Fire Safety Journal 44 (2009) 497–503

Contents lists available at ScienceDirect

Fire Safety Journal

journal homepage: www.elsevier.com/locate/firesaf

Flame-retardant impregnants for woods based on alkaline silicates

Andrea M. Pereyra [a], Carlos A. Giudice [b],*

[a] CIDEPINT (Centro de Investigación y Desarrollo en Tecnología de Pinturas), Calle 52 e/121 y 122, 1900 La Plata, Argentina
[b] UTN (Universidad Tecnológica Nacional), Calle 60 y 124, 1900 La Plata, Argentina

ARTICLE INFO

Article history:
Received 4 May 2006
Received in revised form
15 November 2007
Accepted 16 October 2008
Available online 2 December 2008

Keywords:
Wood
Flame-retardant impregnant
Soluble alkaline silicates
Limiting oxygen chamber
Two-foot tunnel

ABSTRACT

The aim of this paper was to determine the fire performance of wood panels (*Araucaria angustifolia*) impregnated in a pressure vessel with post-cured alkaline silicates (water glasses). Several commercial silicates based on sodium ions and potassium ions with 3.0/1.0 and 3.5/1.0 silica/alkali molar ratios were selected. Various treatments for curing were applied for polymerization, creating metal silicate polymers of high water insolubility.

Experimental panels were tested in a limiting oxygen chamber (limiting oxygen index) and in a two-foot tunnel (flame-spread index and panel consumption). Test results displayed a high fire-retardant efficiency of some post-cured alkaline silicates.

1. Introduction

The use of soluble alkaline silicates is varied and it goes back many years (detergents, water purification, adhesives, zinc-rich coatings, etc.); in the field of fire retardation, the alkaline silicates were also used in the formulation of non-flammable coatings and varnishes.

To make wood flame-resistant, soluble alkaline silicates were also used with a subsequent treatment with solutions of metallic salts to produce insoluble silicates [1]; later, on the basis of the previous method, other patents were developed [2–5]. However, in all of these cases, the silicate-based treatment compositions can be leached from the wood by exposure to environmental water and moisture, which eventually causes that the treated wood loses its resistance against fire action.

In a previous unpublished paper by Giudice et al., the flame-retardant performance of a low-density wood (*Araucaria angustifolia*) impregnated with sodium silicates and potassium silicates (2.5/1.0 and 3.0/1.0 silica/alkali molar ratios) was studied. To facilitate silicate polymerization inside pores of the wood, different treatments were considered. The results indicated that heating at 90 °C for 24 h and acid treatment were insufficient to make the silicates insoluble or at least of reduced solubility. Consequently, in use the silicates can be leached by steam condensation on the surface, during continuous immersion, etc. and the desired performance against fire is not achieved. Experiments with the named alkaline silicate solutions spread on glass allowed the inference to be made that with higher silica content in their composition, the films show a higher curing rate as well as a smaller water dissolution rate.

In the present paper, the silicates used were of higher silica/alkali ratio than in the previous experiment developed by the same authors; an acid treatment was used to form, in the first stage, a silicic polymer of increased molecular weight and then, in the second stage, a treatment with cations to form a metal silicate polymers of high insolubility. For reference, the same treatments were used separately. Concerning the acid treatment, this was carried out with the dibutyl amine salt of phosphoric acid (dibutyl amine phosphate), which in contact with an alkaline medium hydrolyzes slowly to release phosphoric acid. For the other treatment, soluble salts of several metals such as aluminum, copper, zinc, magnesium and calcium were used.

2. Methods

The experimental part included (i) the selection of commercial soluble alkaline silicates and the curing methods to fulfill the polymerization of soluble alkaline silicates impregnated under pressure in low-density wood panels of *Araucaria angustifolia*, (ii) the determination of some characteristics of inorganic polymers formed by precipitation with some cations, (iii) the operative conditions of the impregnation process and finally (iv) laboratory tests to establish the behavior of the treated wood panels when exposed to fire.

---

* Corresponding author. Fax: +54 221 4271537.
E-mail address: cagiudice@yahoo.com (C.A. Giudice).

0379-7112/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.firesaf.2008.10.004

2.1. Soluble alkaline silicates and curing agents

Since impregnated soluble alkaline silicates could be leached from the interior of the wood during use, three methods for curing were used to reduce the solubility of the impregnants.

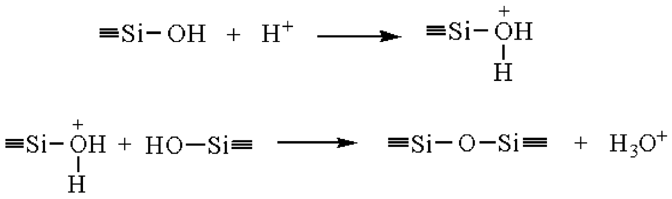
The four commercial soluble silicates used in the experiments included ones based on sodium ions and ones based on potassium ions; for each type, silicates with 3.0/1.0 and 3.5/1.0 molar ratios were used. Table 1 shows some characteristics of the colloidal alkaline solutions which were determined in laboratory tests.

In this paper, to achieve the polymerization of soluble alkaline silicates impregnated in low-density wood panels of *Araucaria angustifolia* the following methods were selected:

- *Series I. Acid treatment*: As above mentioned, the acid treatment involved the use of dibutyl amine salt of phosphoric acid (dibutyl amine phosphate).
  Soluble alkaline silicates contain some silanols and alkoxy groups; these silanols chemically react with hydrogen ions liberated from phosphoric acid protonating the oxygen of the silanol. This intermediate reacts with the silanol forming a siloxane bond, Fig. 1. When the pH of the system is very low, reaction rate is slow due to the repulsion between two positively charged groups (protonated oxygens). Consequently, the pH of the system defines the dehydration rate for forming polymeric silicic acid.
  In this experiment, a 10% dibutyl amine phosphate alcoholic solution was used for acid treatment.
- *Series II. Reaction with cations*: The silanol groups of alkaline silicates react with di- and tri-valent cations forming metal silanol heterobridge, which then react to give metal silicate polymers liberating hydrogen gas, Fig. 2.
  Solutions at 10% of aluminum, copper, zinc and magnesium sulfate (0.29, 0.63, 0.62 and 0.83 M, respectively) as well as calcium hydroxide (1.35 M) were used.
- *Series III. Acid treatment/reaction with cations*: The first stage involves the reaction of the phosphoric acid with the soluble alkaline silicates for allowing polymerization to form silicic acid of high molecular weight. The second stage includes the reaction between silicic acid and metal cations to generate a metal silicate polymer, Fig. 3. A secondary reaction is the formation of insoluble metal phosphates that would be randomly located in the structure of the glass. Table 2 shows the identification of the samples.

Table 1
Some properties of the alkaline silicate solutions at 20 °C.

Silicate type	Silica/alkali molar ratio	Density (°Be)	Viscosity (cP)	pH
SiO_2/Na_2O	3.0/1.0	24.0	12.0	11.3
SiO_2/Na_2O	3.5/1.0	25.2	12.5	11.0
SiO_2/K_2O	3.0/1.0	17.2	10.2	11.3
SiO_2/K_2O	3.5/1.0	18.3	10.7	11.1



$$\equiv Si-OH + H^+ \longrightarrow \equiv Si-\overset{+}{O}H-H$$

$$\equiv Si-\overset{+}{O}H(H) + HO-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + H_3O^+$$

Fig. 1. Formation of siloxane bond.

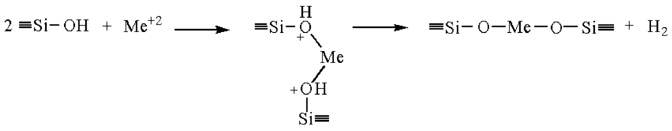


Fig. 2. Reaction to give metal silicate polymers liberating hydrogen gas.

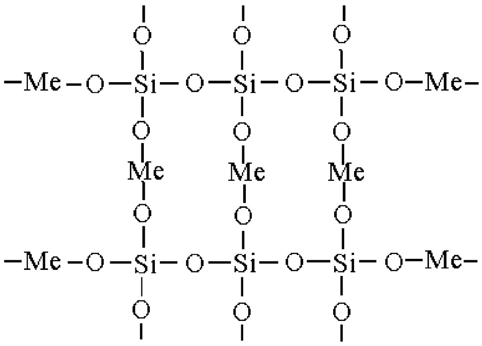


Fig. 3. Structure of metal silicate polymer.

2.2. Formation and thermal stability of metal silicate polymers

To gain an understanding of some aspects of the inorganic polymer formation, water-soluble salts of the selected metals were added to the soluble silicate solutions (aluminum, copper, zinc and magnesium as sulfate solutions; calcium as hydroxide solution); in addition, coefficients of thermal expansion were measured to estimate the stability of the impregnated wood to changes of temperature.

2.3. Operative conditions of the impregnation process

Test panels for these experiments were prepared on *A. angustifolia* since it is a porous wood, which is of low density (497 kg m^{-3}) and easily penetrable. To obtain good impregnation [6–8], the test panels were kept under laboratory conditions until the moisture content ranged from 15% to 18% [9].

The impregnations were carried out at 20 °C in a vertical pressure vessel of 25 l capacity, provided with a vacuum pump and an air compressor. In all the cases, the vessel was loaded with the test panels to be impregnated; then the pressure was reduced by 400 mm Hg for 30 min to remove air and vapor from the wood cells.

The impregnants were added at the reduced pressure until ratio of wood/solution was 1/3rd by volume; in all cases, the surface tension of the solution was reduced to 40 dyne cm^{-1} by adding a tensioactive agent (sodium dodecyl sulfate).

Later on, the pressure was gradually increased until a final value of 4781 mm Hg (6.5 kg cm^{-2}) to facilitate the penetration; this stage lasted for 120 min (Series I–III). The wood/solution ratio that was selected ensured that in all the cases the test panels were completely submerged in the solution of the impregnant for the duration of the process.

The next stage consisted of creating a slight vacuum (approximately 50 mm Hg for 10 min) to eliminate the excess of soluble silicates. Then, to promote the formation of the inorganic polymer, the samples in Series I and II were immersed in the 10% dibutyl amine phosphate alcoholic solution and the 10% solution of above-mentioned cations, respectively. In every case, the wood/solution ratio was 1/3rd by volume. The pressure was gradually

Table 2
Identification of samples.

Treatment	Silicate		A[a]/B[b]
Series I (Acid treatment)	1. SiO_2/Na_2O	3.0/1.0	I.1
	2. SiO_2/Na_2O	3.5/1.0	I.2
	3. SiO_2/K_2O	3.0/1.0	I.3
	4. SiO_2/K_2O	3.5/1.0	I.4
Series II (Reaction with cations)	1. SiO_2/Na_2O	3.0/1.0	II.1.Al; II.1.Cu; II.1.Zn; II.1.Mg; II.1.Ca
	2. SiO_2/Na_2O	3.5/1.0	II.2.Al; II.2.Cu; II.2.Zn; II.2.Mg; II.2.Ca
	3. SiO_2/K_2O	3.0/1.0	II.3.Al; II.3.Cu; II.3.Zn; II.3.Mg; II.3.Ca
	4. SiO_2/K_2O	3.5/1.0	II.4.Al; II.4.Cu; II.4.Zn; II.4.Mg; II.4.Ca
Series III (Combined treatment)	1. SiO_2/Na_2O	3.0/1.0	III.1.Al; III.1.Cu; III.1.Zn; III.1.Mg; III.1.Ca
	2. SiO_2/Na_2O	3.5/1.0	III.2.Al; III.2.Cu; III.2.Zn; III.2.Mg; III.2.Ca
	3. SiO_2/K_2O	3.0/1.0	III.3.Al; III.3.Cu; III.3.Zn; III.3.Mg; III.3.Ca
	4. SiO_2/K_2O	3.5/1.0	III.4.Al; III.4.Cu; III.4.Zn; III.4.Mg; III.4.Ca
Reference	No silicate		R

[a] Air-dried panels in laboratory conditions.
[b] Air-dried panels in laboratory conditions and then immersed in distilled water for 48 h.

increased to 2942 mm Hg (4.0 kg cm^{-2}) and the test panels remained in these conditions for 20 min.

For Series III, the procedure described above for Series I was followed, a slight vacuum was created to eliminate the excess of the alcoholic solution (approximately 50 mm Hg for 10 min) and the solution of corresponding cations was added. A pressure of 2942 mm Hg (4.0 kg cm^{-2}) was held for 10 min.

Finally, after reducing the pressure, the test panels were removed and rinsed with distilled water. Before starting the tests to establish their behavior in fire, a set of panels was air-dried under laboratory conditions (20–22 °C; 50–55% relative humidity) until reaching constant weight. These were designated "Group A".

"Group B" consisted of another set of panels, also air-dried under the same laboratory conditions, then submerged in distilled water for 48 h and finally air-dried until reaching the equilibrium moisture content.

For reference, wood panels (*Araucaria angustifolia*) without any treatment were also tested.

2.4. Flame-retardant tests

Two fire test equipments were used to provide comparative measurements of the fire performance of the untreated and treated wood samples. These were the two-foot tunnel (ASTM D 3806) and the limiting oxygen chamber (ASTM D 2863). It is important to emphasize that the methods employed in these tests are not representative of the real behavior of a material exposed to fire.

2.4.1. Two-foot tunnel [10,11]

Results from this test included a flame-spread index (FSI) and a panel consumption (PC) value. The top of the apparatus is a 600 mm × 100 mm section constructed of angle iron and inclined 28° from the horizontal. The 610 mm long, 100 mm wide, 10 mm thick test panels of *Araucaria angustifolia* were prepared and placed in the opening. A 215 mm high, 40 mm diameter natural gas burner inserted in the enclosed space below the specimen to provide the fire exposure for 4 min. Based on measurements taken every 15 s in the first 4 min, the average of the three highest consecutive readings of the flame advance in millimeters was calculated. In addition, the samples were weighed before and after the test. An asbestos-cement board (zero flame-spread) is also tested. For this study, the FSI of the panels was computed using the equation $FSI = (L_s - L_0)/(L_b - L_0)$, where L_s is the average of the three flame-advance readings for the test specimen, L_0 the average of three flame-advance readings for the zero flame-spread board and L_b the average of three flame-advance readings for the untreated wood panels of *Araucaria angustifolia*. In ASTM D 3806, L_b is the result for a known standard material and this ratio is multiplied by the ASTM E 84 FSI of the standard material. ASTM E 84 is the regulatory flame spread in the US. The weight loss in grams was reported as the panel consumption.

2.4.2. Limiting oxygen index (LOI)

Testing according to ASTM D 2863 determines the minimum oxygen concentration that just support combustion of a material under equilibrium conditions as candle-like burning. It is one of the favorite tests in the assessment of the fire-retardant treatments of polymeric materials because it gives reproducible numerical results [12]. The LOI chamber consists of a glass tube with a perforated plate and glass beads at the bottom that facilitates the mixing of the oxygen and the nitrogen, a clip to support the sample of test panel, devices for controlling and measuring the gases (filters, gauges, micro valves, flow meters, etc.) and a propane flame ignition system. A 150 × 10 × 10 mm specimen was clamped vertically on the approximate centerline of the column with the upper edge of the sample at least 100 mm below the top of the open glass column. Then, the flow valves were set so that the desired concentration of oxygen flows through the glass column. The total flow rate was 3.2 cm s^{-1}. After purging the system with the oxygen–nitrogen flow for 30 s, the top of the specimen was ignited with the propane flame so that the top of the test specimen was well alight. If the specimen continued to burn after the igniter flame was removed, a new specimen was inserted and the oxygen concentration was adjusted to a lower level. If the specimen did not continue to burn, the oxygen concentration was increased to an intermediate value for the subsequent specimen. Testing continued until the minimum oxygen concentration was established. The determination of the LOI was done in triplicate.

3. Results and discussion

3.1. Formation and thermal stability of metal silicate polymers

Formation of inorganic polymers starting from soluble silicates and aluminum, copper, zinc, magnesium and calcium cations (water-soluble salts of above-mentioned cations were added to the soluble silicate solutions) indicated a quick formation of gel at the interface followed by propagation of the reaction into the aqueous phase. In the most cases, a coagulated mass separated out. The precipitates were predominantly amorphous and their composition depended on the silicate type, the pH of the solution, the concentration of reactants and the temperature [13,14].

At the lower temperatures, expansion increased almost linearly with temperature, whereas a faster rate of rise was noted at higher temperatures. The volumetric coefficients, in total correspondence with those of linear dilation, showed a reduced expansion inclusive at temperatures between 25 and 800 °C (approx. those registered in a fire): the values ranged from 3.2% to 3.4%. This would favor the stability and resistance of the treated wood during a conflagration. The melting point of metal silicate polymers is greater than 1000 °C in all cases.

3.2. Retentions and penetrations

After completing the treatment, the retentions were calculated gravimetrically while the penetrations were carried out through visual and microscopic observations of cuts on the test panels [15].

The retention, which is the quantity of solids from the impregnant solution absorbed by unit of volume of wood, was in the narrow margin between 122 and 126 $\mathrm{kg\,m^{-3}}$; the average value for all treated woods was 123 $\mathrm{kg\,m^{-3}}$ while the standard deviation was 1.28. Concerning penetration (the depth reached by the impregnant solution), this was full thickness for 85% of the cases while in the remaining 15%, the penetration was slightly irregular. Final average density of the test panels after impregnation was 542 $\mathrm{kg\,m^{-3}}$ with a standard deviation of 3.55.

3.3. Performance in the fire tests

The experimental results are in Tables 3–5. With the purpose of determining the value of each variable, in the first stage the values of FSI, PC and LOI were established on a scale that varied between 0 and 10. Therefore, values 0 and 10, respectively, were assigned to 1.00 and 0.00 (FSI), to 7.38% and 0.00% (PC) and to 16% and >55% (LOI); it is important to note that in all the cases, the 0 corresponded to the lowest value obtained whereas the 10 was the best registered performance in each test.

For the interpretation of results, the average of each variable was calculated, Table 6. The best performance corresponds to the highest average value.

Results of Tables 3 and 4 show a better performance of all panels treated in comparison with the reference *R* (without treatment) as well as a marked difference between the performances of the designed treatments (Series I–III). In addition, panels for the "Group A" (impregnated panels and air-dried to reach equilibrium moisture) showed generally higher performances than those of "Group B" (panels air-dried, then immersed in distilled water for 48 h and finally air-dried again to reach equilibrium moisture).

As for the type of treatment, the Series III was the best, followed by the Series II and the Series I in this order; it is important to mention that in the case of the Series III, the panels with and without immersion in distilled water after impregnation ("Group A" and "Group B", respectively) showed the same performance in the fire tests.

Table 3
Results of Series I[a].

	FSI	PC (%)	LOI (%)
Group A[b]			
I.1	0.30	2.80	36
I.2	0.32	2.73	38
I.3	0.28	3.53	37
I.4	0.27	3.48	38
Group B[c]			
I.1	0.44	4.43	27
I.2	0.41	4.12	28
I.3	0.43	3.95	30
I.4	0.39	3.79	31
R	1.00	7.38	16

[a] Average of three determinations.
[b] Un-leached panels.
[c] Leached panels.

The impregnation with alkaline silicates (Series I, acid treatment) improved the performance compared with untreated wood; however, this treatment led to reduced efficiency for the panels immersed in distilled water. This behavior could be attributed to the high solubility of those alkaline silicates polymerized by acid treatment; the high solubility was corroborated by the significant concentration of the above-mentioned alkaline cations, which was evaluated by atomic absorption in the solution where the panels were submerged.

The application of catalyst (Series II, reaction with cations) would have favored the formation by dehydration of polymeric silicates of high molecular weight. In consequence, glasses of higher melting point, with the previously mentioned reduced thermal expansion, could be responsible for the improved performance against fire. However, also in this case, when panels were immersed in distilled water before starting the fire tests the efficiency in general decreased. The degree of polymerization was not enough to keep the whole of the impregnants into the panels after immersion; the level of alkaline cations found in the distilled water in which the panels had been submerged also demonstrated the high solubility of polymeric silicates formed by application of catalyst.

The partial leaching of soluble silicates being the "Group B" (Series I and II) was also verified by low values of retention and penetration of the impregnated materials after immersion of the panels in distilled water. In both series, the value of retention decreased by about 10% as maximum in the panels for LOI test and 6% also as maximum in the panels used in the two-foot tunnel test. The depth of the distribution observed by microscopy indicated a very small presence on the surface (up to 1 mm, depending on the type of treatment) and an increasing profile towards the interior: greater than 2 or 3 mm depth homogeneous retention similar to that at the core of the panel was detected.

On the other hand, the panels of the Series III (acid treatment/reaction with cations) showed no significant differences in the values of retention and penetration after immersion in distilled water for 48 h, which explains the similar performance in fire tests demonstrated in experimental trials ("Group A" and "Group B").

The results also reveal that the sodium silicates and the potassium silicates showed no appreciable difference in performance, but the variable silica/alkali molar ratio showed that the highest value of improved performance against fire.

Table 4
Results of Series II[a].

	FSI	PC (%)	LOI (%)
Group A[b]			
II.1.Al	0.24	2.46	40
II.1.Cu	0.24	2.51	39
II.1.Zn	0.25	2.54	38
II.1.Mg	0.26	2.53	38
II.1.Ca	0.26	2.51	37
II.2.Al	0.23	2.36	41
II.2.Cu	0.24	2.43	37
II.2.Zn	0.25	2.51	38
II.2.Mg	0.26	2.51	37
II.2.Ca	0.26	2.51	36
II.3.Al	0.22	3.25	40
II.3.Cu	0.22	3.25	41
II.3.Zn	0.23	3.24	40
II.3.Mg	0.23	3.31	40
II.3.Ca	0.24	3.39	38
II.4.Al	0.20	3.10	42
II.4.Cu	0.21	3.17	41
II.4.Zn	0.21	3.18	42
II.4.Mg	0.22	3.25	40
II.4.Ca	0.22	3.32	39
R	1.00	7.38	16
Group B[c]			
II.1.Al	0.32	3.37	36
II.1.Cu	0.31	3.39	35
II.1.Zn	0.34	3.48	34
II.1.Mg	0.36	3.62	33
II.1.Ca	0.36	3.65	32
II.2.Al	0.30	3.08	37
II.2.Cu	0.30	3.15	36
II.2.Zn	0.32	3.38	35
II.2.Mg	0.3	3.45	35
II.2.Ca	0.34	3.57	34
II.3.Al	0.29	2.92	37
II.3.Cu	0.29	3.00	37
II.3.Zn	0.30	3.12	36
II.3.Mg	0.31	3.25	36
II.3.Ca	0.32	3.39	35
II.4.Al	0.27	2.61	40
II.4.Cu	0.28	2.71	39
II.4.Zn	0.28	2.82	37
II.4.Mg	0.29	2.93	36
II.4.Ca	0.30	3.07	35
R	1.00	7.38	16

[a] Average of three determinations.
[b] Un-leached panels.
[c] Leached panels.

Table 5
Results of Series III[a].

	FSI	PC (%)	LOI (%)
Group A[b]			
III.1.Al	0.16	1.96	48
III.1.Cu	0.17	2.26	46
III.1.Zn	0.17	2.11	45
III.1.Mg	0.18	1.96	46
III.1.Ca	0.18	2.18	44
III.2.Al	0.15	1.77	50
III.2.Cu	0.16	1.85	49
III.2.Zn	0.17	1.91	47
III.2.Mg	0.17	2.00	47
III.2.Ca	0.17	2.00	48
III.3.Al	0.13	2.65	52
III.3.Cu	0.14	2.66	50
III.3.Zn	0.13	2.74	50
III.3.Mg	0.14	2.79	49
III.3.Ca	0.15	2.95	48
III.4.Al	0.10	2.42	>55
III.4.Cu	0.11	2.51	>55
III.4.Zn	0.11	2.57	>55
III.4.Mg	0.11	2.58	>55
III.4.Ca	0.13	2.65	54
R	1.00	7.38	16
Group B[c]			
III.1.Al	0.16	2.37	48
III.1.Cu	0.17	2.50	47
III.1.Zn	0.18	2.50	45
III.1.Mg	0.18	2.61	45
III.1.Ca	0.19	2.62	44
III.2.Al	0.15	2.27	50
III.2.Cu	0.17	2.29	48
III.2.Zn	0.17	2.37	47
III.2.Mg	0.17	2.44	47
III.2.Ca	0.18	2.53	46
III.3.Al	0.14	2.21	51
III.3.Cu	0.14	2.25	50
III.3.Zn	0.14	2.33	50
III.3.Mg	0.14	2.43	50
III.3.Ca	0.15	2.55	49
III.4.Al	0.10	2.00	>55
III.4.Cu	0.11	2.11	>55
III.4.Zn	0.12	2.17	>55
III.4.Mg	0.13	2.23	54
III.4.Ca	0.14	2.35	51
R	1.00	7.38	16

[a] Average of three determinations.
[b] Un-leached panels.
[c] Leached panels.

Taking into account the effect of cation type, a clear difference in performance was observed; an increase in efficiency in the order calcium, magnesium, zinc, copper and aluminum was found.

The different solubility of the metal silicate polymers could explain these results: a decrease in the solubility of those polymers was determined by analyzing the content of cations in distilled water after the immersion of the panels. The inorganic polymers formed by precipitation with aluminum were the most insoluble, since a negligible Al^{+3} level was leached from the treated wood into the distilled water. In addition, the values of retention and penetration after immersion were consistent with the other results described here.

The charge of the alkaline ions would affect the water dissolution of metal silicate polymers: cations of higher valence are more firmly placed into the glass structure since their mobility is less than the ions with smaller bonding capacity.

Table 6
Statistical results.

Condition after impregnation	Average value
Group A	7.7
Group B	7.0

Treatment type	Series I	Series II	Series III
Group A	6.6	7.2	8.4
Group B	4.9	6.1	8.4

Silicate type	Sodium silicate	Potassium silicate
Group A	7.7	7.7
Group B	7.0	7.1

Silica/alkali ratio	3.0/1.0	3.5/1.0
Group A	7.6	7.8
Group B	6.8	7.3

Cations	Al	Cu	Zn	Mg	Ca
Series II/III					
Groups A/B	7.8	7.7	7.6	7.5	7.4
Series II					
Group A	7.4	7.2	7.2	7.1	6.9
Group B	6.7	6.6	6.4	6.2	6.0
Series III					
Group A	8.6	8.5	8.4	8.4	8.3
Group B	8.6	8.5	8.4	8.4	8.3

Note: Group A, un-leached panels; Group B, leached panels.

On the other hand, the larger ions would be held more strongly within the structure of the metal silicate polymers than the smaller ones. Copper, zinc, magnesium and calcium have in that order an increasing ionic volume; nevertheless, the small size of single ions generates a strong electrostatic field in their surroundings and therefore they attract a higher number of water dipoles than the ions of large size. This would explain why the copper cation forms metal silicate polymers that are more insoluble than those formed with the calcium cation.

In summary, the best performance of all the panels was reached with samples III.2.Al and III.4.Al: combined treatment (acid catalyst and aluminum-like cation for the polymerization of silicates) and 3.5/1.0 silica/alkali molar ratio, with the two types of soluble alkaline silicates (as mentioned, this variable did not exert a significant influence on performance).

For example, panel B.III.4.Al displayed the highest average value in this experiment: 8.77. The latter was attained with a FSI of 0.10 (only 57 mm beyond the flame advancement registered in the panel of reference of asbestos-cement), a PC of 2.00% (a very low consumption of panel) in two-foot tunnel and a LOI greater than 55% (self-extinguishing behavior, indicating that requires greater concentration of oxygen in a mixture with nitrogen than the available in the air to maintain the combustion under equilibrium conditions in limiting oxygen chamber) [16].

4. Conclusions

In the fire tests, the performance of all the panels of *Araucaria angustifolia* impregnated with alkaline silicates was improved in relation to those untreated (the average value of the retention of impregnants was about 123 kg m^{-3}).

The results also allow to conclude that the wood panels previously treated with soluble alkaline silicates, then with an acid and finally with cations lead to formation of the metal silicate polymers that show low water solubility; the latter avoids the leaching of impregnants in contact with water and in addition it assures the maintenance of the performance against fire.

Finally, it is very important to mention a significant advantage of alkaline silicates for the wood treatment, beyond those previously mentioned like the high efficiency against fire and the low thermal expansion: the generation of smoke of low toxicity during a conflagration and their low-cost constitutes other excellent factors. Of the disadvantages, it must be mentioned that the high alkalinity of the solutions demands special attention for their handling.

Acknowledgments

To CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), to UTN-FRLP (Universidad Tecnológica Nacional Facultad Regional La Plata) and to CIC (Comisión de Investigaciones Científicas de la Provincia de Buenos Aires) for their sponsorship for this research.

References

[1] Allen G. Lilla, R., Product and method for forming in situ insoluble metal silicates in wood pores for fire retardation and preservation, US Patent no.3,974,318, 1976.
[2] Grantham et al., Method of pressure treating boards, US Patent no. 6,235,349, 2001.
[3] K. Shiozawa, Wood preservative composition, process for treating wood with the same, wood treated with the same, US Patent no. 5,478,598, 1995.
[4] Slimak, K., et al., Enhancing the strength, moisture resistance, and fire-resistance of wood, timber, lumber, similar plant-derived construction and

building materials, and other cellulosic materials, US Patent no. 6,146,766, 2000.

[5] Slimak, R., et al., Enhancing the strength, moisture resistance, and fire-resistance of wood, timber, lumber, similar plant-derived construction and building materials, and other cellulosic materials, US Patent no. 6,040,057, 2000.

[6] I. Imamura, Effect of combined boro compounds and furfuryl alcohol treatment on termite and decay resistance in wood, High-performance utilization of wood for outdoor uses, Report on Research Projet, Grant-In-Aid for Scientific Research, 2001, pp. 97–103.

[7] E. Baysal, et al., Amount of leachant and water absoption levels of wood treated with borates and water repellents, Bioresource Technology 97 (18) (2006) 2271–2279.

[8] O. Grexa, E. Horváthová, O. Besinová, P. Lehocky, Flame retardant treated plywood, Polym. Degrad. Stabil. 64 (1999) 529–533.

[9] I. Usta, Amenability of European silver fir (*Abies alba* Mill.) to preservative treatment by the full-cell process in longitudinal, tangential, radial and triplex flow pathways on the base of wood drying, Build. Environ. 41 (8) (2006) 1027–1033.

[10] M. Caciolai, Testing resistance to fire, Anticorrosione 7 (25) (1999) 29–33.

[11] R. Shaw, The use of flame retardant coatings on wall and ceilings, J. Oil Col. Chem. Assoc. 72 (5) (1999) 176–180.

[12] R. Hindersinn, Historical aspects of polymer fire retardance, in: G. Nelson (ed.), Fire and Polymers, ACS Symposium Series, Washington, USA, 1990, pp. 87–96.

[13] M. Tsai, P. Huang, W. Wu, The study of formation process of colloidal silica, Mater. Res. Bull. 40 (2005) 1609–1616.

[14] M. Dietzel, Dissolution of silicates and the stability of polysilicic acid, Geochimica Cosmochimica Acta 64 (19) (2000) 3275–3281.

[15] W. Gindl, F. Zargar-Yaghubi, R. Wimmer, Impregnation of softwood cell walls with melamine-formaldehyde resin, Bioresour. Technol. 87 (2003) 325–330.

[16] L. Wake, J. Brown, Z. Mathys, Reconsidering the shipboard use of chlorinated alkyd paints, J. Coat. Technol. 67 (844) (1995) 29–36.