ACTA FACULTATIS XYLOLOGIAE ZVOLEN, 59(2): 5−22, 2017
Zvolen, Technická univerzita vo Zvolene
DOI: 10.17423/afx.2017.59.2.01

IMPACTS OF INORGANIC CHEMICALS USED FOR WOOD PROTECTION: A REVIEW

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ABSTRACT

Wood and wood products in proper conditions are durable for centuries. However, there are bio-based materials and thus are prone to deterioration by fungi, insects, and other organism. Another undesirable feature of wood products is their flammability. Wood and wood products are protected by treatment with various chemicals for prolong their longevity, however many of them have adverse impact at their properties as well at the environment; e.g. waterborne preservative treatments generally reduce the mechanical properties of wood. This paper compiles important research findings related to both negative and positive impacts of inorganic chemicals on wood for better understanding and comprehension of the chemical aspect of this problem.

Key words: wood protection, inorganic salts, degradation, chemical composition, mechanical properties.

INTRODUCTION

Wood is one of the most widely used biological materials, especially for constructional application due to its unique physical and mechanical properties in addition to its renewability and environmental friendly nature. However, the application of wood has still some limits due to its easy burning when subjected to flame source or direct heat under suitable conditions. Moreover, wood-degrading fungi, insects, bacteria and marine borers cause damage resulting in billions of dollars being spent on repair and replacement of wooden structures every year. The equivalent of one-tenth of the forest products produced every year is estimated to be destroyed by these agents (GOODEL *et al*. 2003, PHROMSAEN *et al*. 2014). The chemical protection of wood is performed with chemical protective agents called “wood preservatives”. The best known are bactericides (against bacteria), fungicides (against fungi), insecticides (against insects), fire retardants (against fire), anti-weathering and anti-corrosive agents (against atmospheric and aggressive-chemical effects) (REINPRECHT 2016).

Wood preservative products are those that claim to control wood degradation problems due to fungal rot, sap-stain, moulds, or wood-destroying insects. Both the treatment process and the use of treated-products can result in exposure to pesticides for both people and the environment. Most of the treatment processes and uses of treated products occur outdoors. There are wood preservatives that support a tolerance for indirect food-contact uses such as wooden crates, pallets, and stakes used to store or grow raw agriculture commodities (OVERVIEW… 2016).

Currently, many chemicals are used to prolong wood lifetime and protect wood against wood-decaying fungi, insects and fire but there is not sufficient information about their possible corrosive effects on wood and its structural components from the perspective of its long-term exposition in unsuitable condition.

Biocides based on inorganic salts can include e.g. mixtures of salts or oxides containing cations as a Na^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, B^{3+}, Sb^{3+}, As^{3+}, As^{5+}, Cr^{6+} or anions as a Cl^-, F^-, SO_4^{2-}, etc. (Reinprecht 2010). Substances with a fire retarding effect on the basis of inorganic compounds cover a broad spectrum of inorganic chemicals, e.g. ammonium salts as an NH_4F, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, $(NH_4)_2SO_4$ and boron compounds as a H_3BO_3, $Na_2B_4O_7.10H_2O$ etc. (Unger *et al*. 2001; Schultz *et al*. 2007; Reinprecht 2016).

Although it is well known that some inorganic chemicals that are components of protective agents, induce chemical changes in wood polymers, effect of inorganic chemicals used for wood protection were meanwhile observed only in terms of application process, fixation, leaching, hygroscopicity, corrosivity to metal fasteners, their thermal stability and dimensional changes of wood mass caused by crystallizing salts from preservative solutions after drying (Johnson, Gutzmer 1990; Lebow 1996; Guizhen *et al*. 2000; Crawford *et al*. 2002; Cook 2003; Zelinka, Glass 2010; Sonowal, Gogoi 2010; Stirling, Temiz 2014; Recommendation 2014). The greatest attention was paid by many researchers to the influence of inorganic chemicals on mechanical properties of treated wood (Reinprecht 1992, Winandy 1995b; LeVan *et al*. 1996; Lebow, Winandy 1999; Ayrilmis 2007; Kartal, Hwang Imamura 2008; Kloiber *et al*. 2010). At present time, several types of inorganic and organic fungicides are commonly used for protection of wood products against termites, moulds, staining and rotting fungi. However, in the near future the wood preservation industry is required for sustainable processes based on environmentally more friendly additives (González-Laredo *et al*. 2015, Reinprecht 2016).

Corrosion of fasteners can be accelerated under condition of high humidity and in the presence if inorganic salts. Wood treated with inorganic flame-retardant salts is usually more hygroscopic than is in untreated wood, particularly at high relative humidity and also their mechanical properties can be reduced (Belgacem, Pizzi 2016).

The aim of this review is to summarize the existing knowledge for better understanding and comprehension of the chemical aspect of this problem, which has so far received less attention.

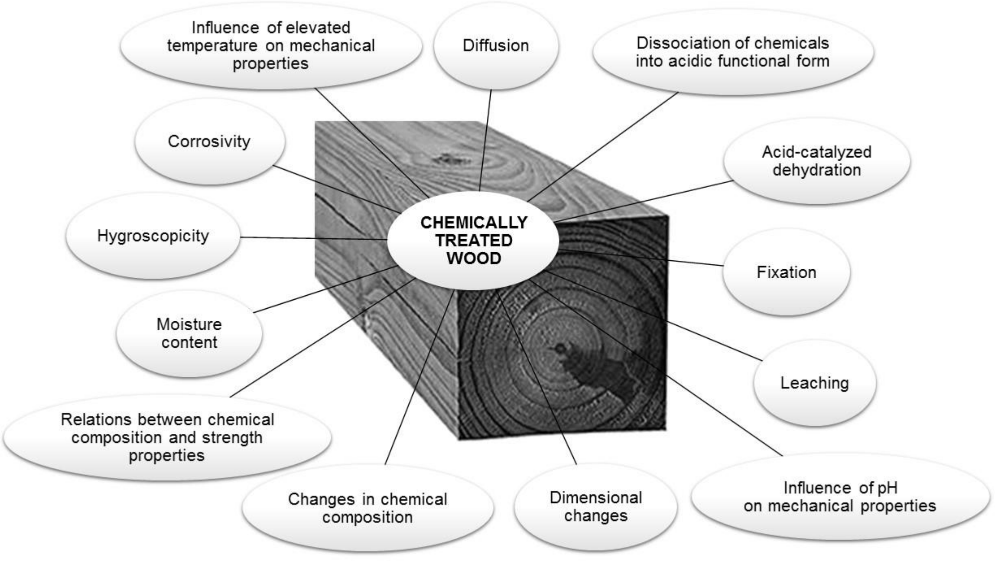

Fig. 1 Particular contributions of different influences, processes properties of chemicals affecting the degradation of chemically treated wood with preservatives.

Corrosivity

Although wood preservatives increase the service life of wood, in some cases these preservatives increase the corrosiveness of the wood toward metal fasteners, simultaneously as some wood extractives (MAKOVÍNY *et al.* 1992). The corrosiveness of preservative-treated wood has been studied since the 1920's when the first treatments were being developed for railroad ties. The amount and intensity of the corrosion research has changed throughout time as wood preservatives of varying corrosivity have been developed and introduced (ZELINKA 2013).

The current mechanism for corrosion of metals in contact with preservative-treated wood was proposed by Baker in the 1980's (1988). The wood preservatives that Baker studied contained cupric ions, which are thermodynamically unstable in the presence of steel and galvanized steel fasteners. Baker's mechanism involves transport of cupric ions through wood to the metal surface where they are reduced at the expense of the fastener, which is oxidized. The destruction of the cellulose component of the wood follows this process, and it is generally accepted that corroding metals promote its oxidative degradation (FABER 1954; BELL, GIBSON 1957; BAKER 1974). The mechanism is believed to be aqueous because the corrosion rate depends strongly on wood moisture content and there is a threshold moisture content below which corrosion does not occur in wood (BAKER 1988; SHORT, DENNIS 1997). Additionally, ZELINKA *et al.* (2008) found that water extracts of treated wood were much more corrosive than dilute solutions of the wood preservative with roughly the same copper concentration. These studies suggest that wood extractives affect corrosion of metals in treated wood; however, the literature on this topic is sparse, and the role of several extractives remains controversial.

In the past years, there have been numerous studies on corrosion of metals in treated wood (KEAR *et al.* 2009; ZELINKA, RAMMER 2009). These studies were focused on determining the corrosiveness of new wood preservatives, such as alkaline copper quaternary (ACQ) and copper azole (CA) (LEBOW 2007) that have become widely used since chromated copper arsenate (CCA) was voluntarily withdrawn by industry for use in residential construction in the year 2004.

Hygroscopicity

One of the main problems with the use of inorganic salts as biocides and fire retardants is that they are highly hygroscopic. The hygroscopic behaviour depends upon the type of chemical, the level of chemical retention, and the size and species of the treated wood (KARTAL *et al.* 2008). It has been reported that some treated wood objects were so hygroscopic that they would actually drip solution at relative humidity of approximately 90% (WILLIAMS 1996). Difference between hygroscopic and in addition hydroscopic properties of wood and salts can lead to detrimental effects, such as stress concentration in treated wood by preservatives based on inorganic salts (BAYSAL *et al.* 2006). This may subsequently lead to dimensional instability, some failure and formation of cracks in wood due to hydrostatic pressures caused by soluble salts during their crystallization and recrystallization. Initial problems of moisture retention on surface as well as in wood structure included corrosion of possible metal fasteners and fittings. BAYSAL *et al.* (2006) also recommended that more dimensionally stable products with reduced moisture contents and increased biological durability it is possible to obtain by adding water repellents to the common wood preservatives.

DULAT (1980) collected sorption isotherms of pine treated with $Na_2B_8O_{13}.4H_2O$, H_3BO_3 and $Na_2B_4O_7.10H_2O$ and compared the isotherms to isotherms of untreated pine. He pointed out that these boron compounds lose their waters of hydration when oven-dried and claimed that wood treated with borates was not more hygroscopic than untreated wood when the waters of hydration were subtracted. However, this analysis assumes that the structure of the hydrated boron compounds remains unaltered within the wood cell wall. From a practical standpoint, though, this extra water is still present in the wood, and it is not clear if it is complexed with the boron compounds or bound to the cell wall.

AWOYEMI and WESTEMARK (2005) concluded that the pre-treatment impregnation with borate salt controversy increased the hydrophobic and antiswelling effects of the heat treatment on wood. This suggests that the bulking effect of the borate salt is more significant than its mitigating effect on the degree of cellulose degradation during heat treatment.

Moisture content

Each fire retardant chemical system alters the equilibrium moisture content (EMC) of the wood. The magnitude of this alteration depends on the attraction of the fire retardant chemical for water, on the temperature and the relative humidity (RH). Moreover, the moisture content is generally higher on the desorption isotherm than on the adsorption isotherm. BENDTSEN (1966) found that most inorganic salts increased the EMC of wood 3–5% depending on the chemical treatment. LEVAN's study (1990) is also in agreement with Bendtsen's results. The significant differences in moisture content (MC) were found between untreated controls and specimens treated with H_3PO_4 and H_3BO_3. Furthermore, the MC results of these specimens indicate a permanent reduction in EMC over the exposure time in the range of 1–2%. This effect was more pronounced for the specimens subjected to the higher EMC conditions (54 °C/73% RH). The negative MC trends in this case can be explained as a permanent loss in the water-holding capacity (hygroscopic affinity for water) of the specimens after long high-temperature exposure. This loss in hygroscopic affinity for water could be primarily due to degradation of the hemicelluloses (SKAAR 1972). In general, at higher moisture contents, wood conducts ions better, and therefore, the corrosion (oxidation) reaction occurs at a faster rate.

Dimensional changes

Wood, like all other fibrous materials, possesses the property of shrinking and swelling upon the loss or gain of moisture. The shrinkage, as manifested by the percentage change in external dimensions, is greatest in the tangential direction, varying from 6 to 12%. In the radial direction it varies from 3 to 7% and in the longitudinal direction it is only a small fraction of 1% (FENGEL, WEGENER 1984). Moreover, the dimensional stability of chemically treated lignocellulosic materials depends upon the type of chemicals and their penetration and how much hydroxyl groups are modified to give adequate cross-linking and bulkiness (SONOWAL, GOGOI 2010).

X-Ray studies have shown that the swelling of a cellulosic fiber by water does not affect its crystal lattice (KATZ 1933). The water must go between the constituent units of the structure rather than within these units (intermicellar swelling as contrasted to intramicellar swelling). Concentrated solutions of certain salts such alkalies, however, change the crystal lattice (KATZ, DERKSEN 1931), showing that their action is intramicellar. Unfortunately, it is extremely difficult to determine the total swelling of fibrous materials from the dimension changes. With wood, where the external dimension changes are easy to follow, it is extremely difficult to even approximate the internal changes that take place in the lumen of the fibers. Data for the absorption of salt solutions by wood, such as those of SCHWALBE and FISCHER (1931), are therefore hardly a measure of the swelling and further give no information as to whether the salts remain in solution in the water which becomes bound, or if they are merely dissolved in the free capillary water. There also seems to be a lack of information on the effect that these salts have upon the subsequent shrinkage of the fibrous materials (STAMM 1934). In any case it is known that a large percentage of wood finish degradation (e.g., paint defects, peeling, and cracking) results from moisture changes in the wood and subsequent dimensional instability, which can be also significantly affected by used waterborne preservatives (WILLIAMS, FEIST 1999).

Diffusion

The solubility and mobility of borates allows them to treat wood species that are difficult to treat with copper based preservatives. Even when not applied on the whole cross section, they redistribute by diffusion if sufficient moisture is available in wood to provide one of the most effective preservation systems available today (LLOYD, MANNING 1995; PEYLO, WELLEITNER 1999). Diffusion into wood is dependent upon a number of factors, including the concentration of the borate applied, formulation, the number of treatments, ambient temperature, age of wood, surface condition of the wood, species of wood and moisture content of the wood.

Borates utilize the natural moisture in the wood to diffuse deeper over time, especially in wood having a moisture level of ≥ 15% (SCHOEMAN, LLOYD 1998). While under conditions of higher moisture content, relatively good liquid diffusion of the borate is observed in the grain direction, diffusion perpendicular to the grain is minimal and glue lines largely hinder liquid transport/diffusion. Borates on the other hand, show little or no gaseous diffusion hence the slight diffusion perpendicular to the grain and through glue lines (FREEMAN *et al.* 2009). ROBINSON *et al.* (2005) found that boron treatment to a depth of already 2 mm in structural wood provides very good insecticidal protection.

Above mentioned researches have discussed how the mobility (diffusible capability) of borates allows their use in many different treatment situations and why this flexibility in treatment procedures gives borates many advantages over potential alternatives. On the other hand, these authors and others (e.g. VINDEN 1984) also list major disadvantages of borate diffusion treatments, including need for and difficulty of assuring high uniform moisture content in wood being treated, high inventory costs of prolonged storage of wood for diffusion, and need for co-biocides to prevent mold and mildew growth on wood during diffusion. The lack of borate fixation and leaching is addressed later (WILLIAMS 1996).

Fixation

The potential environmental impact of treated wood can be minimized by specifying that the wood be treated using methods that ensure chemical fixation and prevent the formation of surface residues or bleeding of preservative. The active ingredients of various waterborne wood preservatives (copper, chromium, arsenic, and zinc) are initially water soluble in the treating solution but become resistant to leaching when placed into the wood. This leaching resistance is a result of the chemical fixation reactions that occur to render the toxic ingredients insoluble in water. The mechanism and requirements for these fixation reactions differ depending on the type of wood preservative (REINPRECHT 2016). Some reactions occur very rapidly during pressure treatment while others may take days or even weeks to reach completion, depending on posttreatment storage and processing conditions (LEBOW, TIPPIE 2001).

Many metallic oxides used in acidic chromium-containing waterborne preservative formulations (pH 1.6–2.5) react with the cell wall components by undergoing hydrolytic reduction upon contact with wood sugars. In this fixation process, the metals are reduced to less water-soluble forms by oxidizing the wood cell-wall components. Fixation is a time-dependent function of temperature that can be accomplished in a couple of hours at ≥ 100 °C (Wood *et al.* 1980), or 4 to7 days at 50 °C, or 2 to 6 weeks at 20 °C (DAHLGREN, HARTFORD 1972). To overcome preservative treatability problems with many refractory species, it is common to use an ammonia-based waterborne preservatives and elevated temperatures. Heat and ammonia cause the wood to swell, thereby increasing preservative penetration. In ammoniacal preservatives, the metals are solubilized by ammonia and become insoluble as the ammonia evaporates (YILDIZ *et al.* 2004). Some of the metals appear to simply precipitate within the wood, while others react with the wood structure. Volatilization of ammonia appears to be a key factor in fixation with ammoniacal preservatives, and this can be accomplished through either air drying or kiln drying, or a combination of the two (LEBOW, TIPPIE 2001). Ammoniacal waterborne preservatives formulations (pH ≥ 11) do not react with the cellulose or the hexose hemicelluloses of the cell wall, but the ammonia can solubilize and/or react with the lignin and pentose hemicelluloses (OSTMEYER *et al.* 1987).

Concerns about inadequate fixation have led to develop standards or guidelines for chemical fixing and leaching minimization from treated wood (AWPA 2000).

Leaching

Leaching of biocides is an important consideration in the long term durability and any potential for environmental impact of treated wood products. The extent of leaching is a function of preservative formulation, treatment methods, and wood properties, type of application and exposure conditions. Wood properties such as permeability, chemistry and heartwood content affect both the amount of biocide contained in the wood as well as its resistance to leaching. A range of exposure factors and site conditions can affect leaching, but the most important of these appears to be the extent of exposure to water (LEBOW 2014).

Borates have frequently been characterized as readily leachable from wood in the presence of water. However, it is more accurate to view the process by which boron is lost from treated timber as diffusion (LLOYD, MANNING 1995). Loss of borate preservatives can only take place when treated timber remains wet throughout its cross section for extensive periods of time, while at the same time having an external sink or destination for boron migration (DRYSDALE 1994; MURPHY 1990; WILLIAMS 1996). Nowadays, borates are more or less restricted for use as stand-alone preservatives in interior situations. Borates in these applications remain mobile in the treated wood and will continue to penetrate, thus providing one of the most effective wood preservative systems available today (LLOYD 1997). The key to extending the use of borates to cover the entire spectrum of wood preservation is improving their permanence in wood while retaining efficacy by retaining limited mobility of the borate, even in situations where there is leaching hazard. Previous reviews suggest that their future lies in the search to fix them within treated timber (NICHOLAS *et al.* 1990; LLOYD, MANNING 1995). On the other hand, these procedures show that while fixing boron may prevent leaching, it may also lock the boron resulting in loss of biological efficacy. Research has therefore been directed to partial fixation systems which conserve sufficient mobility to maintain preservative action (PIZZI, BAECKER 1996; THÉVENON *et al.* 1999). Formulation of borates in forms other than simple inorganic aqueous solutions is beginning to develop. The borate physical and chemical properties make borates suitable as components of more complex formulations in combination with copper (LLYOD 1997; AMBURGEY 1990; DUBEY *et al.* 2007), zinc, chromium, quaternary ammonium, or organic ligands (FREEMAN *et al.* 2009). OBANDA *et al.* (2007) reviewed research in laboratories around the world and published several other strategies that are used to reduce leaching and increase the potential range of boron-based preservative products.

Dissociation of chemicals into acidic functional form

LEVAN *et al.* (1996) as well as WINANDY (1995a, b) observed the trend that once degrades had begun at some certain temperature, the fire retardant chemicals had a similar rate of strength loss. The implication of these findings is that once the elevated temperature has imparted sufficient energy to cause a fire retardant chemical to dissociate into its acidic functional form (the form that provides the fire retardancy mechanism), the strength degrade rate in any fire retardant-treated wood is similar. Thus, the essential difference between most fire retardant chemicals systems is the time and energy required for each chemical to dissociate at a given temperature into its acidic functional form. In the case of phosphates fire retardants that acidic functional form would be phosphoric acid. For borates, that form would be boric acid (WINANDY 1995a).

The mechanical property results indicated that qualitatively similar responses occurred in the wood and the quantitative differences between the fire retardant chemicals can be explained by two major factors: the initial pH of the fire retardant-treated wood and the potential, as measured by the dissociation constant (K_a), dictates the temperature and cumulative exposure time needed for the fire retardant chemical to produce its acid functional unit. The resulting acid then accelerates the thermal degrade process. In general, the influence on strength properties is apparently highly dependent on the initial acidity and on the thermal stability of each formulation. Specifically, the effect of fire retardant chemicals on the strength properties of wood apparently depends on the type of chemical and the cumulative temperature exposure level (WINANDY 1995a). The effect of heat treatment on the strength properties of wood is complex and some effects might be less or more severe as a result of additional factors such as exposure period, temperature, heating medium, wood moisture content and pressure (FENGEL, WEGENER 1984).

Acid-catalysed dehydration

The extent of wood degradation is believed to be due to acid-catalyzed dehydration in many cases (LEVAN, WINANDY 1990), which is influenced by acidity, temperature and also magnified by the high moisture content induced by the water solvent in the systems. Acids in wood, especially when accelerated by acidic fire retardant treatments, cause dehydration reaction and further can hydrolyze the branched hemicellulose and the longer cellulose chains. Cellulose is often thought to be primarily responsible for the strength of the wood fiber; therefore, reducing the length of the cellulose molecules (degree of polymerization - DP) would cause a reduction in macro-strength properties. This theory of hydrolytic cellulose depolymerization was originally proposed by IFJU (1964), modified to also include hemicelluloses content by Sweet and WINANDY (1999), and verified by various chromatographic methods (size exclusion chromatography coupled with diode array detector and multi-angle light scattering detectors, and asymmetrical flow field-flow fractionation combined with multi-angle light scattering detector) (KAČÍKOVÁ *et al.* 2013, KAČÍK *et al.* 2016). Cellulose treated with the acid charred and depolymerized very rapidly (LEVAN, WINANDY 1990). The increase in brittleness of the phosphoric acid-treated wood due to chemical action of acid was observed. Brittleness was probably due to embrittlement of the wood fibres caused by crystal formation within the wood cell-walls or cross-linking between cellulose or hemicellulose molecules (AYRILMIS 2007). It is also known that the alkaline treatments produced a smaller reduction on unaged and aged internal bond strength than do the acid treatments.

Influence of pH on mechanical properties

There is a direct relationship between the effect of chemical treatment and the effect of treatment pH on mechanical properties. For example the H3PO4 treatment has very low pH, and it has a greater negative effect on mechanical properties. The hydrogen ion concentration of H_3PO_4 is approximately 100 times higher than that of $NH_4H_2PO_4$. This difference in pH at the same loading concentration accounts for the severe effect of H_3PO_4 on mechanical properties. On the other hand, the $H_3BO_3/Na_2B_4O_7.10H_2O$ treatment has pH level that is close to neutrality. This treatment exhibits the least effect on strength properties. However, $H_3BO_3/Na_2B_4O_7.10H_2O$ reduces flame propagation only slightly (WINANDY *et al.* 1991).

MIDDLETON *et al.* (1965) published on this topic that the $NH_4H_2PO_4$ treatments reduced strength properties most severely and the boron based formulations reduced strength properties to a lesser extent. KARTAL *et al.* (2008) concluded that the pH of the treated specimens with boron based compounds decreased remarkably after wet-thermal accelerated aging. However, the pH of the untreated wood specimens decreased slightly depending on the heating temperature, moisture and time. As expected, the pH levels of the $Na_2B_8O_{13}.4H_2O$ and $Na_2B_4O_7.10H_2O$ treated specimens were significantly higher than those of the H_3BO_3 treated specimens. During accelerated aging it is possible that some of the $Na_2B_8O_{13}.4H_2O$ and $Na_2B_4O_7.10H_2O$ are further converted into H_3BO_3, decreasing the pH of the treated wood specimens. The decreased acidity of the aged wood may be also assumed to be caused by the removal and leaching of organic acids, especially acetic acid, from the wood. Acetic acid is believed to originate from acetyl groups in the wood carbohydrates (FENGEL, WEGENER 1984). In the study of LEWAN *et al.* (1990) the pH of plywood treated with fire retardant formulations decreased dramatically during the first 60–160 days of exposure at 66 °C. All treatments studied caused large, rapid decreases in pH, with the most rapid decreases occurring with formulations containing H_3PO_4. The pH of some groups of treated wood continued to decline during subsequent exposure, but much less dramatically. Untreated specimens also began to suffer a slight, but significant, decrease in pH after 160–290 days of exposure. Past research has noted that exposure of untreated wood to elevated temperatures and moisture content can eventually cause an increase in acid production (HILLIS 1975). So, regardless of chemical formulation or processing parameters, the pH of all treated specimens decreased markedly after treatment, redry, and subsequent high temperature exposure.

According to REINPRECHT (1988, 1991) corrosion by acidic solutions causes shrinkage of wood in a larger scale and the density of wood treated with acids usually does not increase significantly. Mechanical properties of these wood objects are reduced not only in wet but also in the dry state and decreasing strength is attributed mainly to a significant depolymerization of hemicelluloses but also the cellulose, and in some cases the degradation of lignin. Wood corroded by alkaline solutions shrinks and swells much more than healthy wood. This is related to the degradation of hemicellulose filling in submicroscopic vanes, which leads to increased moisture deformability of cell walls. Mechanical properties can even improve in the dry wood due to increasing its density as a result of wood shrinking and forming hydrogen bonds. However, the strength of alkaline treated wood in the wet state is significantly reduced and in the presence of water molecules there are not applied any reinforcing hydrogen bonding and van der Waals interactions (REINPRECHT 1992).

The trends in pH reduction for all the fire retardant treated groups paralleled the trends of decreasing of modulus of rupture (MOR) and work to maximum load (WML), but this is not case immediately after treatment, because the pH of the treated wood decreased much more significantly than did either MOR or WML. For the treated plywood, strength loss and pH attributed to thermal degradation were closely correlated during the first 160 days of high temperature exposure. During the final days of exposure, pH tended to stabilize, while strength losses continued to decline. It is probable that the chemical reactions that cause a decrease in the pH reach equilibrium much more rapidly than the subsequent reactions that cause strength losses in wood. These findings suggest that the pH of treated plywood is a good indicator of the potential for future strength loss if the plywood is early in its exposure to high temperatures (LEBOW 2007).

Influence of elevated temperature on mechanical properties

Field problems of reduced strength capacity have developed in some situations where material treated with fire retardant is exposed to elevated temperatures (APA 1989; NAHB 1990). The effects of waterborne preservative treatment on mechanical properties appear to be directly related to several key wood material factors and pretreatment, treatment and post-treatment processing factors. The key factors included: preservative chemistry or chemical type, retention, species, material size and grade, product type, mechanical property, initial kiln-drying and post-treatment drying temperature and incising, if required (WINANDY 1995b). In most cases there were observed mainly mixing effects of chemicals and thermal treatments on the chemical composition and strength properties, and it is therefore difficult to distinguish how these factors contribute to the properties evaluated. However, the effect of heat treatment on mechanical properties was much clearer at the highest temperature. Generally, as exposure temperature, relative humidity and duration increase, mechanical properties of treated wood are progressively reduced. Each mechanical property is affected by waterborne preservative treatment differently at various temperatures (WINANDY *et al.* 1991).

In summation, the effects of waterborne preservative treatment on the mechanical properties of wood under standard-specified conditions (AWPA 1994) are as follows:

- Modulus of elasticity (MOE) of the various treated specimens, except the H3PO4 treated specimens, is generally unaffected (BENDTSEN *et al.* 1983; BARNES, MOORE 1987). And this applies not only for room temperature, but also for almost all temperatures and exposure times. Therefore, the evaluation of treatment effects based solely on MOE would not give a realistic evaluation of the impact of chemical type, exposure conditions, and exposure time (WINANDY *et al.* 1991).
- Maximum crushing strength may be differently affected by waterborne preservatives as shown by reported decreases (NISHIMOTO, INOYE 1955; WAZNY, KRAJEWSKI 1987), no changes (KOUKAL *et al.* 1960), or slight increases (SHIBAMOTO, INOUE 1962; WOOD *et al.* 1980; MITCHELL, BARNES 1986; BURMEISTER, BECKER 1963) as retention increases when air dried. However maximum crushing strength can be significantly reduced when redrying temperatures exceed 70 °C (WINANDY *et al.* 1985).
- Bending strength is the most studied wood property. A comprehensive review of the waterborne preservative treatment literature concluded that modulus of rupture (MOR) is more sensitive to treatment effects than MOE and is often reduced from 0 to 20%, depending on the preservative chemistry, retention and severity of the redrying temperature employed (BURMEISTER, BECKER 1963; WINANDY 1995b). While thermal-induced effects were apparent at 82 °C for all specimens including controls, these effects were not as severe as those resulting from H_3PO_4 and $NH_4H_2PO_4$. But the rate of strength degradation (slopes of the lines) was similar for treated and untreated material even though large differences in strength occurred (LEVAN *et al.* 1990).
- Energy-related properties are usually reduced from 10 to 50% (PECHMAN, AUFSESS 1968; BURMEISTER, BECKER 1963; BENDTSEN *et al.* 1983). The work to maximum load (WML) is an indication of the brittleness of materials, and treatments tend to cause embrittlement (WINANDY, ROWELL 1984). This property is a sensitive to the influence of chemical type, exposure conditions, and exposure time. In the LeVan's study the H_3PO_4 treatment had the greatest detrimental effect on WML, followed by $NH_4H_2PO_4$. All other treatments were not as severe as these chemicals. However, except for H_3BO_3 treated specimens, all other treated specimens and the untreated controls had reductions in WML over time at 82 °C (LEVAN *et al.* 1990).

Changes in chemical composition

A partial review of the effects of metals on wood has been published by THOMPSON (1969). Experimental evidence for deterioration of wood near rusting iron has been provided by the comprehensive investigations of MARIAN and WISSING (1960) and by the earlier investigations of BEACHLER (1954) and FABER (1954).

BAKER (1974) explained using describing the chemical reaction around isolated iron, copper and cooper alloys fasteners in terms of crevice corrosion in an acidic environment the reason why wood degrades around individual metal fasteners in wood. Emery and SCHROEDER (1974) have found a decomposition of all wood constituents when analyzing the wood meal and polysaccharides exposured by iron powder under conditions favourable for rusting. These authors also published that rusting iron causes oxidative degradation of wood constituents via two pathways: 1st - direct formation of organic free radicals and their subsequent oxidation through a chain reaction and 2nd - oxidation by intermediate hydroxyl and perhydroxyl free radicals, which should be responsible for most of the wood deterioration. Contrary PANDEY (1998) published that the treatment of wood with ferric compounds indicates no reaction with any of the wood constituents.

- Deterioration of isolated cellulose has been reported by BELL and GIBSON (1957). HEUSER (1944) noted that cellulose in situ can be shielded from chemical attack by lignin. All from above mentioned authors have suggested the analogy between alkaline oxidation and the deterioration of polysaccharides. BLATTNER and FERRIER (1985) studied the oxidation speed of cellulose in the presence of iron and other metals. Their results have shown that iron ions have a general accelerating effect on oxidations by either oxygen or hydrogen peroxide. In the presence of iron, cupric salts initially inhibiting the cellulose oxidation, but eventually accelerating its degradation when compared to the reaction speed catalysed by iron only. Copper ions themselves significantly accelerate the oxidation of organic compounds by Fenton's reagent. The presence of chromate ions had a marked inhibitory influence on the action of iron ions when cellulose oxidation, whereas the presence of chromium alone causes a distinctive cellulose oxidation. Neither arsenic, aluminium, zinc nor CCA (solution of Cr^{6+}, Cu^{+} and As^{3+}) affect the speed of catalysed oxidation, but CCA without the presence of iron has the oxidative effect on cellulose, too.
- In general, hemicellulose content is significantly reduced depending on the type of preservative chemical, temperature, and the specific hemicellulose residue examined. The magnitude of the reduction in hemicellulose components is a function of the chemical treatment and the cumulative exposure. The wood carbohydrates are significantly degraded in the heat-boron treated specimens, suggesting depolymerization and alterations through the cleavage of acetic acid from the acetyl side chains. Some of the changes of properties in treated wood have been directly and individually linked with changes in wood acidity, i.e. hydrolytic mechanism (HODGIN, LEE 2002). KARTAL *et al.* (2008) published that in all treated specimens with H3BO3 and Na2B8O13.4H2O exposed to elevated temperature (220 °C for 4 h), rhamnans were degraded and the arabinan content of the same specimens decreased in the range of 90–87% and 84% for untreated specimens. In the treated and heated specimens, mannan, xylan and galactan were the least affected hemicellulose types; glucan was the most resistant to thermal degradation and the reduction in its content was 10–12% for the untreated and H_3BO_3 treated specimens, respectively 34% for the $Na_2B_8O_{13}.4H_2O$ treated specimens in comparison to the untreated, unheated specimens.
- KULIK *et al.* (1989) were interested in binding of metal ions into lignin structure. They have found out that copper and zinc bind themselves to lignin with a stable covalent bond and that it is difficult to leach them back from lignin with water. The formed copper complex compound being more stable than the zinc one, because that bonds of copper are influenced mainly by carboxyl groups in the aromatic ring of lignin, whereas bonds of zinc are intermediated by the hydroxyl (phenol) group in the aromatic ring. Apparent increases in the amount of Klason lignin were found in heat-chemical-treated specimens (KARTAL, AYRILMIS 2005; FENGEL, WEGENER 1984; FUNAOKA *et al.* 1990), probably because of the ongoing removal of hemicelluloses during thermal degradation or because of the effect of strong acid. Given the effect of H_3PO_4 acidity on the carbohydrates, we believe this increase resulted solely from the

drastic reductions in the other sugar residues, leaving a larger percentage of Klason lignin. However, SWEET and WINANDY (1990) found the Klason lignin content decreased in southern pine with drying at 66 °C for 560 days. Similarly, KAČÍK *et al*. (2016) reported the decrease the acid-insoluble lignin content during pine wood heat sterilization (60 and 120 °C, 10 h). These studies suggest that the exposure time, wood species and heating medium are as important as temperature in thermal degradation of lignin. There also appeared to be a direct correlation between the observed changes in the percentage of arabinose and the acid-soluble lignin (LEVAN 1990). If the arabinose percentage showed a decreasing trend for a given treatment group, the acid-soluble lignin showed an increasing trend, when it was determined by UV absorbance at a wavelength of 205 nm. It is suspected that the fraction collected and identified as acid-soluble lignin includes both actual lignin components and carbohydrate degradation products. But according to (PEARL, BUSCHE 1960) it is known that carbohydrate degradation products from the hydrolytic procedure do not interfere with the 205 nm measurement. So some further research is necessary to positively identify the products that cause the increase in acid-soluble lignin or it would be suitable to find some method for precisely determination of only acid-soluble lignin.

Relations between chemical composition and strength properties

An evaluation of changes in the chemical composition of wood clearly indicated that hemicellulose is the key component of thermal-related strength loss and increased brittleness (LEVAN *et al*. 1990; WINANDY 1995b). Although this finding does not minimalize the critical importance of cellulose and lignin in the overall initial strength of wood products, these results do show that the wood is viewed as a collection of organic components, the degradation of hemicellulose almost exclusively accounts for the first 10–25% loss in initial strength.

Of note is the fact that the side groups of major hemicelluloses are most affected by treatment. These side groups are suspected of bonding with lignin (SJOSTROM 1981). It is possible to speculate that the cleavage of these side groups between the lignin and hemicelluloses releases the linkage by which one microfibril of a wood fiber shares the load with another microfibril. Disruption of such load-sharing would result in increased brittleness. This loss in load sharing in combination with disruption in the hemicellulose backbone chains would also cause a gradual reduction in strength (WINANDY, ROWELL 1984).

The relationship between changes in chemical composition, especially loss in hemicellulose composition, and strength appears quantitative. These results have been also used to develop a nonlinear kinetics-based model to predict strength loss from fire retardant-related degrade (KARTAL *et al*. 2008).

CONCLUSIONS

The extent of wood deterioration, i.e. the magnitude of changes in its structure and properties, depends on the extent of damage to its chemical, microscopic and macroscopic structure. The chemical structure of the wood consists of polymers: cellulose, hemicelluloses and lignin, which form the structure of the cell wall and intercellular matrix. Degradation of the chemical structure is subsequently reflected by changes in the microscopic and macroscopic structure of treated wood, e.g. cracks, surface defibrillation or shape deformation that negatively affect the changes in wood properties. Therefore, the reduction of mechanical properties of treated wood with aqueous solutions of inorganic salts is not only a consequence of the swelling and shrinking of wood, but also a result of chemical reactions of these chemicals (with acidic/basic character commonly described by pH value or oxidation effects) with wood polymers.

It is obvious that the chemicals already enter into reaction with the wood during their application and fixation into wood structure. Deterioration of wood polymers in varying extent occurs by direct reaction of the chemical compounds with wood and/or due to their catalytic action (PANDEY 1998; GOLDSTEIN 1984; EMERY, SCHROEDER 1974). The most significant corrosion damage is probably reduction of the degree of polymerization of polysaccharides and decline of lignin amorphous three-dimensional network. The main degradation reactions include mainly hydrolysis, depolymerization and oxidation of polysaccharides and lignin as well as substitution and crosslinking reactions. In addition certain metal cations ($Fe2^{+}$, Fe^{3+}, Cu^{2+}, Zn^{2+}) can react with wood extractives to produce characteristic colouring or they have an influence on the formation of radicals which catalyze the above mentioned decomposition of the wood polymers (BLATTNER, FERRIER 1985). The introduced reactions occur simultaneously and influence each other. The relative proportions of these competing reactions and their impact on the degradation of the wood components have not been elucidated yet (HILL *et al*. 1995; EMSLEY *et al*. 1997; ZERVOS, MOROPOULOU 2005; BANSA 2002). The difficulties lie in the complexity of the monitored systems and in the combination of different acting factors in the aging process of lignocellulosic materials.

Moreover, elevated temperature, increased relative humidity and the higher concentration of aggressive chemicals can easily accelerate wood degradation resulting in wood damage. The magnitude of changes in the molecular structure of wood, as well as in micro and macrostructure, depends on the properties of wood, dissociation constant of the chemical, exposure time and exposure conditions.

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ACKNOWLEDGMENTS

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-16-0326 (50%) and by the VEGA agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic No. 1/0521/15 (50%).

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