



Potentials of silicate-based formulations for wood protection and improvement of mechanical properties: A review

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Received: 30 August 2020 / Accepted: 15 April 2021 / Published online: 30 April 2021
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Abstract

Silica or silica-precursor systems are attractive for the protection of wood against biotic and abiotic damages and for improvement of the fire resistance. Alkali metal silicate solutions, also known as water glasses, colloidal silica (nanosilica dispersions) and other inorganic–organic hybrids resulting from the sol-gel chemistry of alkoxysilane compounds, are products available for this purpose. These chemicals are increasingly considered to formulate wood modification products or to develop surface coatings. This review article is focused on in-depth treatments of wood through dipping, soaking or vacuum-pressure impregnation methods. The techniques used to convert monomers and low molecular weight silicate species in water glasses into less soluble and leaching-resistant silica particles, such as heat treatment, acid treatment and reactions with multivalent metal cation salts, are discussed. The similarities and differences between the various raw-impregnation materials and the properties of the final products are highlighted. Water glasses after appropriate curing, colloidal silica and tetraalkoxysilane-based formulations all lead to deposition of silica particles (SiO_2) at the surface of the cell walls, in lumens and pores. Low molecular weight organosilanes and other organo-modified formulations that are able to penetrate the wood cell walls and react with wood components are good dimensional stabilizers. The treated wood exhibits, in general, increased mechanical properties (strength, hardness) and improved resistance to biodegradation and fire retardancy. The efficiency of the treatments can significantly be enhanced to a level fulfilling the requirements for industrial applications by the addition of biocides, ultraviolet absorbers or antioxidants, fireproofing compounds (boron or phosphorus-based compounds, multivalent metal salts) and hydrophobic alkylalkoxysilanes. Silica acts as a barrier/support to many of these additives preventing them from leaching.

Introduction

Wood is a versatile material used in building construction and civil engineering for a variety of structural and non-structural applications. It has several advantages such as renewability, aesthetic appeal, lightweight, amenability to processing and ease to maintain, low thermal conductivity, and relatively high mechanical strengths. However, wood is vulnerable to various abiotic and biotic factors, and its utilization usually requires special attention and treatments to increase the lifespan of constructions and other wood-based products, and fire safety. The rate of degradation of wood in an environment depends on the intrinsic properties of the wood as well as the harshness of the environment.

Among the abiotic damaging agents, moisture is the most significant. Because of the hydrophilicity of cell wall components and its porous structure, wood can absorb water more than 100% of its weight. This moisture is permanently exchanged to maintain balance with the environment. When the moisture content is below the fibre saturation point (around 30 wt%) as it is generally for wood in above-ground applications, moisture changes result in swelling and shrinkage of the wood inducing mechanical stresses at the origin of cracks and deformation (e.g. bow, twist, or cup) (Reinprecht 2016). Temperature, oxygen, and impact of other particulates dispersed in air, atmospheric pollution and solar radiations also contribute to the degradation of wood causing, during ageing, damages such as surface erosion and roughening, and discolouration. Wood cell walls are composed of three main polymeric components, two carbohydrates (cellulose and hemicelluloses) and lignin an aromatic compound. These components, by absorbing sunlight especially ultraviolet-light, undergo photo-oxidative chemical reactions responsible for discolouration of the wood surface. With a high concentration of chromophores, lignin is by far the component most affected and degraded by light (Teacă et al. 2013).

Biodegradation is a natural process in which wood components are decomposed and eaten by microorganisms (bacteria and fungi), insects or marine borers leading to different types of damages from visual discolouration, small holes, craters and galleries inside the wood, loss of mechanical properties to complete disaggregation of wood (Levy 1987). The biodegradation of wood is closely related to its moisture content. Moisture has to be high enough to promote a flow path for enzymes and the products of enzyme actions and to soften fibres, yet low enough to prevent waterlogging, which might produce an anaerobic habitat hostile to the common and more aggressive white rot and brown rot fungi and termites (Brischke and Alfredsen 2020; Kim and Singh 2000; Oberst et al. 2019). Hydrolytic enzymes, ligninolytic enzymes secreted by these organisms or symbiont species as well as non-enzymatic oxidative systems are used to depolymerize and fragment carbohydrates and lignin of cell walls (Andlar et al. 2018; Mester et al. 2004; Talia and Arneodo 2018). Soft rot and some bacteria, which are more tolerant towards high moisture and reduced oxygen conditions can attack submerged wood, but they are less aggressive for wood compared to brown rot or white rot (Kim and Singh 2000).

Flammability of wood is another matter of great concern in the built environment (Östman 2006; Lowden and Hull 2013; Reinprecht 2016). Wood

components undergo thermal degradation and exothermic combustion when heated at elevated temperatures. The ignition-point temperatures for wood are between 220 °C and 280 °C in normal conditions (Kollmann 1960). Wood thermal degradation produces gases, primary water vapour, carbon dioxide, formic and acetic acids, glyoxal, and highly combustible gases when temperature increases (carbon monoxide, methane, hydrogen) and tars in the form of smoke particles (Beall and Eickner 1970). In a fire scenario, the smoke released poses severe risks to the safety of occupants of the buildings (reduction in visibility, irritation, and lethal effects) and is responsible for increasing requirements regarding the utilization of wood especially in the escape routes (corridors and stairs) (Lowden and Hull 2013).

Wood treatments are usually carried out to afford the limitations and fulfill the quality requirements for use in a specific application. A superficial treatment such as application of an appropriate coating can be enough in many cases, but for some exigent applications and depending on the natural grade of the wood, service solicitations and aggressivity of the environment, and the necessity of fulfilling the requirements of a particular standard, in-depth modifications are needed. Wood and wood-based products are now framed by many standards which provide a number of performance criteria to measure and grade the materials according to their resistance to biodegradation, reaction to fire and fire resistance, ensuring the quality and consumer satisfactions. The European standards for fire performances are presented in Östman (2006), Östman and Mikkola (2006) and Reinprecht (2016), and standards for the evaluation of natural durability of wood and resistance to biodegradation of wood and wood materials can be seen in Kutnik et al. (2017).

Three in-depth treatment methods commercially used are chemical, thermochemical and impregnation modification. The treatment by impregnation method is an ancient and the most implemented full-treatment method in the field of wood technology and consists of the introduction of biocidal agents, hydrophobizing agents and/or flame-retardant compounds within wood. Pure liquids, solutions or dispersion mixtures containing the active ingredients are applied to wood and allow to penetrate and migrate within the wood using the interconnected network of pores and pits. The treatment is performed by soaking/dipping wood in an impregnation product for a specific period, and may be assisted by vacuum-pressure forces. The chemicals can diffuse to the heart of the wood piece affecting the material in its whole volume (full-depth modification). Water-soluble chemicals forming strong chemical bonds and/or physical interactions (e.g. hydrogen bonds, van der Waals interactions) with wood surface components, water-insoluble and hydrophobic chemicals filling pores are resistant against leaching and perform durably. The chemical structure of wood is not fundamentally changed, but because of the various physicochemical interactions between the introduced chemicals and wood cell walls and ensuing macroscopic changes, impregnation is commonly classed among the wood modification methods. A preservative product must be efficient against the targeted drawbacks and produce a material that would be disposed at the end of service life without presenting any environmental hazard. The hazard risks related to conventional inorganic copper-based and organic creosote or pentachlorophenol preservatives and

their increasing restrictions around the world have led to the search for environmentally friendly and sustainable alternatives and other modification methods.

The chemical modification of wood is based on the reactivity of hydroxyl groups of wood components, which undergo various chemical reactions such as etherification, esterification or furfurylation. The conversion of hydroxyl groups responsible for the hydrophilic nature of wood into hydrophobic groups (e.g. acetate) reduces its affinity with moisture and dimensional instability, and increases its resistance to biodegradation (Mantanis 2017). The thermal modification of wood is performed at a temperature range between 150 °C and 240 °C under a controlled dry atmosphere (air, vacuum, inert gases) or wet atmosphere (water, saturated steam) (Hill et al. 2021). The decrease in oxygen/carbon ratio and hydroxyl group content, degradation of amorphous carbohydrates, and modification of the chemical structure of lignin are some notable changes associated with the thermal treatment of wood. The chemical and thermal modifications of wood increase the resistance to moisture and dimensional stability of wood but usually lead to the reduction in mechanical strength.

Inorganic silica-wood composites have always been present in nature as fossil petrified wood, and have shown resistance to biodegradation for thousands of years (Ballhaus et al. 2012; Dietrich et al. 2013; Sigleo 1979; Trümper et al. 2018). The concept of wood protection with silicate-based formulations for building applications has been envisaged at least two centuries ago in Germany. Water glass—“sodium silicate solution” was studied for the protection of wood against fire (Fuchs 1825, in Pries and Mai 2013a). This idea was intensively reconsidered since the end of the twentieth century. The development of nanosilica, sol-gel chemistry and wood nanotechnology have extended the possibilities of treatment with silica-based products.

Numerous starting materials including water glasses of different modules, colloidal silica, non- and pre-hydrolyzed alkoxysilanes and curing methods have been used in this literature to produce silica and siloxane-treated wood. This work presents the various formulations available for wood impregnation: preparation, physical properties and chemistry, and toxicity. The methods used to apply and cure the silicates within the wood are discussed. A global insight into what has already been done regarding the treatment of wood with silica-precursors and the chemical processes involved are presented. In general, modified wood exhibiting increased mechanical properties (bending and compression strength, surface hardness, a slight change of the elastic modulus), improved resistance to biodegradation and fire retardancy can be obtained with these formulations. To the best of the authors' knowledge, the most recent review articles addressing mainly this research topic date back to 2004 (Mai and Miltz 2004a, 2004b). In the authors' opinion, there is a need to update the data and scientific achievements in the field. The results are discussed, and comprehensive explanations are provided as a contribution for better knowledge of these systems and future research and development of new products.

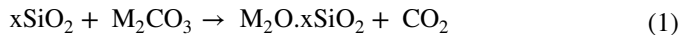
Silicate-based formulations

Silicon sources

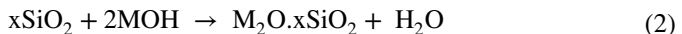
Silicon is the second most abundant chemical element in the earth crust following oxygen. Silicon is found in nature combined with oxygen in silica or silicate minerals. Silicon compounds account for around 90% of the mass of the crust; feldspars and quartz being the most important (Rafferty 2012). Silica sand or quartz sand, a crystalline form of SiO_2 , is largely available all around the world and easy to mine for industrial applications. It is currently the main raw material for the production of silicate glasses, water glasses, silicon and other silicon-based products. Other silica sources such as feldspars, clays and silica-rich ashes can also be used, although their conversion requires purification and elimination of other elements (Aphane et al. 2020; Cha and Park 2001; Liu et al. 2016; Park et al. 1997; Zulfiqar et al. 2016).

Water glasses

Water glass is an aqueous solution of an alkali metal silicate. Alkali metal silicates are compounds of formula $\text{M}_2\text{O}\cdot x\text{SiO}_2$ ($\text{M}=\text{Na}, \text{K}$, and eventually Li) prepared usually by fusing quartz sand with a metal carbonate (Eq. 1) (PQ Corporation Europe 2004).



The stoichiometry of the reaction (Eq. 1) is set to yield a glassy solid with silicate to alkali $\text{SiO}_2/\text{M}_2\text{O}$ molar ratio (often simply called module) between 0.5 and 5. The solubility of alkali metal silicates in water decreases with their module. Water glass can also be produced by direct thermal dissolution of quartz sand in an alkaline hydroxide solution (Eq. 2) (Pfeiffer et al. 2019).



Several types and grades of water glasses are now commercially available. The marketed products are differentiated by their metal ion, module, and solid content. Sodium silicate accounts for approx. 92% of the worldwide production and consumption of metal silicates and it is the least expensive silicate. Sodium is available for exploitation, mainly in large reserves of NaCl or trona ores; potassium is less used for silicates because of high demand in fertilizer industries, while lithium is a minor element in the earth crust.

Water glasses are complex mixtures of monomeric (silicic acid and silicate species) and oligomeric silicate species (oligomers of silicic acid with some negatively charged, non-bridging oxygen atoms) (see Fig. 1).

Alkali metals in the solutions are in the form $\text{Si-O}^-\text{M}^+$ and MOH . pH, viscosity and particle size distribution of a water glass are dependent on the module and the mass concentration. For instance, solutions of sodium metasilicate (Na_2SiO_3) are highly alkaline with pH typically ranging from 12.4 to 12.7, while pH for a sodium

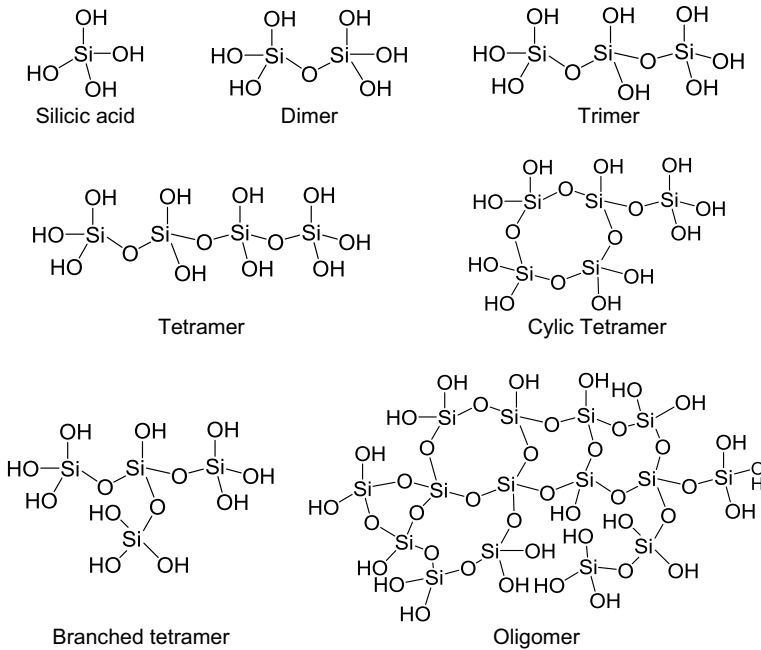


Fig. 1 Some model species present in silicic acid solutions (pH < 8–9). At high pH values, a part of silanol (Si–OH) end-groups are converted to silicate groups (Si–O[–]M⁺)

silicate with module 3 is around 11.5. Water glasses have a “buffer capacity”; pH decreases slowly through dilutions.

The particle sizes of dissolved species in a water glass are a function of concentration, pH, metal counterion, and temperature (Schubert 2015). The mean particle size increases with the module and decreases when the temperature increases. At pH below 9, silicate solutions contain mostly silicic acid species (Fig. 1). When the pH increases above 9, there is a progressive formation of ionic silicate species through depolymerization of oligomeric species and neutralization of the silanol groups. An increase in the temperature also causes depolymerization increasing the concentration of particles in the solution. The depolymerization-solubilization due to temperature and pH variations has been demonstrated in many studies devoted to the solubility of amorphous silica in water (Alexander et al. 1954; De Lucas et al. 2004; Krauskopf 1956; Vogelsberger et al. 1992). The equilibrium in water glass is then controlled by polymerization-depolymerization reactions involving silanol groups; an increase of the pH depolymerizes and increases the concentration of low molecular weight species in solution (Krauskopf 1956; Weldes and Lange 1969). Drying of silicate solutions also causes polymerization. During drying, the solution becomes more and more concentrated by the evaporation of water; the silanol groups of the silicate species brought closer progressively react leading to the formation of a gel (Krauskopf 1956). However, this process is reversible. Depolymerization occurs and gel could be solubilized through the addition of water. Polymerization occurs

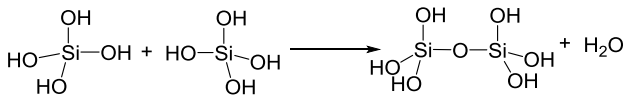
by condensation reactions between two silanol groups resulting in chain structures (and not a network structure) which produce, as the reaction progresses, growing nanoparticles (Fig. 2). When the module is brought to a significantly high value, water glass is converted into a dispersion of nanoparticles that can be stabilized to form colloidal silica (Bergna 2006).

Colloidal silica

Colloidal silica, also known as silica-sol, consists of dense, amorphous particles of SiO_2 . A colloidal silica dispersion is defined by its particle size distribution, pH, solid mass content, and counterion (type and concentration). The particle sizes are usually between 10 and 100 nm, but dispersions with particle sizes up to 10 μm can also be included. The most popular method for the production of colloidal silica uses sodium water glass as raw material and ion-exchange techniques. Traditionally, the water glass is diluted with water to a mass concentration around (3–5) %, and then it is passed through a cation exchange resin where sodium ions in the solution are substituted by hydrogen ions at the exchange sites of the acid resin and then the pH is adjusted (Lim et al. 2010; Qomariyah et al. 2018). The mean particle size and surface area of colloidal silica are influenced by the conditions of the preparation such as temperature, the concentration of silicic acid and alkaline solutions, and titration rate (Karami et al. 2008). Colloidal silica products with a wide range of pH from basic (pH between 8 and 10) to acidic (pH between 3 and 4) are now available on the market. Colloidal silica is generally stable in the pH range between 8 and 11 while exhibiting a short gel time in neutral to acidic pH (3–8). Colloidal silica products, stable at low pH (acidic), are obtained by surface modification of the silica particles by the addition of aluminium (Al) ions which change the overall charge at the surface of the particles from common anionic to cationic (Tsai and Wu 2004).

Colloidal silica can be produced using various other methods and starting materials such as neutralization or electro dialysis of aqueous silicates, direct oxidation of silicon, or peptization and milling of silica gel or silica powder, or hydrolysis and condensation of alkoxy silane compounds.

Condensation reaction between two silicic acid monomers



Formation of a silica nanoparticle via polycondensation reactions

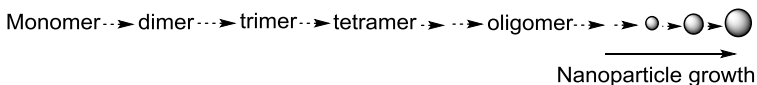


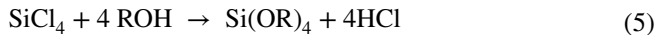
Fig. 2 Polycondensation in silicate solutions and formation of silica particles

Alkoxysilane-based products

Alkoxysilanes are products of the silicon-metal production sector. More than 8 million tons of silicon (silicon metal and ferrosilicon) were produced in 2020 in the world with major applications in aluminium alloys, siloxanes resins, and semiconductors and solar energies industries (Schnebele 2021). Silicon is extracted from abundant silica sand (quartz) by reaction with carbon at a temperature between (1500–1800) °C in the main process (Eq. 3).



The halogenation of silicon provides halogenated silanes (e.g. trichlorosilane SiHCl_3 , tetrachlorosilane SiCl_4), precursors for alkoxysilanes through etherification and alkylation reactions as shown in Eqs. 4 and 5 for production of tetraalkoxysilane (Khananashvili et al. 2006; Maurits 2014).

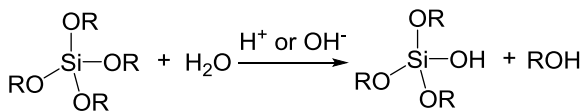


Many organosilanes containing various organic moieties and exhibiting different properties are commercially produced. The most common is tetraethoxysilane (TEOS, also called ethyl silicate). Alkyltrialkoxysilanes with different alkyl chains and other organosilanes are available alternatives or additions for modification of the properties of silica end products (Spataru et al. 2013).

Alkoxysilanes undergo polycondensation reactions when in contact with water via the sol-gel process and have found many applications in material sciences (Ciriminna et al. 2013; Danks et al. 2016; Burger et al. 2016; Rahman and Padavettan 2012). In alkoxide-based systems, hydrolysis reaction of Si-OR groups to generate Si-OH groups is a prerequisite for condensation (Fig. 3) (Ro and Chung 1989; Esposito 2019).

The main difference between alkali silicates and alkoxysilanes is that polycondensation occurs in aqueous silicate systems by pH or temperature changes and by addition of water (hydrolysis reactions to generate Si-OH groups) in alkoxysilane

(a) Hydrolyse



(b) Condensation

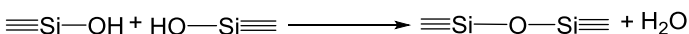
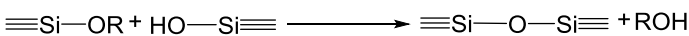


Fig. 3 Hydrolysis and condensation of alkoxysilanes

systems. An acid or a base catalyst is often added in alkoxy silane systems to accelerate the hydrolysis of alkoxy groups and the condensation of silanol groups. Sol-gel processing of tetraalkoxysilanes, $\text{Si}(\text{OR})_4$, results in pure inorganic silica, SiO_2 , at completion while alkyltrialkoxysilanes ($\text{R}'\text{Si}(\text{OR})_3$) could yield the so-called silsesquioxanes, $\text{R}'\text{SiO}_{3/2}$ (Baatti et al. 2017; Issa and Luyt 2019; Schubert 2015). The structure evolution in the sol-gel polymerization of organotrialkoxysilanes is dependent on the type of the organic substituent R' , temperature, water/silane molar ratio, organic solvent, and catalysts. An increase in the size of R' slows down the polymerization, the intermolecular reaction being sterically hindered and cyclization favoured. The trialkoxysilanes with long substituents do not lead to high-molecular-weight polymers and do not gel even at high conversion rates (Matějka et al. 2001). Trialkoxysilanes with long substituents are generally used as additives to improve the hydrophobicity of nanoparticles of silica or silsesquioxanes and could exhibit a plasticizing effect leading to more uniform surfaces. There also are many other silanes with only a single and two hydrolysable groups which form dimers, or linear/cyclic silicon polymers.

Toxicity of silicon compounds

Silicate compounds have been found to be of low toxicity and approved for use in various consumer products such as food additives, water treatment, detergents, and cosmetics. Sodium metasilicate has been granted GRAS (Generally Regarded As Safe) status by the US Food and Drug Administration FDA (21 CFR 182.90). The US Environmental Protection Agency has classified potassium silicate as non-toxic to the environment and a product not requiring the environmental hazard statement on the end-use product's label. According to the data available to the European chemicals agency (ECHA) in the classification, labelling and packaging (CLP) section, no hazards have been classified for sodium silicate (ECHA 2019a). It has been reported for potassium silicate risks of eye damages and skin irritations (ECHA 2019b). Care must be taken to prevent contact, especially when manipulating concentrated water glasses because of their high alkalinity (pH above 11). Their low vapour pressure reduces the risks of intoxication by inhalation. The median lethal dose (LD_{50}) for accurate oral toxicity of silicate compounds (sodium) was reported to be superior to 5,000 mg/Kg (Vattem et al. 2012) suggesting low toxicity with regard to food safety and water quality and in potential pharmaceutical applications. Soluble silicates have low acute toxicity by the oral route because of their high solubility in water. Sodium silicate is readily absorbed from the alimentary canal and excreted in the urine when ingested orally in authorized foods or drinks. Because of their very low lipophilicity and moderate particle sizes, dermal bioavailability is limited.

The toxicity of colloidal silica has been studied in the literature. The toxicity of silica nanoparticles in in-vitro analyses has appeared to be size, dose, and cell type-dependent and nanoparticles synthesized by wet route have exhibited noticeably different biological effects compared to those prepared by the thermal route. In vivo, adverse effects are mainly reported in acute exposure, while no significant signs of

toxicity are noted in chronically dosed animals (review from 2010 to 2016 in Murugados et al. 2017). The no-observed-adverse-effect levels have been found around 2,000 mg silica /kg and no target organ has been identified in laboratory specimens of either sex for two colloidal silica dispersions with mean particle size 20 nm and 100 nm (Kim et al. 2014). Laboratory specimens exposed to ultrafine colloidal silica particles (14 nm) or fine colloidal silica particles (230 nm) showed some pulmonary lesions, but the severity and incidence of these lesions were reduced after a 3-month recovery period (Kaewamatawong et al. 2005). Exposure of laboratory specimens to silica vapour of a commercial colloidal silica (Ludox) at different concentrations revealed pulmonary inflammation at higher concentration (50 and 150 mg/m³), but in most cases return to normal conditions following a 3-month post-exposure period was observed (Lee and Kelly 1992; Warheit et al. 1999). Ludox deposits have cleared rapidly from the lungs with half time approximately between 40 and 50 days for specimens exposed to 50 and 150 mg/m³. 10 mg/m³ of Ludox was found to be a no-effect concentration; the alterations were not significant in any measured parameters at any time after exposure.

The toxicity of alkoxysilanes is related to their volatility. The lethal concentration LC₅₀ for 4-h TEOS exposure is found greater than 1000 ppm and that the kidney and nasal mucosa are the target organs for TEOS inhalation (Nakashima et al. 1994, 1998). No effects were seen in animals exposed to 1, 5, and 10 ppm tetramethoxysilane (TMOS). Nevertheless, TMOS can cause severe ulceration, inflammation, and necrosis of epithelium at high concentrations (e.g. at 45 ppm) (Kolesar et al. 1989). Special care must be taken to avoid prolonged exposure to volatile alkoxysilanes in general.

Alkali metal silicates, alkoxysilanes and colloidal silica dispersions offer a wide range of possibilities for wood treatments: alkaline to acidic impregnation products, monomeric- or oligomeric solutions to nanoparticle dispersions.

Impregnation of wood with silicate formulations

Water glass-based formulations

Water glasses with different modules are commercially available and have been used for wood impregnation. The module and concentration define the pH, density, viscosity, and sizes of dissolved silicate particles in the solution. The pH range is generally between 10 and 13; below this range water glass systems gel by polycondensation of silicate species in solutions.

Impregnation

The particle sizes of chemical species in water glasses (monomer and small oligomers silicates) are normally sufficiently small to ensure the penetration into wood by any conventional impregnation route. Wood has shown a great affinity with silicates in water and is able to attract and fix these species from an aqueous solution. Silicification

is the most important process in the natural petrification of wood (Ballhaus et al. 2012; Dietrich et al. 2013). When a piece of wood is placed in an aqueous environment containing dissolved silicate species, the wood accumulates progressively these compounds by diffusion–advection processes through the pores. The silicate transport is triggered by a pH gradient established between the wood (pH 4–5) and the silicate solutions (pH 9–10). The silicate species are fixed within the wood via hydrogen bonds with the polysaccharides of the cell walls and progressively precipitated in the form of a porous silica gel at early stages of the process (Ballhaus et al. 2012; Dietrich et al. 2013). Artificial silicification of wood was successfully achieved by dipping wood in a water glass in the laboratory scale as well as by storing wood in a silicate-rich natural river water. Wood specimens placed in a hot spring water lake were silicified to nearly 40% by weight over a period of 7 years by the deposition of amorphous silica spheres in cell lumina of wood tissue (Akahane et al. 2004). Commercial water glasses have been used for wood impregnation. The diffusion-penetration ability of silicate compounds in wood has been reported by Furuno et al. (1993) and Furuno and Imamura (1998), who showed that wood samples with relatively high silicate contents can be obtained using a two-step process involving a pre-saturation of wood with water and further soaking of water-saturated specimens in a water glass solution. Simple dipping or soaking also works as reported in Slimak et al. (2000), Slimak and Slimak (2004), Slimak and Slimak (2007). However, vacuum and pressure methods, when well combined, allow reducing the impregnation time. Vacuum is used to remove air filling wood lumens and pores before the introduction of the impregnation solution; afterwards pressure is applied to force the chemicals into wood (Li et al. 2020; Zhou et al. 2020). Wood pre-treatments with electron beams (100–300 KiloGrays(KGy)) are reported to significantly enhance the penetration of water glass inside the wood (Son et al. 2012).

The amount of chemicals introduced in a wood specimen expressed as weight per cent gain WPG (%) of the specimen (or retention rate in kg/m^3) can be relatively high (Furuno and Imamura 1998; Li et al. 2020; Peng et al. 2010; Pereyra and Giudice 2009). WPGs up to approx. 50% is reported in some studies (Li et al. 2020; Zhou et al. 2020). The penetration of silicates into wood can reach the full-thickness (the heart of the wood pieces), as reported by Pereyra and Giudice (2009).

The in-depth impregnation treatments of wood with water glasses result mainly in the deposition of silicate compounds at the surface of the cell walls, in lumens and pores. The inorganic compounds fill the wood lumens and pits without infiltrating the cell walls as observed by scanning electron microscopy and energy-dispersive X-ray analyses in many studies (Chen 2009; Garskaite et al. 2019; Nguyen et al. 2019). It is also well accepted in natural petrification that wood silicification occurs initially by a void-filling mechanism, the so-called permineralization, in which exposed wood surfaces serve as a template for silica deposition (Ballhaus et al. 2012; Dietrich et al. 2013; Sigleo 1979).

Curing

Natural silicification is a long process starting from the formation of a porous silica gel in wood known as opal. In nature, it is silicic acid that enters the wood and

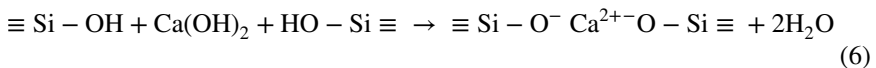
because of the relatively low pH (<9) and low solubility of silica in this pH domain, amorphous silica precipitates easily in wood. Silica deposit matures to more stable crystalline forms such as chalcedony, moganite, or α -quartz supported by a continuous supply of silicate species, hydrothermal conditions, and modification of wood cell wall components (Dietrich et al. 2013). In the laboratory experiments, water glasses are more alkaline, and the acidity of wood is not sufficient enough to provide conditions for gelation of silicates and the formation of a protective layer resistant to water. Silicates introduced must be cured by an external route.

Three routes have been applied to cure silicates in impregnated wood: (i) heat treatment, (ii) reaction with an inorganic acid or an organic acid and (iii) reaction with polyvalent metal cations. The heat curing is utilized to increase the dehydration state of the silicates layer above limits being achieved by drying at ambient temperature. Slimak et al. (2000) developed a particular process in which a heat treatment is applied to completely wet, partially or totally dry wood treated with sodium water glasses. The silicate-treated wood was hot-pressed between plates and baked at temperatures up to 260 °C or microwaved. Silicate products quite insoluble throughout wood were claimed by these authors after impregnation and a sequential curing procedure including thoroughly drying of treated wood, then dipping in water for 5 min and heating at 260 °C for 2.5 min, or air-drying for 24 h and microwave treatment for 5 min.

Polymerization of silicate species occurs through acidification. Water glasses are alkaline solutions (pH > 10); this alkalinity is reduced by the acidity of wood in the first step towards the polycondensation process, but an additional acid treatment is required to produce insoluble silica. Inorganic or organic acids, strong as well as weak acids have been investigated in the field. Inorganic acids are phosphoric acid (Chen 2009; Giudice and Pereyra 2007; Pereyra and Giudice, 2009), sodium bicarbonate (Thougaard and Hayden 2014) or boric acid (Furuno et al. 1992), while organic acids are citric acid, malic acid, acetic acid or p-toluenesulfonic acid (Hellberg and Öhrn 2012). A second impregnation treatment with the acid curing solution is generally carried out following the impregnation of wood with the water glass (Furuno et al. 1992; Giudice and Pereyra 2007). However, the wood treatment can also be performed in a single impregnation procedure using an acidified silicate formulation. A silicic acid solution resulting from acidification of an aqueous sodium silicate solution with a cation-exchange resin was explored for wood impregnation (Yamaguchi 2002). As previously mentioned, this method is one of the processes used for the preparation of colloidal silica and the impregnating mixtures applied by the author are probably closer to silica dispersions than to the common water glass. Curing under carbon dioxide atmosphere has also been reported. Wood treated with sodium water glass was stored for weeks in a carbon dioxide atmosphere (Pfeffer et al. 2012). Carbon dioxide in water forms with a water molecule carbonic acid (H_2CO_3) which neutralizes the alkalinity of water glass causing the polymerization of silicate species to silica. In a study of silica precipitation, Gorrepati et al. (2010) revealed that precipitation proceeds through two distinct steps. First, the monomeric form of silica is quickly depleted from solution as it polymerizes to form primary particles of about 5 nm in diameter. Secondly, the primary particles formed then flocculate. The authors also showed that adding metal salts

to the solutions accelerated both particle formation and growth rates in the order: $\text{AlCl}_3 > \text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl} > \text{CsCl} > \text{no salt}$.

Multivalent metal cations react with silicate species to form metal silicates of low solubility in water. Chloride or sulphate salts of metals such as Ca^{2+} , Zn^{2+} , Cu^{2+} , Mg^{2+} , Ba^{2+} and Al^{3+} have been investigated for curing and insolubilization of silicates in wood (Furuno et al. 1991; Furuno et al. 1992; Furuno et al. 1998; Hellberg and Öhrn 2012). A multivalent metal cation in contact with the alkaline silicate solution in wood forms metal hydroxide $[\text{M}'(\text{OH})_n]$ (e.g. $\text{Ca}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$), and the latter reacts with silanol/silicates groups yielding new insoluble compounds through silicate-metal Si–O–M' bonds. An example of metal silicate bonds is shown in Eq. 6; a bridging calcium ion is in the interlayer between two silicate chains.



The preparation of calcium silicate hydrates from mixtures of various sources of calcium and silica including sodium silicates has been widely studied and successfully achieved in the field of cement and inorganic binders (Zhu et al. 2016; Wang et al. 2019). The synthesis of polyaluminium silicate sulphate binders by the reaction of aluminium sulphate with sodium silicate solutions acidified at various pH for wood fibres boards was reported (Chen et al. 2015). Aluminium ions (Al^{3+}) give rise to various ionic species ($\text{Al}(\text{OH})_4^-$; $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^+$ or $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$) in aqueous solutions, which results in an increase in its solubility both in acidic and alkaline pH range and the reaction with silanol groups to form hydroxyaluminium silicates (Beardmore et al. 2016; Chen et al. 2015; Gabelich et al. 2005; Gayer et al. 1958; Savenko and Savenko 2011). Aluminium ion has appeared to provide an accelerating effect on the growth of polysilicic acid particles and on the rate of decrease in the concentration of monosilicic acid due to the formation of aluminium hydroxide on the surface of polysilicic acid (Yokoyama et al. 1989). The presence of sodium ion Na^+ or potassium ion K^+ in a relatively high amount significantly influences the formation of multivalent metal silicates. It was found in preparation of calcium silicate that high concentration of the sodium ion in the reaction mixture increases the amount of sodium ions combined in the interlayer and reduces the polymerization of the divalent metal silicate (Zhu et al. 2016).

It is possible to combine the curing methods to produce silicate-treated wood in a single or multi-step impregnation procedure. Acid curing and heating, acid treatment and reaction with polyvalent cations, and even a combination of the three have been used to produce metal silicates in wood (Canosa et al. 2011; Giudice and Pereyra 2007; Hellberg and Öhrn, 2012; Pereyra and Giudice 2009; Thougard and Hayden 2014). A process comprising impregnation of wood with sodium bicarbonate solution and further impregnation with sodium silicate solutions at a temperature between (20–100) °C followed by optional drying at a temperature of at least 70 °C was claimed by Thougard and Hayden (2014). Water glass-based single products for wood impregnation containing an alkali metal silicate, an insolubilizing agent (a mineral or organic acid) and polyvalent metal cations can be formulated and designed in such a manner that the mixture is close to gelling but convenient enough to avoid gelling before the impregnation for a long shelf pot life (Hellberg

and Öhrn 2012; Hicks 1984). Hellberg and Öhrn (2012) recommended further drying at a temperature between 20 °C and 100 °C and heat-curing at a temperature between 60 °C and 150 °C.

A two-step treatment comprising impregnation of wood with a sodium silicate solution and further treatment of the impregnated wood samples by vapour deposition of a thin molecular layer coating of silicon monoxide has also been proposed (Slimak and Slimak 2004, 2007). The combined application of sodium silicate and silicon monoxide was found to provide a product that was moisture-resistant and potentially effective for internal and external uses.

Alkoxysilane formulations

Alkoxysilane formulations are precursors of silica nanoparticles and silsesquioxanes in wood. They can be applied to wood at various stages corresponding to different mean particle sizes of the impregnation mixtures and viscosity: (i) formulations with very low advancement of hydrolysis and condensation, (ii) after a level of advancement of the polymerization reactions or (iii) at almost complete hydrolysis and condensation (colloidal silica). The impregnation of wood with low molecular unpolymerized silanes is not demanding and comparable to the application of water glasses. However, the advancement of polycondensation reaction produces more viscous and complex mixtures with particles of high dimensions more difficult to penetrate the wood. The impregnation of wood with monomeric silane solutions leads to relatively higher WPGs than impregnation with pre-hydrolyzed oligomeric silanes (Donath et al. 2004). Size and reactivity of the particle species are key factors for efficient impregnation of wood, as shown by Unger et al. (2013) with a TEOS-sol. These authors proposed that sol-gel synthesis has to be performed in such a way that the particles remain very small (< 2 nm) and reactive, for the completion of the sol-gel process in wood. The reactions in wood result in additional reactions between silanol groups and hydroxyl groups of the wood cell wall components (Bücker et al. 2014). The impregnation of highly polymerized sols will be presented in the next section devoted to colloidal silica (silica sols). It should be noticed that additional curing treatment is not required for silanes and alkoxysilanes; water in wood is enough for the completion of the polymerization reaction. Heating can be applied to accelerate the hydrolysis and condensation and drying of the treated wood. After completion of the reaction, tetraalkoxysilanes generate within the wood silica particles while organosilanes produce organic–inorganic hybrid silicon particles.

The impregnation of wood with alkylalkoxysilanes results in a notable bulking effect of wood specimens attributed to the penetration of the silanes in the wood cell walls. This effect is more important when wood is treated with non-pre-hydrolyzed silanes (Donath et al. 2004; Broda et al. 2020). It is important to mention that alkoxysilane formulations are often solvent-based systems containing a high amount of organic solvents (e.g. ethanol) owing to the low solubility of the silanes in water. The organic solvents contribute to the swelling of wood and the penetration of silanes in the cell walls.

Colloidal silica

Colloidal silica dispersions are available in a wide range of particle sizes and pH. They also differ by the nature of counterion. Commercial products containing colloidal silica include Ludox (Grace), Levasil (Bayer), Betol (Wöllner GmbH), Nyacol/Benzil (Eka chemicals-Akzo Nobel) Köstrosol (Chemiewerke Bad Kos-tritz), Sicadol (Nippon Chemical Industrial) or Sebosil (Kallies Feinchemie AG). Colloidal silica products are also commercially distributed in the form of powder as Aerosil (Evonik). The primary difference between colloidal silica and silicate solutions—“water glasses” or low molecular weight silanes described previously—is the size of the particles, which are higher in colloidal silica (usually few nanometers up to 100 nm). However, wood contains a pore size distribution with macropores and mesopores of sufficiently high sizes to allow penetration of nanoparticles. Indeed, four pore size classes could be distinguished in wood: macropores (radius (58–2) μm and (2–0.5) μm), mesopores ((500–80) nm), and micropores ((80–1.8) nm) (Plötze and Niemz 2011). Nanotechnology is gaining importance in the field of wood preservation and protection, and several types of nanoparticles (metal, metal oxide, or inorganic–organic hybrid) and particles with relatively high sizes such as micronized copper have been applied to wood (Akhtari and Nicholas 2013; Borges et al. 2018; Civardi et al. 2016; Matsunaga et al. 2009). Nanoparticles can be introduced in wood by using all the common methods, i.e. coating methods, dipping, soaking or vacuum-pressure techniques. Silica nanosols are among the most studied systems. The uptake of nanoparticles from sol is dependent on the impregnation method and time (dipping, vacuum-pressure), solid content of the nanosols and type of wood (Mahltig et al. 2008). A low-density wood is prone to take up more nanosilica than a denser wood, and sols of high solid content lead to higher WPG values. There is no relation between particle sizes and WPG, but the pH (acidic, neutral or alkaline) seems to have an influence on the product uptake (Jiang et al. 2018; Pries and Mai 2013a). It is assumed that the acidic sols are compatible with the acidic pH of wood. Acidic sols do not considerably change their pH in contact with wood and penetrate the fine pore system without aggregation-precipitation leading to better WPGs. Whereas for neutral or weakly alkaline sols (pH 7–9), the particles could undergo aggregation at the surface of wood due to neutralization of the sol by the wood acidity blocking the penetration pathways for capillary uptake. A sol with a pH high enough (e.g. pH = 11) and low particle sizes can give good WPG (Jiang et al. 2018).

By using vacuum-pressure impregnation, significant WPGs (up to (30–35) %) can be obtained (Jiang et al. 2018; Mahltig et al. 2008; Palanti et al. 2017; Pries and Mai, 2013a and 2013b; Xu et al. 2020). By applying several cycles of impregnation-drying, it is possible to increase the WPG of impregnated wood as reported by Locs et al. (2008) who obtained with a TEOS sol a WPG up to 56%.

The depth of penetration of colloidal silica in wood has also been studied. A penetration depth of 3.5 mm could be reached with colloidal silica via cross-section impregnation of wood by dipping (immersion) (Rosenthal and Bues 2010). Important depths of penetration (more than 4.5 mm) were reported for vacuum-pressure

as well as for dipping impregnation (Mahltig et al. 2008). The major differences between the impregnation methods are WPG and the concentration of particles at each depth that are quite low when the dipping method is used.

Nanosilica treated wood shows in general a low-bulking effect or even a slightly negative one related to the inability of nanoparticles to penetrate the wood cell walls (Jiang et al. 2018; Pries and Mai 2013a; Unger et al. 2013). Organosilane-based sols tend to increase the bulking effect. Bulking rates of 0.7% for TEOS-sol treated and 7.1% for PTEO-treated wood were reported for example (Donath et al. 2004).

Resistance to leaching

Leaching of water glass-based products

A wood protection product should be resistant to leaching by water for long-term efficacy. Leaching of wood treated with water glass has been studied in the literature using standard and non-standard procedures. Wood treated with sodium metasilicate solution, dried at 103 °C for 24 h, and exposed to leaching according to EN 84 (1997) showed minimal water resistance; the silicate compounds were even completely leached in some specimens (Hautamäki et al. 2020). Drying at relatively low temperatures below 100 °C has also appeared in other studies to be less suitable for insolubilization of silica (Giudice and Pereyra 2007). High-temperature treatments were claimed in some patents as being able to reduce the leaching of silicates, but the experimental data concerning leaching tests were not presented (Slimak et al. 2000; Thouggaard and Hayden 2014). The alkalinity and the presence of alkali metal ions (e.g. sodium ions) are factors promoting the solubilization of amorphous silica. Under high pH conditions, the rate of Si–O–Si cleavage and redissolution is catalyzed by hydroxyl groups (OH⁻) and alkali metal ions (Crundwell 2017; Schubert 2015). In a solubility study of amorphous silica, solutions containing sodium ions showed a significant increase in the proportions of monomeric silicic acid compared to equivalent sodium-free ones. Sodium ions attract water shells, which initiate the separation of monomeric silicic acid from polymeric silica groups. Sodium ion also tends to surround silicate species preventing them from polymerization (Lunevich 2019). Silicate layers cured only by heat treatment would more probably be of low stability because the product remains alkaline and contains alkali metal ions that could act as a catalyst for solubilization of silica upon contact with water.

Curing of water glass-impregnated wood with polyvalent metal salts (aluminium chloride, calcium chloride and barium chloride) also appears to be not efficient in insolubilization of silica. In a leaching study of silicate-treated wood cured with polyvalent metal ions using Japan Industry-standard leaching procedure JIS A 9201 (1991), a decrease in WPGs by (97–99) % with respect to the initial WPGs was reported (Furuno and Imamura 1998). In contrast, silicate-treated wood samples cured with acetic acid or with boric acid resisted better to leaching in the same study, WPGs were decreased only by (32–35) %. Similar results were reported by Chen (2009) regarding wood treated with a sodium water glass followed by curing with a phosphoric acid solution. Leaching experiments performed according to

the ASTM D1413-99 (1999) caused weight losses of approximately one-third of the chemicals introduced, which can be attributed to leaching of by-products and wood extractives. Normally, in addition to silica particles formed in wood during curing of wood treated with water glass, by-products made of sodium ion (potassium ion) of the water glass and counterion of the curing agent are formed in wood (e.g. NaCl, Na₃PO₄, NaCH₃COO). These by-products are not incorporated in silica structure and are dissolved and removed during leaching. Water-soluble extractives of wood also contribute obviously to the leached products. A combination of acid curing and polyvalent cations curing has been used to produce leaching-resistant treatments (Altun et al. 2010; Pereyra and Giudice 2009). It emerges from the whole literature that curing is efficient for insolubilization of the silicates in wood when an acid treatment is involved. Acid treatment increases the pH in the wood and induces the polymerization of silicate species to form amorphous silica less soluble in water.

Sodium hexafluorosilicate (Na₂SiF₆) is also recognized for curing water glass (sodium), as shown by Zhou et al. (2020), who applied an additional impregnation with Na₂SiF₆ to reduce leaching and reduce water absorption of the water glass-treated wood.

Water glasses can be used to prevent the leaching of biocidal compounds such as boron or copper from wood. Even non-acid and non-polyvalent cation-based boron compounds such as borax, potassium borate or ammonium borate, form with water glass, silicate compounds more resistant to water (Furuno et al. 1993; Furuno and Imamura 1998). The utilization of the water glass-boron systems yields treated wood with improved dimensional stability and lower hygroscopicity (Furuno and Imamura 1998).

Leaching of alkoxysilane-based products and colloidal silica

Colloidal silica-treated wood exhibits generally low weight losses through leaching due to the low solubility of silica particles in water and a low amount of by-products (Götze et al. 2008; Pries and Mai 2013a, b; Yamaguchi 2002). Weight losses around (1–2) % are achieved (Pries and Mai 2013b). The treatment of wood with colloidal silica does not impart considerable water repellency and dimensional stability to wood, because of the hygroscopic characteristic of silica (Pries and Mai 2013b; Temiz et al 2006). A decrease in water uptake is reported in few cases depending probably on the nature of the impregnated silica; an example is the treatment with a cationic silica sol (Pries and Mai 2013a). An increase in the water contact angle was obtained by Xu et al. (2020).

Wood treated with alkoxysilanes is generally resistant to leaching because condensation polymerization gives directly insoluble compounds in wood. In addition, most silanes used are hydrophobic and then resistant to water. The water repellency of wood treated with alkoxysilane-containing formulations is initially overestimated due to non-hydrolyzed organic alkoxy-groups remaining in the silica-siloxane layers. A decrease in this property is noticed with ageing because the progression of the hydrolysis to completion replaced non-hydrolyzed hydrophobic alkoxy groups by hydrophilic silanol groups (Donath et al. 2004, 2006, 2007). Wood treated with

TEOS-based sols displays almost the same features after complete hydrolysis as wood impregnated with water glass and cured with an acid solution regarding leaching and water uptake. Water-repellent properties are reached more effectively by the addition of highly hydrophobic silanes such as 2-heptadecafluoro-octylethyltrimethoxysilane (HFOETMOS) or decyltrimethoxysilane (Saka and Uneo 1997; Saka and Tanno 1996). Functional silanes can be used to fix leachable biocides in wood. Silica xerogels containing amine functional groups prepared from TEOS/APTES mixtures were used for copper (Hao et al. 2021; Palanti et al. 2010, and 2012a; Vignali et al. 2011) and boron (Palanti et al. 2012b) in wood. The amine functions of APTES anchor both copper and boron through coordinative and ionic interactions preventing them from leaching (Palanti et al. 2017). The leaching of antifungal salicylic acid from wood was reduced by coating salicylic acid microcapsules with silica using a sol-gel of TEOS before impregnation (Yan et al. 2021).

Impact on physical and mechanical properties

Impact on physical properties

Wood modification with silicate-based formulations increases, in general, the density of wood, especially at high WPGs. The increase in the density of the treated wood up to (40–60) % compared with untreated wood was reported in some studies (Li et al. 2020; Zhou et al. 2020). The influence of the treatment on the dimensional stability of wood varies with the ability of the chemicals to enter the wood cell walls and the water-repellent effect conferred by the modification. Wood treatment with water glass can cause shrinkage of the treated wood due to alkaline dissolution of wood components as reported by Liu et al. (2021). This effect is moderated when using for the impregnation water glass with high module and diluted (low mass concentration), or other low alkaline formulations (e.g. alkoxy silanes formulations, modified water glass formulations). Wood dimensional stability determined by the anti-swelling efficiency (ASE) is increased by treatments involving bulking of wood such as impregnation with low-molecular weight silanes (Donath et al. 2004, 2006), or impregnation with a melamine-urea-glycose (MUG)-sodium silicate (Liu et al. 2021). The reduction in moisture uptake decreases the swelling and shrinkage of the wood. The best stabilizers for wood are chemical compounds able to penetrate the cell walls and containing functional groups able to form stable coatings at the surface of the wood cell walls through strong chemical interactions with wood components, and imparting hydrophobicity to the treated wood (Broda et al. 2020; Donath et al. 2004, 2006; Liu et al. 2021).

The water glass-based impregnations cause only slight colour change of wood keeping the wood surface features still visible as can be seen in pictures shown by Neyses et al. (2017) and Pfeffer et al. (2012). The treatment can provoke darkening when the alkalinity of the impregnation products increases (Neyses et al. 2017). The alkoxy silane-based formulations and colloidal silica products have also little effect on the colour and appearance of wood. The weathering studies have shown that the silica-siloxane modifications fail in the protection of wood against natural

photodegradation in the long term. The treatments with water glass-based products or nanosilica delay the colour changes of the wood surface compared with the untreated samples, but finally, the surface turns grey (Donath et al. 2007; Pfeffer et al. 2012; Temiz et al. 2006). Fourier transform infrared analysis of the wood surface shows mainly the reduction in bands associated with lignin degradation (Pfeffer et al. 2012). Water glass-based products can even accelerate the greying of wood. A potassium silicate formulation mimicking the natural ageing process of wood and accelerating the formation of silver-grey appearance on the wood surface is even commercialized by Sioo:x, Göteborg (Sioo wood protection AB 2021).

The addition of UV-light stabilizers significantly enhances the effectiveness of the protection and leads to higher colour stability during weathering (Donath et al. 2007). Colloidal silica dispersions and organoalkoxysilane-based sols treatments do not provide any reduction in crack formation during exposure to weathering (Donath et al. 2007). Water glass can slightly change the acoustic characteristics of wood decreasing the acoustic constant and speed of sound in wood leading to a different effect (attenuation or amplification) of low and high frequencies (Daníhelová et al. 2015).

Impact on mechanical properties

Water glass-based impregnation products with appropriate module and concentration have no detrimental effect on mechanical properties of wood. The formulations with high module and low concentration must be used to reduce the alkalinity and the impact on the wood components. When such conditions are fulfilled, the treatment induces improvement in mechanical strengths (flexural/bending and compressive), surface hardness and the elastic modulus of wood, and this effect grows with WPG and is substantial at high WPG values. The increase in bending and compressive strengths of treated wood to nearly twice the values of untreated wood is observed at WPGs around 50% (Li et al. 2020; Peng et al. 2010; Zhou et al. 2020). The Young's modulus is usually not highly affected by the modification, but the addition of cellulose nanofibrils at a ratio (1–2) % in water glass has increased considerably the values (Peng et al. 2010). An increase in the surface hardness of wood after treatment is also reported (Garskaite et al. 2019; Li et al. 2020). Similar increases in the modulus of elasticity, bending and compression strengths (longitudinal direction and radial direction), surface hardness, tensile strength (parallel to grain) and shear strength (parallel to grain) were achieved for wood treatment with nanosilica and silica-organic polymers (Chen et al. 2020; Nguyen et al. 2019; Xu et al. 2020). The results can be explained by the filling effect of wood cell lumina with silica compounds; wood becomes denser and more compact, and therefore more resistant and stiffer.

Water glass reduces the mechanical properties of wood only when the treatment is performed with strong alkaline solutions, which are solutions with low modules (e.g. sodium metasilicate solution). The strength loss reported in a previous review by Mai and Militz (2004a) concerns mainly such silicate systems. A high pH of the impregnation products (pH around 12–13) causes rather degradation-solubilization

of wood components and leads to a reduction in the mechanical performances. This explains the reduction in bending strength reported by a few authors (Borůvka et al. 2016; Furuno et al. 1992; Saka and Ueno 1997). An increase in the curing temperature exacerbates the impact of these solutions on wood; the strength of the treated wood could remain unchanged or even slightly increased after air drying (25 °C) while a high-temperature drying (103 °C) causes a significant strength reduction (Saka and Ueno 1997). High pH and temperatures promote the hydrolysis of the cell wall components.

Alkoxysilane-based products also increase the mechanical properties of wood as previously reported with water glasses or nanosilica. The flexural strength of wood modified with various alkoxysilanes and mixtures of alkoxysilanes was higher than that of untreated wood, while the elastic modulus was slightly modified (Hung et al. 2019). The mechanical characterization of treated wood was extended further to creep behaviour. Creep test measures the strain of a material specimen subjected to constant stress at a constant temperature, and informs on the long-term performances (deformation, stiffness) of the material, particularly of structural elements. The creep resistance of wood was improved with MTMS and TEOS sols compared to untreated wood. The best reduction in time-dependent modulus was obtained with wood treated with MTMS (26% after 50 years) (Hung et al. 2019). Wood treated with a formulation containing propolis extract, 3-(trimethoxysilyl)propyl methacrylate and TEOS showed an increase in bending strength and work to maximum load and exhibited higher creep compliance than unmodified wood (Woźniak et al. 2021).

Resistance to biodegradation

A preservative agent can act as (i) a biocide poisoning wood, (ii) a barrier layer at the surface of wood or (iii) an hydrophobizing agent reducing the moisture content of the wood. Silica gel has a desiccant effect that has been long exploited industrially for the protection of goods against moisture. Silica gel has a strong affinity for water molecules and can absorb relatively high amount of moisture without any significant swelling. Studies have reported the efficiency of cured silicates to protect wood against different fungi and termites even though the treated wood exhibits in most cases no considerable modification of their hydrophilic/hydrophobic property or even higher hydrophilicity compared with the untreated wood (Chen 2009; Furuno and Imamura 1998). It has been found that for water glass-treated wood, the inhibition of fungal growth is not influenced by the reduction in the moisture content of the treated wood (Chen 2009; Furuno et al. 1991, 1992; Furuno and Imamura 1998). Wood specimens treated with sodium water glass, post-cured with phosphoric acid and submitted to a standard leaching test exhibited only a 0.2% weight loss when exposed to a brown-rot fungus (*Gloeophyllum trabeum* (Pers.) Murrill), and a weight loss between 3.4 and 5.2% when exposed to a white-rot fungus (*Trametes versicolor* (L.) Lloyd). The weight loss of the control (non-treated wood) was 32.2% and 30.2% by *G. trabeum* and *T. versicolor*, respectively (Chen 2009). Wood impregnated with water glass and cured

metal salts or acetic acid subjected to the attack of a virulent subterranean termite *Coptotermes formosanus* (Shiraki), a brown-rot fungus, *Tyromyces palustris* (Berk. & M.A. Curtis) Murrill and a white-rot fungus, *Coriulus versicolor* (L. ex Fr.) showed globally positive activities against the degradation agents causing mortalities of termites (workers and soldiers) (Furuno and Imamura 1998). The resistance to fungi was especially observed for treated wood cured with an acid (e.g. acetic acid). The efficiency of the treatments with polyvalent metal cations was difficult to determine in the studies because of their high leachability. Wood treated with colloidal silica or with TEOS-based sols are comparable to wood treated with a water glass and post-cured with an acid solution regarding the bioactivity against fungi and termites. Indeed, all these treatments result in the deposition of silica in the wood structure.

The alkalinity or acidity of the silicate compounds within the wood could contribute in some ways to the protection of wood against biodegradation agents. The hypothesis of alkalinity was advanced in many works since highly alkaline media are known to be able to influence spore germination and mycelia growth (Abubakar et al. 2013; Furuno et al. 1992; Pfeffer et al. 2011). The protection of wood impregnated with water glass and cured with an acid compound which logically neutralises the alkalinity of water glass and leads to the formation of acidic polysilicic compounds is also reported (Furuno and Imamura 1998).

However, it is likely that silicon compounds in wood act as a protective layer/barrier at the wood cell wall reducing the access to wood components for fungi and termites. For instance, different silica sols (alkaline and acidic sols) have imparted some protection to wood against fungi without really exhibiting an intrinsic biocidal effect in culture media as observed by Pries and Mai (2013a). A relevant biocidal effect was noticed only for a cationic sol product. Addition of 2% cationic sol to a malt-agar growth medium caused growth inhibition of between 40 and 50% of the wood decay fungi *Coniophora puteana* (Schumach.) P. Karst and *Trametes versicolor* (L.) Lloyd while the other colloidal silica (alkaline) had not significant bioactivity (Pries and Mai 2013a). The ability of colloidal silica with low intrinsic activity against degradation agents to protect wood to a certain extent can be attributed to the barrier effect and maybe also due to a local depletion of moisture in organic matter by silica.

Addition of other bioactive compounds such as boron-compounds was exploited to increase the protection. Boric acid is the most interesting compound for this purpose. Boric acid acts jointly as an acid curing agent and a biocide, and the formed silica prevents boric acid from leaching (Altun et al. 2010; Palanti and Feci 2013; Yamaguchi 2003). Wood treated with formulations containing water glass (sodium silicate) and a boron compound (boric acid, borax, ammonium borax) showed better termite resistances with negligible weight losses of the specimens and high mortalities of workers and soldiers (Furuno and Imamura 1998; Yamaguchi 2003). Water glass-boron systems were also found to significantly enhance the decay resistance. The incorporation of boron in the insoluble inorganic substances contributes much to the enhancement of biological resistance. Silicic acid-boric acid treated wood has shown very high resistance to leaching and resistance to biodegradation to such an extent that it could be recommended for outdoor applications. Wood treated with a

silicic acid-boric formulation and exposed to termite attack in a field test showed no damage after three years of exposure (Yamaguchi 2003).

Addition of multivalent metal cations (FeCl_2 , ZnCl_2 , CoCl_2 , CuCl_2) has also improved the resistance of treated wood to fungi (brown-rot fungus *Fomitopsis palustris* (Berk. & M.A. Curtis) (Yamaguchi 2002).

The organo-alkoxysilanes compounds such as methyltrimethoxysilane (MTMS), propyltriethoxysilane (PTEO) and isobutyl-triethoxysilane (IBTEO) contribute to further increase in resistance to biodegradation by raising the hydrophobicity and anti-swelling efficiency of the treated wood (Donath et al. 2004, 2006; Saka and Ueno 1997). The functional silanes (e.g. APTES) can be used to fix biocidal agents such as copper and boron in wood for an efficient resistance to leaching and long-term protection (Hao et al. 2021; Palanti et al. 2011, 2012b, 2017; Vignali et al. 2011).

Temiz et al. (2006) found, by comparing the behaviour of silica-treated wood samples in laboratory test and above-ground field test, that only laboratory test is not enough for evaluation of the durability of modified wood. Silica-treated wood showed in above-ground test (standard lap-joint test ENV 12,037:1996) significantly better performances against fungal discolouration than control and the efficacy was comparable to that of CCA impregnated controls. Silica-treated wood can be viewed as a permanent reactive system particularly in the exterior where it is exposed to moisture, carbon dioxide and soil minerals. The elements could induce various modifications of the silica layer consolidating the efficacy of the protection during weathering including a restructuring of amorphous silica and recrystallization to more stable quartz-like layer as reported for natural silicification of wood (Akahane et al. 2004; Mustoe 2017; Trümper et al. 2018).

Fire retardancy

One of the primary objectives of the treatment of wood with silicate-based products is the improvement of its fire resistance. Fire-retardant compounds are added to flammable materials such as wood and plastics to modulate and minimise some aspects of their fire behaviour including ignitability, flame spread, burning droplets or smoke production and toxicity. They are particularly useful at the early stages crucial for the safe evacuation of a burning building.

The flame-retardant compounds intervene in a combustion process through various mechanisms: (i) change of the pathway of pyrolysis, (ii) formation of an insulating protective layer at the surface, (iii) change of the thermal properties of the material (e.g. wood), or (iv) dilution of the pyrolysis gases (Brown 1998; Popescu and Pfriem 2020). Flame retardants act in the condensed phase by forming an inorganic glass layer or enhancing the formation of a char layer at the surface in contact with flame, both protecting the material beneath and reducing the supply of decomposition products potentially flammable to the burning gas phase. They can undergo endothermic decomposition reactions withdrawing locally heat from the gas phase and producing non-flammable gaseous products (e.g. water) diluting the flammable

gas. The flame-retardant particles can also absorb many volatile species and fragments contributing to the smoke reduction.

Inorganic compounds (e.g. $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, Sb_2O_3 , $\text{B}(\text{OH})_3$), inorganic–organic phosphorus and phosphorus–nitrogen are available in the market. Boric acid and borax are some examples of chemicals considered for fire protection of wood. Boric acid catalyzes the dehydration of wood components and some oxygen-eliminating reactions at relatively low temperatures (approximately (100–300) °C) and may also catalyze the isomerization of the newly formed polymeric materials to aromatic structures that promote charring and fire retardation of wood (Wang et al. 2004; Yu et al. 2017). The potential toxicity and leachability of fire retardants remain major concerns in the field of wood science inciting further research for alternatives solutions.

Fire tests used to assess the reaction to fire of the silica-treated wood include bench-scale methods such as cone calorimetry (ISO 5660–1:2015, ASTM E1354–02), and more simple methods such as limiting oxygen index (ISO 4589–1:2017, ASTM D2863-19 2019) and two-foot tunnel (ASTM D3806—19a).

Cone calorimetry is among the most suitable fire test methods providing data for prediction and modelling of fire behaviour of materials. In this technique, the oxygen concentration in the combustion gases of a test specimen subjected to an external heat flux ((10–100) kW/m^2) is measured and related to the flow gases. The fire parameters such as the heat release rate (HRR) per unit time and surface area of the specimens, maximum or peak of heat released rate curve (PHRR), time of ignition (TOI), time of combustion or extinction (TOF) and total smoke release (TSR) are deduced. The mass loss during combustion and the amount of carbon monoxide and carbon dioxide released are also recorded. This method is approved for wood specimens and a typical curve for wood exhibits an initial increase in HRR to a PHRR, following a drop to a steady state, and a second peak as the final portion of the specimen is consumed (White and Dietenberger 2004). The two-foot tunnel determines some aspects of fire behaviour such as flame spread index (FSI), panel consumption (PC), after-flaming time (AFT), and after-glow time (AGT). LOI measures the minimum concentration of oxygen in a mixture of oxygen and nitrogen that is needed to support the flaming combustion of a material (White 1979). Materials with LOI values less than 21% are classified as combustible, while those with LOI greater than this value are classed as self-extinguishing since their combustion cannot be sustained at ambient temperature without an external energy.

Silicate-based compounds are effective flame retardants for wood given that they are able to increase TOF and decrease the FSI, PC, and total amount of smoke produced. The early works on the treatment of wood with silicate systems showed that water glass applied to the wood surface increased the fire resistance of wood by melting and forming an insulating foam layer on the surface. However, the efficiency of the treatment was of short duration because of the neutralization of the silicate in contact with air, which resulted in a reduction in the foaming capacity and detachment of the coating from the surface (Metz 1942 as cited in Pries and Mai 2013b). The same phenomenon was reported by Slimak et al. (2000): wood treated with sodium silicate foams when exposed to fire and insoluble silica particles are formed. When (sodium) water glass is not properly cured, an important amount of

water remains in the system in the form of bound and free water, and is responsible for the foaming effect and unfortunately also for the low stability of the treatment. Wood impregnated with sodium silicate solution and thermally cured (120 °C, 24 h) has shown lower HRR, PHRR, THR, smoke production rate, and total smoke production (Li et al. 2020). The sodium silicate treated wood has good smoke suppression effects. Similar results were reported for silica treated wood (Liu et al. 2020). However, water glass-treated wood without appropriate post-curing exhibits lower thermal degradation temperatures compared to the reference untreated wood as revealed by thermogravimetric (TG) and differential thermogravimetric (DTG) analyses (Li et al. 2020; Garskaite et al. 2019). The difference in thermal behaviour between untreated and treated wood can be attributed to additional chemical reactions between wood and alkaline components of water glass. Indeed, when the alkalinity of the impregnation product is reduced as it usually is the case for treatments with silica sols, the thermal behaviour of the treated wood is comparable to that of the untreated wood (Liu et al. 2020), and even silica sol or organoalkoxisilane-based sols could enhance the resistance of wood to thermal degradation at higher temperature (Hung and Wu 2017; Jiang et al. 2018). The amount of the thermally stable and non-flammable inorganic silicate compounds in the treated wood should be considered in the data generation in the authors' opinion for a more convincing interpretation of the results and a better understanding of the thermal behaviour of the treated wood.

Wood treated with sodium, potassium or lithium silicate solutions and cured by acid treatment and/or by multivalent metal cation treatment was found to improve the fire resistance in all cases compared to untreated wood (Canosa et al. 2011; Giudice and Pereyra 2007, 2010; Pereyra and Giudice 2009).

Sodium and potassium silicate treatment showed no appreciable difference in performance. However, wood treated with water glass with higher modules exhibited better fire performance compared with the ones treated with lower module water glass. Better fire performances were also reported when treatment with water glass was followed by treatment with metal cations (Pereyra and Giudice 2009). A clear difference in the reaction to fire was observed with an increase in the efficiency following the order of polyvalent metal cations: calcium, magnesium, zinc, copper and aluminium. As stated before, multivalent metal cations react with silicate species of water glass to form metal silicate systems which have been found more effective in the fire protection of wood. The improvement of fire performances measured with these systems can also be due to the formation of metal hydroxides known for their fire-retardant properties.

Wood treated with colloidal silica also reveals in a simple flammability test a reduction in burning time, velocity of mass loss and the glowing of the formed charcoal is completely prevented (Pries and Mai 2013b). The efficiency of the treatment increases with WPG (the amount of silica introduced in the wood). Silica may have the same mechanism of action as metal oxides and performs through a physical mechanism achieved by the formation of a protective layer on the surface of the wood at high temperatures (Canosa et al. 2011; Giudice and Pereyra 2010). In a direct line with this approach, a mechanism based on physical processes in the condensed phase instead of chemical reactions was proposed by Kashiwagi et al. (2000)

to explain the flame retardancy efficacy of fumed silica or silica gel in polypropylene and polyethylene oxide. Silica accumulates near the surface of the plastic materials and acts as a thermal insulation layer. In a study of the combined effect of aluminium hydroxide and silica on the fire properties of ethylene–vinyl acetate copolymer (EVA), Sonnier et al. (2016) found that silica provides benefits when the amount and properties of the fillers allow the formation of an insulating mineral layer. Fire performances increase with silica content until a concentration of 20%. This is in line with the work of Unger et al. (2013) who proposed that a WPG > 20% is a pre-condition for efficient protection of wood with nanosols (TEOS-based nanosols). The treatment of wood with silica and silica-precursor compounds may require relatively high chemical retention, WPG values above 20% to be fully effective. The barrier effect acts for resistance to biodegradation as well as for fire retardancy.

As previously reported concerning silicate–boron systems for the protection against biodegradation, the fire-retardant properties of silica-treated wood are clearly enhanced when boron compounds (e.g. boric acid) are added (Altun et al. 2010; Yamaguchi 2003). Wood treated with boric acid-modified silica sol showed for example better improvement in fire retardancy than wood-treated with silica sols alone (Liu et al. 2020). Alkoxysilane-based formulations can also be used to retain organo-phosphorus or organo-boron compounds such as trimethylphosphite, ethylphosphite and trimethylborate within the wood to improve fire resistance and prevent leaching of the fire-retardant additives to ensure long-term treatment effectiveness (Miyafuji et al. 1998; Saka and Tanno 1996).

Conclusion

Alkali metal silicate solutions—“water glasses”, colloidal silica, and alkoxysilanes are silicon-based products commercially available for wood treatment. Water glass and colloidal silica are generally of low toxicity while alkoxysilanes can be of great concern when humans are exposed to their vapours for a relatively long time. These compounds can be introduced into wood in the form of a solution or nanoparticle dispersions with significant penetration depth, using the simple dipping or vacuum-pressure methods. Water glass-based impregnation requires specific post-curing treatments including thermal procedures and/or reaction with organic or mineral acids, sodium hexafluorosilicate, or multivalent metal cations to convert the water-soluble silicate species into water-insoluble and non-leachable polymeric particles; acid curing is emerging as the most promising method for this purpose. In contrast, only heat treatment is enough for curing of alkoxysilane-treated wood. After an appropriate combination of curing and insolubilization processes, the treatment with water glass produces modified wood with properties equivalent to those of pure inorganic colloidal silica-treated wood or fully hydrolyzed tetraalkoxysilane sol-gel-treated wood. Pure inorganic silica does not impart considerable hydrophobicity to the wood. Water resistance can be improved by the utilization of alkylalkoxysilanes and/or addition of highly hydrophobic alkoxysilanes with long-chain alkyls such as 2-heptafluoro-octylethyltrimethoxysilane, hexadecyltrimethoxysilane or decyltrimethoxysilane. Silica in wood is resistant to leaching, increases the resistance of

wood against fungi and termites, and fire resistance (reduces heat release and smoke production). Wood protection can be considerably enhanced by systems containing additional biocides (boron compounds and copper ions) and fire-retardant agents (boron and phosphorus compounds), where the silica layer performs as a support/barrier preventing the additives from leaching. Bending and compression strengths, surface hardness, and scratch resistance of silica-treated wood increase with weight percent gain (retention), while impact resistance decreases. Silica-treated wood samples exhibit improved creep resistance. All these results show the interesting potentials of these systems for the protection of wood.

Acknowledgments The authors are grateful to the Slovenian National Research Agency (ARRS) for financial support (The project “SilWoodCoat” N4-0117, and the research programme “Wood and lignocellulosic composites” P4-0015).

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