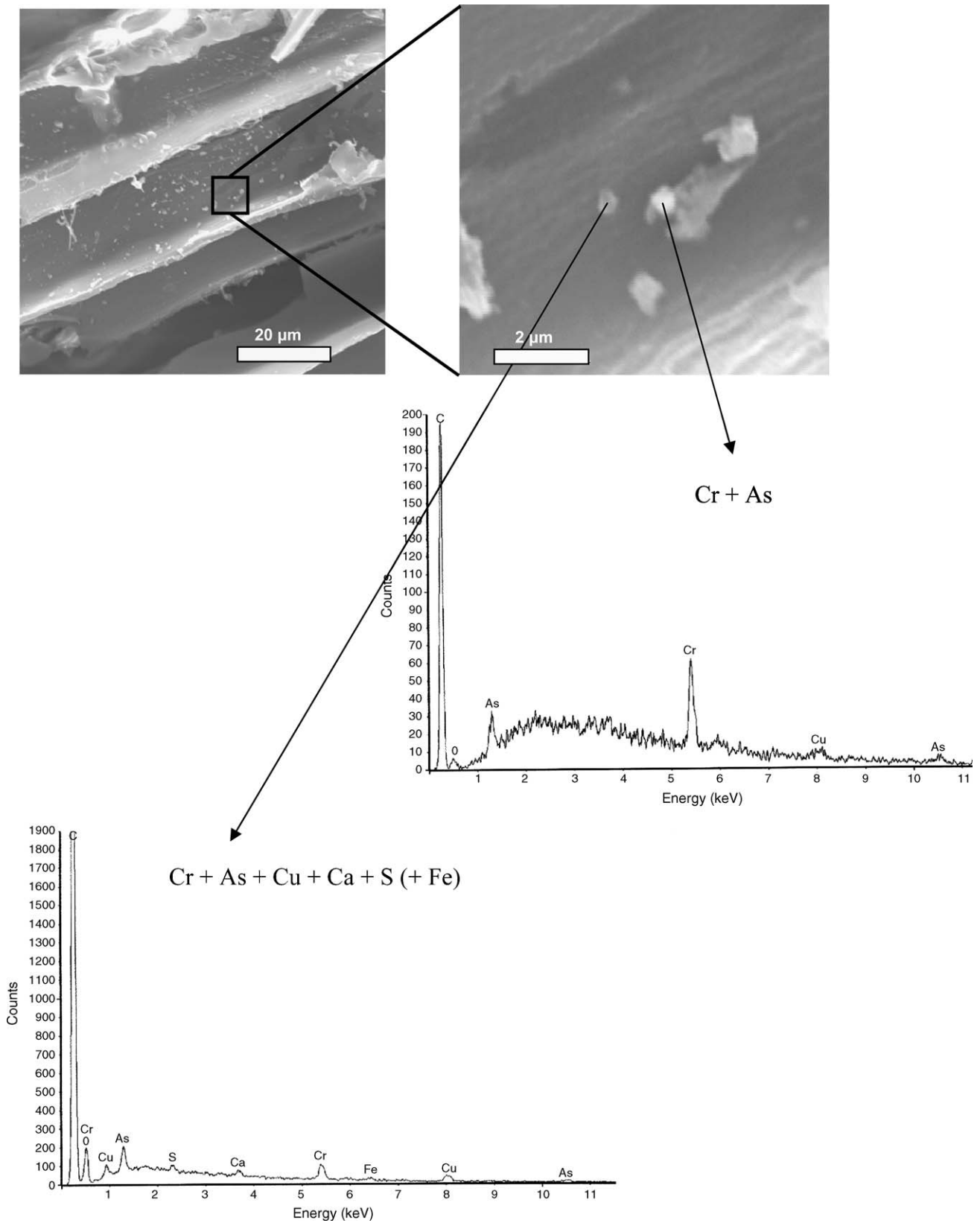


Fig. 9. Detail of Carmath resulting from CCA treated wood: SEM-EDX analysis of spots (agglomerates) containing metals (and minerals).

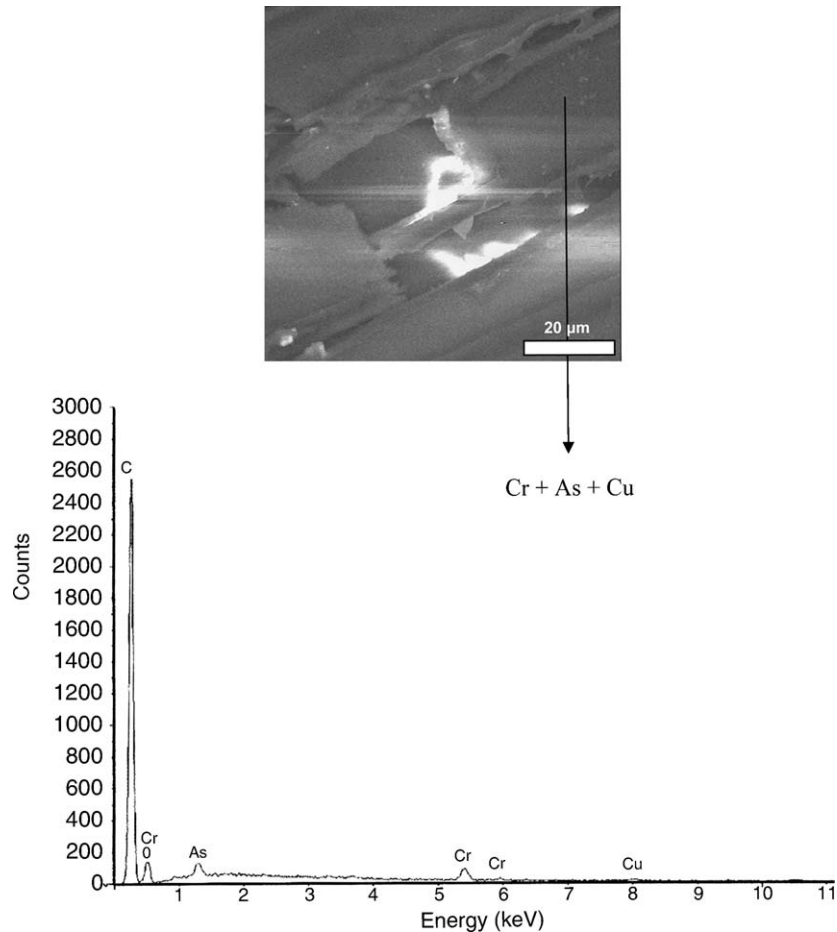


Fig. 10. Detail of Carmath resulting from CCA treated wood: SEM-EDX analysis shows that Cr, Cu and As are diffused in the Carmath matrix.

3.1.2. Sapwood samples

The anatomical structure of the sapwood samples was less porous compared to the peeling samples. CCA analysis performed on random locations showed that the CCA concentrations were lower in sapwood, which can be explained by the singular treatment of these samples.

Again the anatomical structure of the pyrolysis product resembled the initial wood structure, however the structure was more open and tears were observed as a result of the decomposition process. The three metals were mostly found together, although some spots contained Cu without Cr or As, or Cr without Cu and As, or Cr and As without Cu, or Cu and Cr without As. Clusters, precipitates or agglomerates consisting of Cr (dominant species), Cu and As were found in ray cells and tracheids, indicating a migration of metal compounds during pyrolysis.

These results suggest that the formation of metal agglomerates might be easier if the input to the process is characterized by higher initial metal concentrations.

3.2. Industrial Chartherm process

3.2.1. Wood samples

The samples can be easily recognized as wood due to the presence of tracheids and ray cells. The difference in treatment,

and thus the heterogeneity of the wood samples, is clear from EDX analysis: some wood pieces contain the three metals Cr, Cu and As, indicating that these wood poles have been treated with CCA, while in other wood pieces only Cu (no As, no Cr) is found, suggesting that these wood poles have been treated with CuSO_4 or other Cu-based preservatives. In all samples analysed by SEM-EDX copper seems to be the metal present in the highest concentration, even in the CCA treated samples. CCA salts, used to impregnate wood, contain the metals in the following decreasing order of concentrations (wt%): $\text{Cr} > \text{Cu} \gg \text{As}$. CCA oxides, on the other hand, contain the metals in the following decreasing order of concentrations (wt%): $\text{Cr} > \text{As} \gg \text{Cu}$ [5]. CCA salts have been used a lot in the past. Nowadays CCA oxides are usually used since they have better fixation properties. The dominant presence of copper in the samples suggests that the CCA poles have been impregnated with CCA salts. However, the Cr concentration of these CCA samples should be even higher than the Cu concentration. Maybe Cr is much more diffused in the matrix and Cu is much more localized in spots and therefore easier to detect by SEM-EDX analysis. The relative concentration of the three metals as determined by XRF analysis of the wood samples confirms the hypothesis that the CCA poles have been treated with CCA salts. Previous studies (e.g. [6]) that have shown the presence of the three metals (Cr, Cu and As) in zones

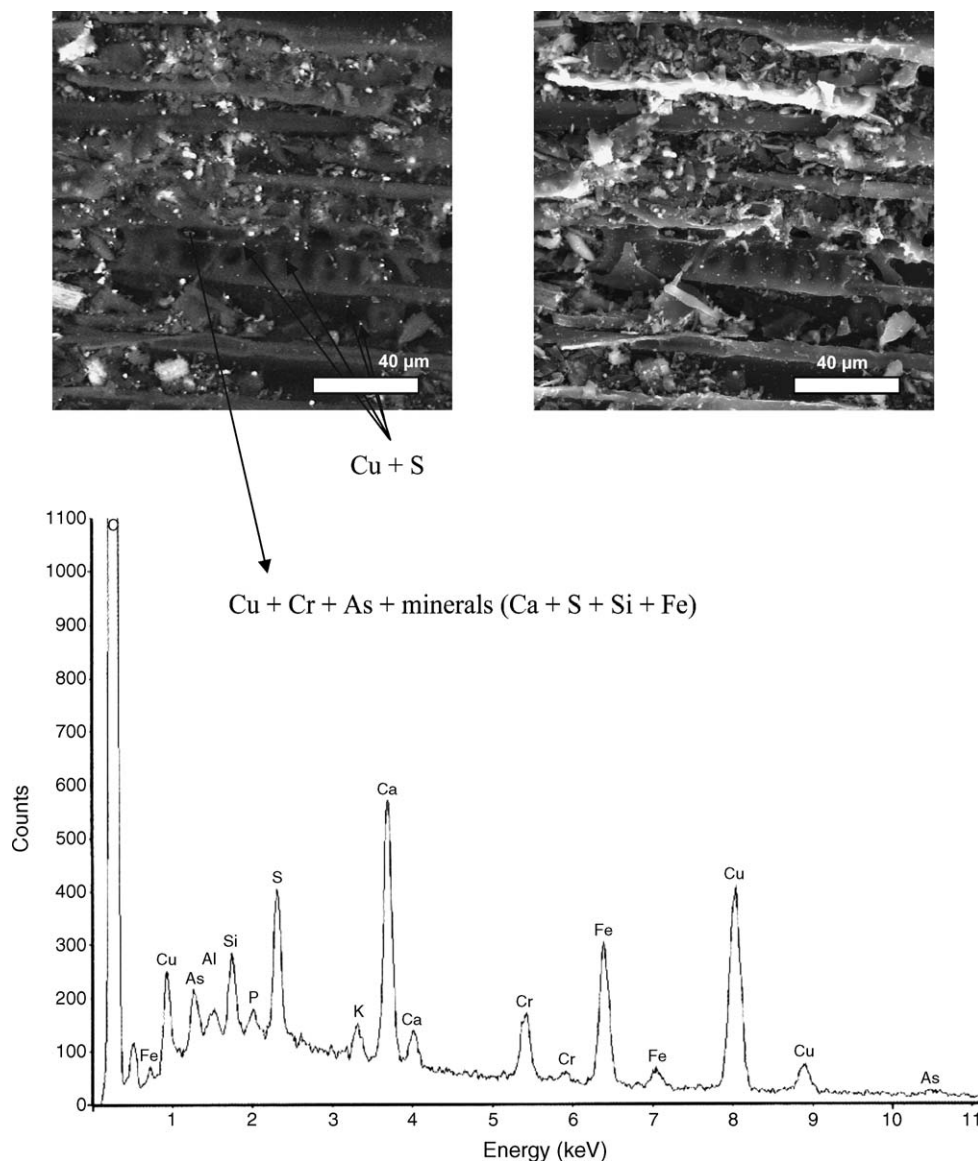


Fig. 11. Detail of Carmath resulting from CCA treated wood: SEM-EDX analysis shows many agglomerates (*left*: image by backscattered electrons, *right*: image by secondary electrons).

and thus a very close binding between the wood matrix and the metals, used wood treated with CCA oxides (such as Boliden K33 that contains CuO , CrO_3 and As_2O_5). The CCA fixation is less perfect in wood treated with CCA salts, resulting in metals concentrated in spots, clusters, . . . Furthermore, samples originating from real wood poles are characterized by lower metal concentrations than freshly treated samples [7]. As a result it is more difficult to find the metals in the wood sample by SEM-EDX analysis.

The wood samples themselves already contain crystals or agglomerates of minerals. Their composition and size are highly variable, ranging from small particles ($3\ \mu\text{m}$) consisting of Si, Al, Fe and K to Si crystals as large as $20\ \mu\text{m}$ in diameter. Some examples are shown in Fig. 4. These mineral agglomerates may serve as a seed for the metal agglomeration process during chartherisation. Sometimes the mineral agglomerates contain

Cu or Cr or As or a combination of these metals. A combination of Cu and minerals is shown in Fig. 4, and a combination of Cr, As and Ca is shown in Fig. 5. The metals may also appear on their own, without other metals and without minerals, for example the spot of As on Fig. 4, either as a distinct particle or diffused in the wood matrix.

3.2.2. Carmath samples

Carmath samples of different dimensions have been examined in order to study the influence of wood chip size on the metal agglomeration process, but no significant correlations were observed. So, the conclusions formulated below hold for all wood chip sizes presented in Fig. 2b.

The Carmath samples still have the typical structure of wood. The presence, size and composition of agglomerates may depend on the type of wood used at the input of the Chartherm pro-

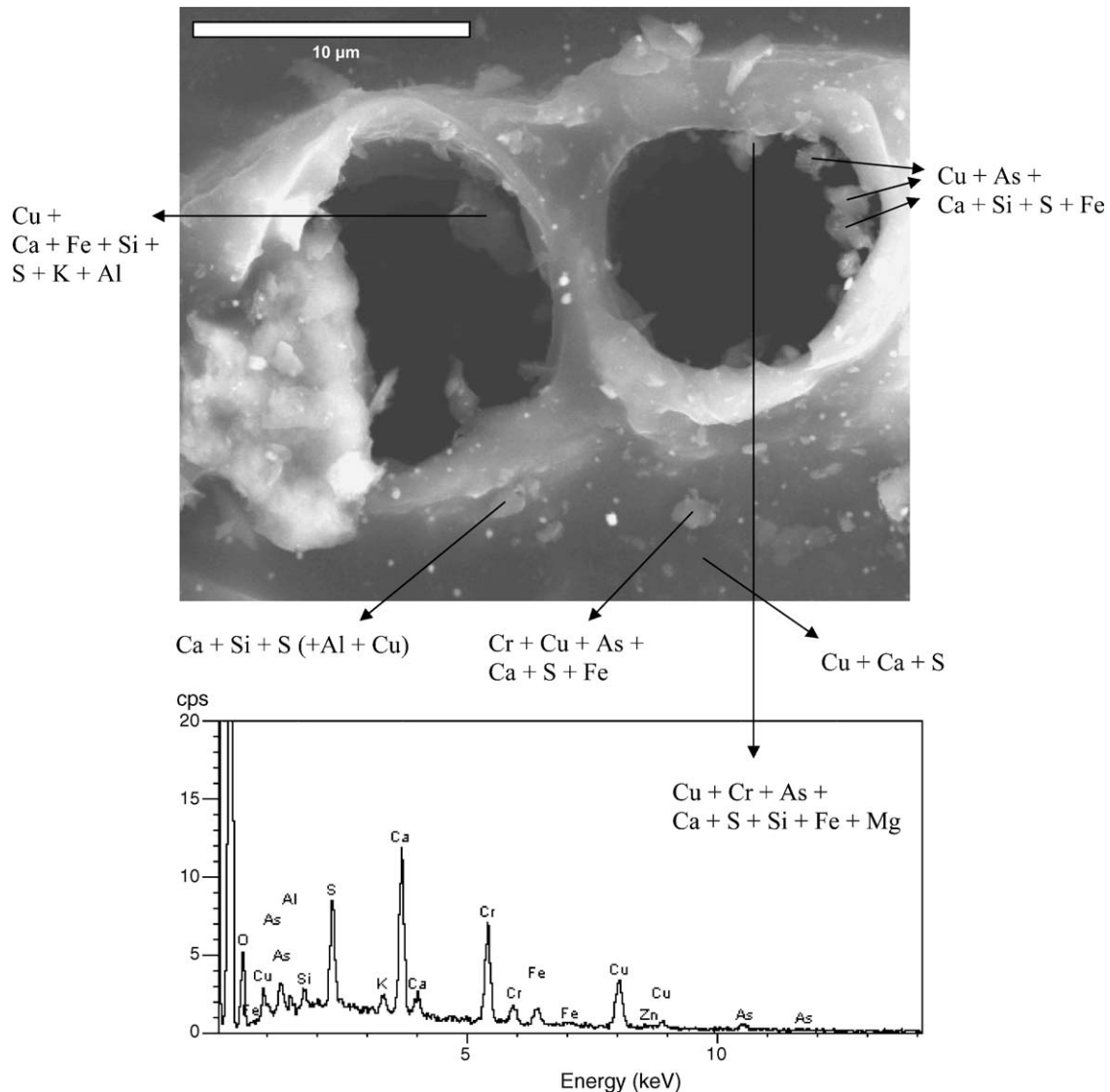


Fig. 12. Detail of Carmath resulting from CCA treated wood: SEM-EDX analysis shows many agglomerates.

cess. Therefore, Section 3.2.2 is divided in different subsections according to the type of wood used as input to the Chartherm process.

3.2.2.1. Carmath samples from untreated or creosoted wood.

Some of the Carmath samples do not contain Cu, Cr or As. Probably these samples originate from untreated wood (centre of poles or untreated poles) or creosoted poles. Even these samples contain agglomerates, ranging in size between less than 1 and 10 μm and being composed of wood minerals. Moreover, the Carmath samples contain significantly more agglomerates than the initial wood samples. Thus, during chartherisation an agglomeration process takes place which results not only in the growth of existing agglomerates but also in the formation of new agglomerates. This means that the metals (Cr, Cu and As) are not needed for the agglomeration process.

3.2.2.2. Carmath samples from Cu-treated wood.

Some of the Carmath samples contain a lot of Cu, but no Cr or As, suggest-

ing that these samples originate from CuSO_4 treated wood. The possibility that these samples originate from CCA treated wood, implying that all arsenic and chromium have been released as volatile compounds, is nihil at the low temperatures used during chartherisation.

A huge amount of agglomerates consisting of Cu, S and wood minerals (such as Ca, Si, Mg, Al, K, Fe, Zn) and measuring about 0.1–3 μm is observed (see Figs. 6 and 7). Since no diffused copper is found, copper seems to agglomerate easily resulting in small copper particles. The high amount of Cu agglomerates may be explained by a high retention of the preservative. Besides the Cu agglomerates, crystals (3 μm in size) of Ca and S (probably CaSO_4), sometimes containing a little bit of Cu, are found. These crystals may be formed from the Ca present in the wood structure and the SO_4 originating from the wood preservative.

3.2.2.3. Carmath samples from Cu/Cr-treated wood.

In some Carmath samples Cu and Cr have been detected. These samples may originate from CFK, CCB or CCA treated wood. However,

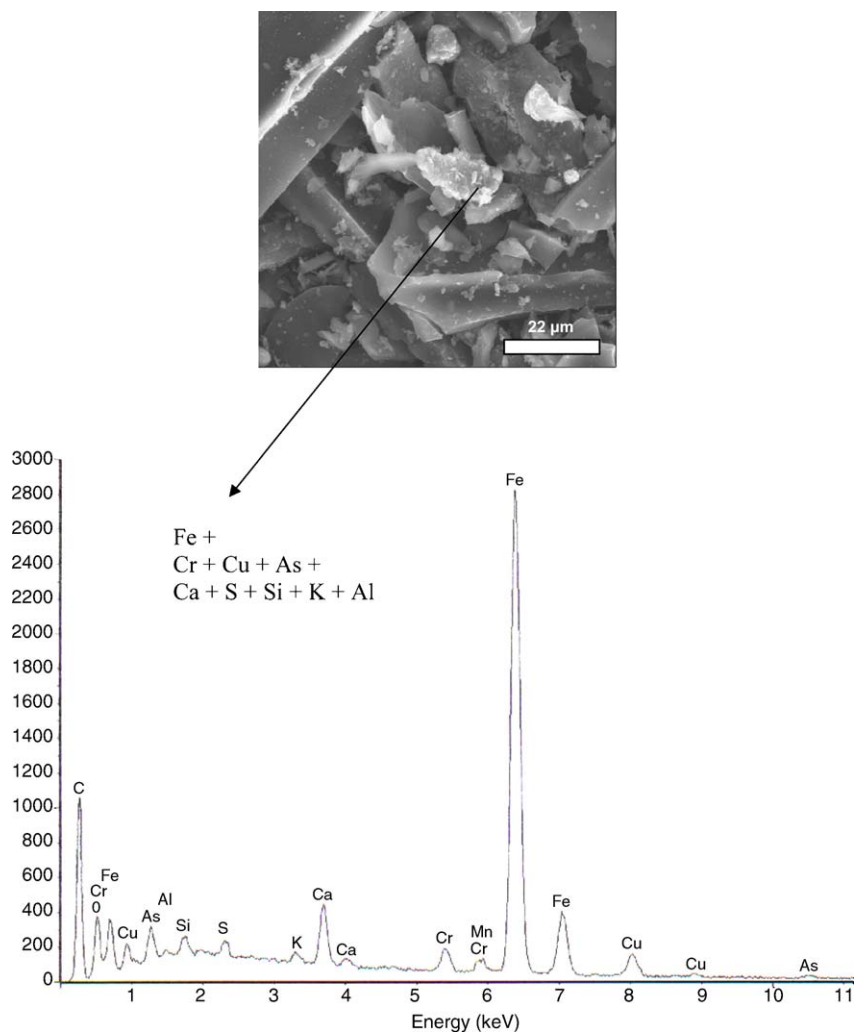


Fig. 13. Detail of Carmath resulting from CCA treated wood: SEM-EDX analysis shows a large Fe particle containing the three metals Cr, Cu and As together with wood minerals.

none of the three elements F, B or As was found by SEM-EDX analysis. If CCA treated wood would have led to these Carmath samples this means that the As concentration in these samples is too low to be detectable by SEM-EDX analysis and thus part of the As has been released during the chartherisation process. However, other Carmath samples do contain As in detectable quantities (see Section 3.2.2.4) indicating that the As initially present in the treated wood is (at least partly) recovered in the Carmath product. Fluorine (and boron) compounds may be more volatile, resulting in non detectable amounts of F (and B) in the Carmath products. The chance that these Carmath samples originate from CuSO_4 treated wood and the Cr was condensed on these samples during the chartherisation process is rather low. Before the Cr is able to move from one sample to another it has to be transformed in volatile products, such as $\text{Cr}(\text{CO})_6$ or CrO_2Cl_2 . The occurrence of this process of evaporation and recondensation has to be checked in future experiments. It is expected to take place with decomposed wood compounds and maybe arsenic, but not with chromium.

Copper seems to be present in much higher quantities than chromium. Cartography, applied to determine the presence of

Cr, Cu and As in a larger zone, confirms the predominance of Cu. The signals for Cr and As are very weak, indicating that the Cr and As concentrations in the sample are too low for detection by cartography. A spot analysis by SEM-EDX, however, has shown the presence of Cr.

A lot of agglomerates, located in certain regions, are found in these samples, as shown by Fig. 8. Different types of agglomerates are observed, such as: very small (0.1–0.5 μm) Cu agglomerates; small (1 μm) agglomerates of wood minerals; medium sized agglomerates (2–3 μm) of Cu, Cr and wood minerals (such as Si, Ca, K, Al, S, Fe); and medium sized (3 μm) agglomerates of Cu and the same wood minerals.

3.2.2.4. Carmath samples from Cu/Cr/As (CCA) treated wood.

In the Carmath samples resulting from CCA treated wood (proven by the presence of the three metals Cr, Cu and As) the metals appear both as agglomerates (see Fig. 9) and diffused in the solid matrix (see Fig. 10). The agglomerates' dimension varies from 0.1 to 3 μm for the small metal agglomerates up to 50 μm for the mineral agglomerates sometimes associated with some metals. The bright white small spots at the surface

of the tracheids are Cu agglomerates while the somewhat larger agglomerates located deeper inside the tracheids consist of Cr, Cu and As. Both types of agglomerates are a combination of metal(s), S and wood minerals (Si, Ca, Fe, K, Al, Cl, Mg), as illustrated in Figs. 11 and 12. Agglomerates of wood minerals without preservative metals are also present, as well as agglomerates of pure copper. Once, a large agglomerate (20 μm) consisting of Fe (main element), Cu, Cr, As, Ca, S, Si, K, Al is found (see Fig. 13). A small iron particle may have attracted the other metals and minerals, resulting in the agglomerate observed. Combinations of two out of the three metals, such as Cr + As, Cr + Cu or Cu + As, with and without wood minerals are also observed. Similar to the Carmath samples originating from CuSO_4 treated wood, CaSO_4 crystals (2–3 μm in size) are found.

Again, cartography is only able to detect the copper. Maybe Cr and As are much more diffused in the matrix and Cu is much more localized in spots and therefore easier to detect by SEM-EDX analysis. Or part of the As and/or Cr has been volatilized during the chartherisation process? To answer this question quantitative analysis with well defined samples is needed. Another question that remains is: do the agglomerates of wood minerals already present in the wood matrix before chartherisation influence the formation of metal agglomerates during chartherisation? Some of the larger mineral agglomerates do contain metals after chartherisation. The mineral agglomerates may thus assist in the metal agglomeration process.

The originality of the results of the present study lies not only in the use of real wood waste and the use of an industrial installation, but also in the analysis of samples for both preservative metals and wood minerals. Earlier studies focused on the detection of Cr, Cu and As only. Real poles contain Cr, Cu and As in lower concentrations, comparable to the concentrations of wood minerals. As a consequence the importance of the behaviour of both groups of elements becomes clear, as well as their interaction during the chartherisation process.

4. Discussion

From this study it is clear that some similarities but also some differences exist between the lab scale observations and the observations in the industrial Chartherm plant. In both reactors a metal agglomeration process takes place. The treated wood inputs, however, differ significantly. While the three metals Cr, Cu and As are found almost everywhere in the wood used in the lab scale study, the real wood samples are characterized by (1) much lower metal concentrations, (2) copper compounds that are much easier to detect by SEM-EDX (compared to Cr and As compounds) and (3) less spots where the three metals are found together. Agglomerates of wood minerals have been observed in both types of wood samples.

Comparing the lab scale pyrolysis residue with the industrial Carmath product reveals the following observations. All the agglomerates examined in the pyrolysis residue of the (double-treated) peeling samples contained the three metals. In the solid residue resulting from the same pyrolysis process applied to

(single-treated) sapwood samples the agglomerates found in the ray cells consisted of the three metals with Cr being the dominant element, whereas at other locations agglomerates of pure Cr, or Cr and As, or Cr and Cu were found. The Carmath product contains agglomerates with a huge variety in composition and size. This is not only attributed to the fact that the wood input to the Chartherm process is a mixture of crushed wood poles which have been treated with different wood preservatives according to different procedures. Even when looking at one Carmath sample originating from CCA treated wood the range of agglomerates' composition and dimension is large. The Carmath product contains agglomerates consisting of the three metals but the major part is a combination of wood minerals and one or two of the three preservative metals. Furthermore, part of the metals are diffused in the solid matrix and do not appear as agglomerates. This comparison leads to the conclusion that the higher the CCA retention in the wood input is, the easier is the metal agglomeration process during chartherisation of CCA treated wood waste. Whether this conclusion also holds for wood impregnated with other metal containing preservatives still has to be verified. From the analyses performed in this study, it seems that copper agglomerates easily, but the resulting particles are small (smaller than micrometer range).

Another important observation is that if small samples (e.g. 20 g of wood or Carmath) are taken for analysis they will be very heterogeneous and therefore not representative for the whole batch. Even two Carmath pieces taken from the same layer inside the Chartherm reactor may be totally different. Therefore, either a well defined wood input is needed for future experiments or a detailed statistical study will be required to be able to draw conclusions that hold for the whole batch, based on analysis performed on a small sample taken out of that batch. If a well defined wood input can be used, it is possible to study the influence of the process conditions (which is expected to be important) on the metal agglomeration process without interference of the influence of the input characteristics.

An extensive literature search has led to only two other publications describing the microdistribution of metals in the pyrolysis residue of CCA treated wood [8,9].

Hata et al. [8] used CCA treated wood powder (size smaller than 100 mesh) as input to a lab scale batch pyrolysis unit. The powder originates from wooden (Western Hemlock) boards that were treated with CCA oxide. The pyrolysis residue analysed by transmission electron microscopy (TEM) resulted from pyrolysing 1 g of CCA wood powder at 450 °C for 10 min in a fixed bed. The wood sample showed a clear wood cell structure but no interesting details linked to CCA treatment. The pyrolysis residue, on the other hand, contained a dense collection of nanoparticles, mostly spherical in shape and 10–50 nm in size. The particles turned out to be $\text{Cr}_2\text{As}_4\text{O}_{12}$, As_2O_5 and As_2O_3 . Copper agglomerates were thus not found and the metal particles were much smaller than the ones detected in the study described in this paper. Whether this is due to the differences in wood input or to the higher temperature used during pyrolysis is not yet clear.

Ottosen et al. [9] performed SEM-EDX analysis on pyrolysis residues (2–5 cm in size) resulting from an industrial

plant (Kommunekemi, Denmark) working at a temperature of 300–400 °C and using treated wood originating from a public recycling centre for waste. The wood was sorted by visual inspection and the waste defined as painted and impregnated wood was sent to Kommunekemi for treatment. The pyrolysis residues had still the wood structure which is in agreement with all other studies. Cu, Cr and As were found inside the solid matrix: Cr and As associated, and Cu without the other metals. Arsenic was also observed in small particles (around 7 µm in size) at the surface of the pyrolysis residue.

Comparing the results formulated by other researchers with the results of the present study reveals that agglomerates of Cr and As and agglomerates of Cu (without Cr and As), as well as As compounds have been found in all studies, irrespective of the impregnation procedure of the CCA treated wood and the operating conditions of the pyrolysis process. The results described in the present paper, however, show a much broader range of agglomerates detected, both with respect to size and composition. The impact of this broad range on the efficiency of the subsequent mechanical separation step applied to the Carmath product is a subject for future research.

5. Conclusions

The most important conclusions with respect to the metal agglomeration process in the industrial Chartherm plant are listed below:

- (1) SEM-EDX analysis has shown that crushed wood poles contain already agglomerates or crystals of wood minerals, while the preservative metals are concentrated in certain zones or diffused in the wood matrix.
- (2) Since real poles contain minerals and metals in concentrations of the same order of magnitude, the behaviour of both groups of elements and their interaction is important.
- (3) During chartherisation new agglomerates are formed and existing agglomerates have grown, both in untreated and treated wood. Thus, the metals (Cr, Cu and As) are not needed for the agglomeration process.
- (4) The agglomerates in the Carmath product consist of wood minerals, sometimes associated with preservative metals in the case of treated wood. Thus, the mineral agglomerates may assist in the metal agglomeration process.
- (5) The preservative metals form agglomerates on themselves too, the Cu agglomerates being the smallest in size and the largest in number. All combinations of metals are observed and the composition as well as the size of the agglomerates exhibits a large variation. This observation is the most significant difference with earlier results of a lab scale study that uses a different wood input and different process conditions.
- (6) The agglomerates are located on the surface of the tracheids or inside the tracheids, in the ray cells or next to the ray cells.
- (7) The smaller Cu agglomerates have been found in both CCA samples and CuSO₄ samples.
- (8) The CCA agglomerates are (evidently) only found in CCA samples, where diffused metals also appear.
- (9) It is not yet clear why copper behaves differently to Cr and As.

Experiments with well defined (but real) treated wood inputs are needed in order to get more insight in the metal agglomeration process during chartherisation. The metal agglomeration process needs to be studied both (but separately) as a function of the wood input (procedure of impregnation, preservative, retention, age of the treated wood, type of wood species, . . .) and as a function of the Chartherm process conditions. Conditions have to be optimized such that all preservative metals form agglomerates that can be separated from the carbon powder in a mechanical way in the subsequent stage of the Chartherm process.

Acknowledgements

During this study L. Helsen was a post-doctoral research fellow of the Fund for Scientific Research of Flanders (Fonds voor Wetenschappelijk Onderzoek (FWO) Vlaanderen) (Belgium). The FWO-Vlaanderen is also acknowledged for financially supporting the study leave of L. Helsen for 2 months in Bordeaux (France). The authors would like to thank Jean Sebastien Hery and David Mateos from the company Thermya for their valuable help during this study. The authors are also grateful to Mrs. Elisabeth Sellier of CREMEM (Centre de Ressources en Microscopie Electronique et Analyse, Bordeaux, France) and Mrs. Annie Richard of the Centre of Electron Microscopy (Orleans, France) for their advice during the SEM-EDX analyses.

References

- [1] L. Helsen, E. Van den Bulck, Review of disposal technologies for chromated copper arsenate (CCA) treated wood waste, with detailed analyses of thermochemical conversion processes, *Environ. Pollut.* 134 (2005) 301–314.
- [2] L. Helsen, E. Van den Bulck, J.S. Hery, Total recycling of CCA treated wood waste by low-temperature pyrolysis, *Waste Manage.* 18 (1998) 571–578.
- [3] L. Helsen, E. Van den Bulck, The microdistribution of copper, chromium and arsenic in CCA treated wood and its pyrolysis residue using energy dispersive X-ray analysis in scanning electron microscopy, *Holzforchung* 52 (1998) 607–614.
- [4] L. Helsen, K. Van den Broeck, C. Vandecasteele, E. Van den Bulck, Low-temperature pyrolysis of CCA treated wood waste: chemical determination and statistical analysis of metal in- and output; mass balances, *Waste Manage.* 17 (1) (1997) 79–86.
- [5] L. Helsen, Low-temperature pyrolysis of chromated copper arsenate (CCA) treated wood waste, PhD Thesis, Katholieke Universiteit Leuven, Belgium, 2000.
- [6] H. Greaves, The microdistribution of copper-chrome-arsenic in preservative treated sapwoods using X-ray micro-analysis in scanning electron microscopy, *Holzforchung* 28 (6) (1974) 193–200.
- [7] P.S. Nico, S.E. Fendorf, Y.W. Lowney, S.E. Holm, M.V. Ruby, Chemical structure of arsenic and chromium in CCA treated wood: implications of environmental weathering, *Environ. Sci. Technol.* 38 (2004) 5253–5260.
- [8] T. Hata, P.M. Bronsveld, T. Vystavel, B.J. Kooi, J.Th.M. De Hosson, T. Kakitani, A. Otono, Y. Imamura, Electron microscopic study on pyrolysis of CCA (chromium, copper and arsenic oxide)-treated wood, *J. Anal. Appl. Pyrol.* 68–69 (2003) 635–643.

- [9] L.M. Ottosen, A.J. Pedersen, I.V. Christensen, Characterization of residues from thermal treatment of treated wood and extraction of Cu, Cr, As and Zn, *Wood Sci. Technol.* 39 (2005) 87–99.

Glossary

Carmath product: solid product of the industrial carbonisation process applied to treated wood waste

CCA: chromated copper arsenate wood preservative used to impregnate wood by a vacuum–pressure–vacuum procedure

CCB: chromated copper boron wood preservative used to impregnate wood

CFK: chromated copper fluorine wood preservative used to impregnate wood

Chartherm process: chartherm stands for thermal chartherisation and refers to the industrial carbonisation process, as schematically presented in Fig. 3

Chartherisation: the thermal carbonisation process

EDXA: energy dispersive X-ray analysis

ICP-MS: inductively coupled plasma mass spectrometry

SEM: scanning electron microscopy

TEM: transmission electron microscopy

XRF: X-ray fluorescence