Mineralization of wooden elements by bypass cement kiln dust

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Abstract. The application of renewable and waste materials for the production of building materials is currently one of the main trends, especially with regard to environmental aspects. This is a reduction in the volume of materials that could be a waste and at the same time a reduction in the cost (including carbon footprint) for special wood treatment products that would have to be produced. One example given in this article is the possible application of a mineralization of wood matrix by kiln dust produced in a cement plant. This treatment can be primarily used in the production of wood-based panels bonded with cement, whose main purpose is to limit the leaching of soluble components, which affect the setting of the cement. If the cement kiln dust is applied for the mineralization of wooden elements, the flammability of wood can be positively influenced. Bypass cement kiln dusts contain significant amount of chloride, which in this case function as a reducing agent. In this article, the effect of the wood mineralization by the cement kiln dust from CEMMAC a.s. Horné Smíre was investigated on thermal degradation of wood by a simultaneous thermal analysis TG / DSC.

1. Introduction

Wood is an organic renewable material that has been and still is preferably used for many construction purposes like ceiling and roof constructions, lintels, claddings, floors, windows, doors, stairway construction, vertical load-bearing structures etc. This wide spectrum of wood application in civil engineering was caused mainly by its low bulk density, good workability, strength, thermal insulation parameters and also by other properties [1]. However, this material is also characterized by some unsuitable properties such as reduced durability and flammability. Various types of treatment products are applied to reduce combustion and promote the formation of a protective carbonized layer [1–2]. On the other hand, the flammability can be also reduced by applying a certain production technology, as in the case of wood-cement panels [3].

Flammability of wooden elements has a direct connection with the amount of ash (non-combustible fraction) and the release of heat during combustion [1–2]. These parameters can be influenced by the application of bypass cement kiln dust (BCKD). Firstly, increasing the non-combustible proportion is determined by the principle of wood mineralization, i.e. a natural phenomenon, which is generally based on the deposition of mineral substances that can partially or completely replace organic substances [4–6]. Conversely, substances acting as oxidizing agents can be used to reduce the released heat especially with larger wood particles. These substances include chlorine, which is a strong oxidizing agent - it reduces itself (increases the oxidation number), thereby reducing the amount of oxygen involved in the reaction during the combustion process (figure 1) [1–2]. At the same time, chloride-based compounds are also used as accelerating agents that technologically affect the setting time and the onset of strength in the early stages in wood-based composites [3].
Thermal analysis is an effective analytical tool for this study because wood with a high content of combustible components is relatively easily decomposed at elevated temperature [1–2, 4]. The basic output is the exothermic and endothermic phenomena observed on the DSC curve and the weight changes detected on the TG curve [1–2, 4, 7]. The results are possible to compare with the thermal curves database in some cases [8] or process in the form of quantitative analysis [7]. Thermal analysis is often used for assessment of basic wood components [9] or targeted treatments with the task of monitoring changes in thermal degradation of material, primarily seen in the changes of mass residue in TG curve, temperature shifts of the thermal decomposition of wood components in DSC curve [2, 4]. For this reason, the characteristics of wood flammability for the reference (untreated) samples and samples treated with a solution of BCKD were determined in the experimental part by using of thermal analysis. It is essential to determine the non-combustible fraction and the shift of temperature milestones of wood thermal degradation by verified and published methodology [2, 4].

2. Materials and Methods

2.1. Wood

Primarily, specimens for the experiment 20 × 20 × 30 mm (R × T × L) were prepared from one representative of softwood species - Norway spruce (Picea abies L.) and one representative of hardwood species - European beech (Fagus sylvatica L.). The specimens were placed in a laboratory environment at the temperature of 20 ± 1°C and the relative humidity of 50 ± 5%. Every specimen was weighted with an accuracy of 0.1 g and measured with the accuracy 0.01 mm.

2.2. Chemicals

For the testing, the BCKD from the CEMMAC a.s. Horné Srnie production plant was used.

**Table 1.** Chemical composition [wt. %] of the bypass cement kiln dust (BCKD) determined by XRF.

| Chemical component | Portion [wt. %] |
|--------------------|----------------|
| SiO₂               | 5.32           |
| Al₂O₃              | 1.46           |
| Fe₂O₃              | 1.22           |
| MgO                | 0.48           |
| CaO                | 34.08          |
| Na₂O               | 0.31           |
| K₂O                | 18.62          |
| TiO₂               | 0.12           |
| SO₃                | 5.16           |
| P₂O₅               | 0.05           |
| Cl                  | 10.49          |
| Br                  | 0.16           |
| MnO                | 0.09           |

The chemical composition of the used BCKD can vary slightly. On the other hand, approximate chemical composition determined by XRF can be found in table 1. The treatment solution was prepared
by mixing the powder sample from BCKD with demineralized water in a ratio of 5, 10, 15 or 25 g of the BCKD to 100 ml of demineralized water. The pH of each solution was measured.

2.3. Preparing of specimens
Wooden specimens were treated with BCKD water solution by a coating or by a dipping method at the atmospheric pressure of \( \pm 100 \) kPa, the temperature of 20 \( \pm 1 \)\(^\circ\)C, and with different immersion time – 30, 60, 180 minutes. The specimens were surface dried with filter paper after removing from the solution. Every specimen was weighted after treatment with an accuracy of 0.1 g. The retention parameters \( R [g \cdot m^{-2}] \) were calculated by (1) from the weight after immersion \( w_{after-treat} \) in relation to the weight before treatment \( w_{before-treat} \) and the specimen surface \( S [mm^2] \).

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R = 1000000 \times \frac{w_{after-treat} - w_{before-treat}}{S}
\] (1)

Subsequently, these specimens were conditioned in a laboratory environment at the temperature of 20 \( \pm 1 \)\(^\circ\)C and the relative humidity of 50 \( \pm 5 \)% until they reached the equilibrium moisture. Reference specimens (without mineral treatment) were also conditioned. For the thermal analysis, superficial cuts in the form of chips were taken by a scalpel. The reference specimens were also taken by a scalpel for thermal analysis, similar to the treated samples.

2.4. Thermal analysis
Thermal analysis was performed by SDT Q600, TA Instruments, which allows a simultaneous combination of thermogravimetric analysis and differential scanning calorimetry (TG/DSC) [10]. The wooden superficial cuts were placed in corundum pans and heated up at a constant heating rate of 10\(^\circ\)C\cdot min\(^{-1}\) to 700\(^\circ\)C in an oxidizing atmosphere of air. The oxidizing atmosphere allows simulation of fire conditions that could confirm the fire retardation effects.

An important output was the shift of values of non-combustible fraction generated after thermal degradation of predominantly volatile and solid components (TG curve), which may indicate a change in material flammability [2, 4]. The shift in the initial temperature (the beginning of hemicellulose decomposition) should be also observed by the TG curve. The evaluation of the DSC curve was added for temperature definition of the peak for thermal degradation of predominantly volatile components and the first peak for the decomposition of solid components [2, 4].

3. Results and Discussion

3.1. The pH measurement
The pH was measured for all solutions, which was made of 5, 10, 15, or 25 g powder samples from the BCKD and 100 ml demineralized water. A relatively high pH of 13.5 was already measured for the solution made from 5g of the BCKD and 100 ml of demineralized water. For all other solutions, the pH values have already been at a maximum of 14. This phenomenon may be advantageous for wood, alkaline nature of the solution can also reduce the development of molds and fungi on this material.

3.2. Weight changes of specimens
For the treated specimens, the retention parameter \( R \) immediately after treatment was determined in relation to the surface of the specimen which is in contact with the BCKD solution (table 2 and 3).

Based on the results it can be stated that the weight of the specimens increases with the increasing exposition time, particularly due to the solution intake and the deposition of the mineral particles. At the same time, it is apparent that solutions of lower concentrations penetrate the wood considerably better [5]. Especially for Norway spruce, it is apparent that the uptake of the solution at the concentration of 10 g of the BCKD per 100 ml demineralized water is significant and a considerable mineral particle deposition can also be expected.
Table 2. Retention parameter R for Norway spruce specimens.

|                  | R [g·m⁻²] | Concentration 5 g per 100 ml | Concentration 10 g per 100 ml | Concentration 15 g per 100 ml | Concentration 25 g per 100 ml |
|------------------|-----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Coating          | 210.6     | 127.9                         | 104.4                         | 206.6                         |
| Immersion 30 mins| 566.6     | 915.8                         | 730.8                         | 520.5                         |
| Immersion 60 mins| 523.3     | 546.5                         | 825.4                         | 845.7                         |
| Immersion 180 mins| 662.6   | 1034.7                        | 1036.6                        | 895.4                         |

Table 3. Retention parameter R for European beech specimens.

|                  | R [g·m⁻²] | Concentration 5 g per 100 ml | Concentration 10 g per 100 ml | Concentration 15 g per 100 ml | Concentration 25 g per 100 ml |
|------------------|-----------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Coating          | 114.6     | 118.2                         | 130.3                         | 153.6                         |
| Immersion 30 mins| 930.9     | 922.6                         | 445.6                         | 599.6                         |
| Immersion 60 mins| 994.3     | 547.1                         | 414.6                         | 611.6                         |
| Immersion 180 mins| 1559.4  | 900.7                         | 725.1                         | 744.2                         |

3.3. Thermal analysis.

The values of non-combustible fraction for the treated specimens are stated in tables 4 and 5. These values can be compared with the reference specimens, for which mass residue take value 0.00% for Norway spruce and 0.20% for European beech.

Table 4. Non-combustible fraction after thermal decomposition for Norway spruce specimens.

|                  | Non-combustible fraction [%] | Concentration 5 g per 100 ml | Concentration 10 g per 100 ml | Concentration 15 g per 100 ml | Concentration 25 g per 100 ml |
|------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Coating          | 0.00                          | 0.00                          | 0.61                          | 3.24                          |
| Immersion 30 mins| 2.40                          | 4.16                          | 5.15                          | 6.52                          |
| Immersion 60 mins| 2.11                          | 7.62                          | 4.07                          | 7.42                          |
| Immersion 180 mins| 2.40                        | 10.32                         | 8.46                          | 6.87                          |

Based on the test results, it can be stated that the non-combustible fraction values increase in most cases with prolonged exposure to the BCKD solution. In terms of solution concentrations, it can be emphasized that too high a concentration of the BCKD solution may not correspond to higher values of the non-combustible fraction, as the retention parameters already showed. However, too low concentrations do not guarantee uniform mineralization. For the above reasons, the concentration of 10 g of the BCKD per 100 ml of demineralized water appears perspective.

Table 5. Non-combustible fraction after thermal decomposition for European beech specimens.

|                  | Non-combustible fraction [%] | Concentration 5 g per 100 ml | Concentration 10 g per 100 ml | Concentration 15 g per 100 ml | Concentration 25 g per 100 ml |
|------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Coating          | 0.00                          | 0.99                          | 0.00                          | 2.75                          |
| Immersion 30 mins| 5.42                          | 5.17                          | 3.40                          | 4.53                          |
| Immersion 60 mins| 2.96                          | 5.21                          | 3.48                          | 7.64                          |
| Immersion 180 mins| 1.02                        | 5.13                          | 6.36                          | 8.15                          |

Thermal analyses of specimens with different exposition in the BCKD solution are shown in figure 2–5. The various figures show the TG curves – monitoring the weight changes in % and the DSC curves – describing heat flow in °C·mg⁻¹. Figure 2 also defines the location of key characteristics for thermal
degradation of wood, namely non-combustible fractions, peaks of predominantly volatile components, first peaks of solid components and initial temperatures.

![Graph showing thermal analysis curves of beech surface chips.](image)

**Figure 2.** Comparison of thermal analysis curves of beech surface chips: reference specimen (ref. beech), treated specimens by coating with solution of 5 g BCKD and 100 ml demineralized water (BN5), with the solution of 10 g BCKD and 100 ml demineralized water (BN10), with the solution of 15 g BCKD and 100 ml demineralized water (BN15) or with the solution of 25 g BCKD and 100 ml demineralized water (BN25).

It is apparent from the graphical records of analysis that low concentration of the solution or short-term exposure in the solution, for example by coating or spraying, does not significantly affect the course of combustion (figure 2).

The opposite is the case with treatment by dipping method (figure 3) or higher concentrations of the BCKD in solutions (figure 4), where the changes in peak size are evident in the DSC curves. It can be stated that increasing intake of the solution results in a smaller peak area thus, less heat is generated. Also, the first peaks of the solids components have a slight shift to higher temperatures, which may also indicate a change inflammability of wood. It is also apparent from the TG curve that the weight changes for these specimens are considerably more gradual.

On the other hand, thermal analyses show new peaks from 450°C, which are hardly found in smaller amount of the BCKD and coating applications. These peaks are always supplemented by weight changes; therefore, some decomposition of the specimen components is a probable cause. Moreover, the peaks do not appear in the case of thermal analysis in the reduction atmosphere. All the results show that the cause may be just high chloride content, which would also confirm the partial retardation effect. However, these reactions cannot be specified without further chemical analyses.
Figure 3. Comparison of thermal analysis curves of spruce surface chips: reference specimen (ref_spruce), treated specimens by dipping method with immersion time 180 minutes and with the solution of 5 g BCKD and 100 ml demineralized water (S180M5), with the solution of 10 g BCKD and 100 ml demineralized water (S180M10), with the solution of 15 g BCKD and 100 ml demineralized water (S180M15) or with the solution of 25 g BCKD and 100 ml demineralized water (S180M25).

Figure 4. Comparison of thermal analysis curves of beech surface chips: reference specimen (ref_beech), treated specimens with the solution of 25 g BCKD and 100 ml demineralized water by
coating (BN25), or by dipping method with immersion time 30 minutes (B30M25), 60 minutes (B60M25) or 180 minutes (B180M25).

A concentration of 10 g of the BCKD per 100 ml of demineralized water for Norway spruce can be seen in figure 5. This concentration appeared to be very effective in terms of non-combustible fraction growth. From the heat flow point of view, it can be seen that for all treatments the peak size of predominantly volatile components decreased. Peaks of solid components are on the contrary narrower compared to the reference specimens. The reason for these reactions is the application of the BCKD with a higher amount of chlorines. The above-mentioned reactions above 450°C occur only for the specimens with higher immersion time.

**Figure 5.** Comparison of thermal analysis curves of spruce surface chips: reference specimen (ref_spruce), treated specimens with solution of 10 g BCKD and 100 ml demineralized water by coating (SN10), or by dipping method with immersion time 30 minutes (S30M10), 60 minutes (S60M10) or 180 minutes (S180M10).

It has been shown that the application of BCKD-based treatments can reduce the flammability of the treated wood. However, prolonged exposure to the solution is required and therefore application in the form of a coating or a spraying is not very suitable. If we observe a parameter associated with flammability, a specifically the non-combustible fraction, higher values can be achieved by a longer immersion time. Furthermore, it has been found that lower concentrations of the solution penetrate much more easily into the specimens. This effect is well known from the petrification process, wherein a faster saturation of the organic matrix with minerals is achieved in solutions with lower concentrations [5, 11]. On the result basis it can be stated that the concentration of 10 g of the BCKD per 100 ml of demineralized water can be optimal for this purpose.

Based on the DSC curves, the thermal degradation of specimens with higher solution retention is limited, especially in the area of thermal decomposition of the basic wood components. The primary cause can be the known effect of chlorines as a fire retardant [1]. However, the effect of the individual chloride salts is usually investigated [2]. In our case, chloride salts, in particular KCl, are also present in the BCKD. On the other hand, the BCKD also contains a number of other substances that can affect
the combustion process [12]. In particular, silicates may form layers on the inner or the outer surface which can partly protect the organic substance against fire, but it may partially decompose during heating [1, 8]. It can be assumed that the resolution of these effects is not fully possible due to the complexity of the problems.

4. Conclusion

The high chloride content limits the use of a bypass cement kiln dust (BCKD) for conventional cement applications. On the other hand, chloride-containing substances are used for some applications related to the application of renewable natural materials. The application of chloride-based substances is frequent in the case of accelerated setting time of the wood particleboard bonded with cement. Chloride salts are also used as fire retardants for timber elements.

The fire-retarding effect of BCKD has been studied by thermal analysis in this experiment. It has been shown that application of BCKD-based treatments can reduce the flammability of the treated wood. The reason for the reduction in flammability is mainly the content of chloride salts and partly silicates in BCKD. On the other hand, prolonged exposure to the solution and lower concentration of the water solution is required. For this case, the concentration of 10 g of the BCKD per 100 ml of demineralized water and the immersion in the order of hours can be recommended. However, further analytical testing should be performed to confirm these conclusions.

For this reason, the treatment method with BCKD water solution can be recommended mainly for the preparation of wood-based composites and potentially for solid wood application.

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