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Adsorption of Cations from a Cement Suspension onto Lignocellulosic Substrates and its Influence on Cement Setting

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Adsorption of Cations from a Cement Suspension onto Lignocellulosic Substrates and its Influence on Cement Setting

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Abstract: The calcium (Ca), sodium (Na), and potassium (K) contents of blue gum, maritime pine, and cork increased after these lignocellulosics were stirred with the filtrate of a cement suspension or a solution of calcium hydroxide. The adsorbed cations could be released easily by treatment with an acidic solution. It is suggested that those raw materials, and lignocellulosics in general, act as cation exchange substrates when they are mixed with cement and water to make wood–cement composites. The implications that such phenomena may have on cement hardening reactions, and how they could hinder them are discussed. The possibility that the phenomenon is related to well-known compatibility problems that many woods present when manufacturing wood–cement composites is discussed.

Keywords: Cement, cations, lignocellulosics, interactions, adsorption, hindrance

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INTRODUCTION

In studies of wood–cement composites, or in a more general sense, composites of cement and lignocellulosic materials, for example, forest or agricultural residues, it has been reported that some substrates are not suitable for manufacturing composites with the desired physical properties.^[1] Some composites exhibit lower physical properties when compared with neat cement, the effect being dependent on the wood species. In some cases there is a total lack of physical integrity. That is why classifications of wood species such as "compatible," "moderately compatible," and "not compatible" have been proposed,^[2] according to the degree of cement hardening hindrance. Several methods for assessing the degree of compatibility have been discussed and recommended.^[3,4]

The extractives of the wood have often been cited as the cause for such incompatibility. In the manufacture of wood-wool cement boards with radiata pine (*Pinus radiata* D. Don) furnish, the heartwood, which has a higher extractives content, was found to severely retard cement hydration, resulting in boards with little structural integrity. On the other hand, boards made from just sapwood have been made industrially and commercialized.^[5] An investigation of several hardwoods and softwoods revealed that hardwoods adversely affected tensile strength and exothermic behavior of cement composites, more than softwoods, and that softwood heartwood affected the same characteristics more than sapwood.^[6]

In addition to the amount of extractives, the chemical nature of the extractives plays a role in the question of compatibility in the composites. Among wood and bark species with the same amount of extractives, different levels of compatibility were measured.^[7] More detailed studies of the extractives revealed that, for example, in the wood of *Acacia mangium* Willd., teracidin with a 7,8-dihydroxy group in a leucoanthocyanidin structure has a strong inhibitory effect;^[8] in the wood of sugi (*Cryptomeria japonica* D. Don) the incompatibility was attributed to sequirin-C and pinitol;^[9] and in beech (*Fagus crenata* Blume) it was mainly due to sucrose.^[10]

Simple removal of the extractives has worked in several cases to render woods more compatible with composite formation. Extraction with just cold water has been enough for several tropical hardwoods,^[11] but some other wood species may require a harsh extraction, for example, with 1% NaOH.^[12] Western larch (*Larix occidentalis* Nutt.), a wood species usually taken as truly incompatible, and that has been used as a standard of such for comparison purposes, showed substantial improvements after extraction with hot water.^[13] The addition of some chemicals, usually chlorides, as cement hardening accelerators, also has the effect of improving the compatibility of some wood species. For example, a study of 30 inorganic and organic accelerators showed that SnCl₂, FeCl₃, and AlCl₃, followed by CaCl₂, gave the best results in a larch-cement-water system, in terms of the higher maximum temperature of hydration and of the shorter time to reach that temperature.^[14]

Because extractives play an important role in making some woods and other lignocellulosic materials incompatible with cement in making composites, extractives of maritime pine (*Pinus pinaster* Ait.), blue gum (*Eucalyptus globulus* Labill.) and cork, the bark of cork oak (*Quercus suber* L.), all grown in Portugal, were quantified as a first step in assessing the compatibility of these materials with Portland cement in preparing composites.^[15] Organic solvents were used in extractions, but the materials were also subjected to inorganic solutions that simulated a cement suspension (pH and cations in solution): 0.1% NaOH, 0.1% Ca(OH)₂, and the filtrate of a cement suspension. The study indicated that with the aqueous Ca(OH)₂ and the filtrate from the cement, calcium ions, and maybe other cations, were being adsorbed by the substrates. This could have a potential impact on the hydration reactions that follow mixing of water with cement, and that lead to the hardening of cement.

In this article we present the results of a study of this adsorption behavior of the woods and the bark referred to earlier, after they were mixed and stirred with aqueous $Ca(OH)_2$ or the filtrate of cement suspensions. The nature of the phenomenon and its implications on the cement hardening reactions is discussed.

MATERIALS AND METHODS

Wood and Cork

Blue gum (*Eucalyptus globulus* Labill.) was provided in the form of chips with a size range of 7-42 mm by a pulp and paper mill located in northern Portugal. This furnish was assumed to be composed predominantly of sapwood, as most of the trees are cut at about 10-12 years. The chips were milled in a Wiley mill until passing a 60-mm screen. The wood meal was then screened on a 1000 µm sieve to remove the fine powder.

Maritime pine (*Pinus pinaster* Ait.) was supplied by a particleboard manufacturer of the same region of the country. The particles had a size range of 0.14–5 mm, which is the range of the particles used in the inner layer of the panels. The particles were used without further processing in subsequent experiments. This stock was also presumed to be mainly sapwood, as the raw material of the particleboard manufacturer comes mostly from small round wood, and the outer slabs from sawmills.

Pine and blue gum heartwoods were also used in this study. They were provided by a furniture manufacturer that separated sapwood and heartwood from lumber. Then, heartwood plunks were sawn in small pieces, and milled in a Wiley mill until passing a 6-mm screen. The wood meal was sieved as described earlier to remove the powdery material.

Cork was supplied by a cork particleboard plant. The fraction used in this work had a size range of 1-2 mm, and was classified as high density

 $(110-130 \text{ kg/m}^3)$. Other fractions of cork particles can have a much lower density. One of the criteria in including cork in this study, beyond an interest in developing potential methods of utilizing recycled cork residues, was to assess the possibility of developing a cement composite of low density, as cork presents a lower density than most woods.

These three raw materials of forest origin can be taken as potential materials for the industrial production of wood-cement boards in Portugal, because of their abundance and wide availability.

Solutions

Several solutions were used in this study to simulate the chemical environment to which wood or cork would be exposed when they are mixed with cement and water. Two cement suspensions were prepared by adding 0.350 kg or 2.22 kg of cement to 1 L of water.

The cement used was Portland, type CEMII/B-L 32.5 N, made by Cimpor, Portugal. The latter cement–water ratio is common for studying wood–cement composite manufacturing. The lower cement–water ratio was used because it is easier to prepare and filter than the higher one, and it could be useful for comparison purposes. These mixtures of cement and water were stirred for 1 h, and then vacuum filtered. The filtrate had a pH of approximately 12.3. The filtrate was analyzed by ICP-OES (inductively coupled plasma-optical emission spectroscopy), for Si, Ni, Fe, Cr, Al, Mg, Ca, Na, and K. Aliquots of 2 mL were taken, stabilized with 3 drops of 3.61 M HNO₃, and diluted to 20 mL. The final pH was *ca.* 1. The filtrate from a cement suspension is referred to hereafter as "cement water." The cement water was used within one week. Before each test, the cement water was analyzed for the main elements, Ca, Na, and K.

Because cement water can be complex and the results with it difficult to interpret, solutions of just calcium hydroxide were also used. Calcium hydroxide was used because of the important role of the calcium ion in cement hydration reactions. A saturated solution of calcium hydroxide was prepared by stirring Ca(OH)₂ powder (0.1 g) with water (100 mL) for at least 20 h, followed by vacuum filtration. The response of the lignocellulosic substrates to this solution could be analyzed more easily than that with cement water because only the one main cation, Ca, is involved.

Sorption Experiments

Lignocellulosic particles were added to 500 mL of either the less concentrated cement water or calcium hydroxide solution and the suspension was stirred for 8 h. The suspensions were filtered, and the lignocellulosic particles and the filtrates were kept separately for further analysis.

For the more concentrated cement water, the wood or cork particles (*ca.* 3.5 g) were added to about 50 mL of cement water. The aim was to closely simulate the experimental conditions used in the manufacturing of wood–cement composites.

Analyses of the solutions were performed by ICP-OES as described earlier for Ca, Na, and K, before and after being mixed with wood and cork. To analyze the substrates, the wood or cork particles were placed in ceramic crucibles and incinerated in a muffle furnace using a heating rate of 1.25° C/min up to 750° C, held at this temperature for 2 h, then allowed to cool to room temperature. The amounts used were about 3 g per sample for the substrates that have been in contact with the three solutions, or 8 g per sample for the fresh substrates. The resulting ashes were dissolved with a mixture of 34% HCl and 65% HNO₃ (3:1, vol). The mixture was heated close to the boiling point for about 1 h, until it became translucent. The resultant solutions were diluted to 50 mL with distilled water, and analyzed by ICP-OES.

Part of the pine and blue gum sapwoods and cork particles that were previously treated with the less concentrated cement water were dried and then leached with an acid solution. Approximately 7 g of each sample was added to 500 mL of 1.2 MHCl and the suspension was stirred for 1 h. The suspension was filtered, and the solid particles were submitted to the same acid treatment two more times. Ca, Na, and K analyses were performed before treatment with cement water, after this treatment, and after the three cycles of acid leaching.

RESULTS AND DISCUSSION

Table 1 presents the concentrations of some cations that enter into solution after mixing cement and water in different concentrations. The main cations are calcium (Ca), sodium (Na), and potassium (K). This is the reason why these cations were selected for monitoring the interactions between the cement waters and the lignocellulosic substrates in order to assess the cation adsorption hypothesis, as suggested previously.^[15]

Table 2 presents the concentrations of Ca, Na, and K, in solution and in the substrates, before and after the lignocellulosic substrates were mixed and stirred with the saturated aqueous $Ca(OH)_2$. It is clear that Ca cation is

Table 1. Concentration of cations present in solution after mixing cement and water

| Proportion | | Concentration of elements (mg/L) | | | | | | | | | |
|----------------------|-------|----------------------------------|-------|--------|-------|-----|-----|-----|-------|--|--|
| cement/water kg/L | Si | Ni | Fe | Cr | Al | Mg | Ca | Na | K | | |
| 0.35 | 6.223 | < 0.1 | 0.204 | 5.055 | < 0.5 | 1.1 | 844 | 132 | 1,090 | | |
| 2.22 | 6.828 | < 0.1 | 0.416 | 17.301 | < 0.5 | 0.8 | 528 | 540 | 4,910 | | |

| | | | Ca | | | | N | la | | Κ | | | |
|--------------------|-------|----------|-----------------|--------|----------|----------|--|--------|----------|-----------------|-------|-----------|-------|
| | | Solution | Solution (mg/L) | | e (mg/g) | Solution | olution (mg/L) Substrate (mg/g) Solution | | Solution | (mg/L) Substrat | | te (mg/g) | |
| | | Before | After | Before | After | Before | After | Before | After | Before | After | Before | After |
| Cork | n | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 |
| | Ave | 246 | 91.1 | 3.43 | 15.65 | 1.3 | 1.46 | 0.25 | 0.02 | 0.91 | 9.41 | 1.22 | 0.02 |
| | Stdev | | 13.6 | 0.035 | 0.273 | | 0.62 | 0.084 | 0.005 | | 0.1 | 0.002 | 0.002 |
| | cv% | | 14.9 | 1.0 | 1.7 | | 42.5 | 33.6 | 25.0 | | 1.1 | 0.2 | 10.0 |
| Blue gum sapwood | n | 1 | 3 | 4 | 3 | 1 | 3 | 4 | 3 | 1 | 3 | 4 | 3 |
| | Ave | 428 | 241.7 | 0.43 | 13.01 | 2.7 | 2.94 | 0.14 | 0.01 | 1.69 | 7.86 | 0.53 | 0.01 |
| | Stdev | | 11.8 | 0.011 | 0.132 | | 0.99 | 0.019 | 0.002 | | 0.95 | 0.12 | 0.007 |
| | cv% | | 4.9 | 2.6 | 1.0 | | 33.7 | 13.6 | 20.0 | | 12.1 | 22.6 | 70.0 |
| Blue gum heartwood | n | 1 | 4 | 2 | 2 | 1 | 4 | 2 | 2 | 1 | 4 | 2 | 2 |
| C | Ave | 556.8 | 269.3 | 0.52 | 21.06 | <1.5 | <1.5 | 0.073 | 0.046 | 4.48 | 5.23 | 0.034 | 0.033 |
| | Stdev | | 31.5 | 0.01 | 0.77 | | | 0.022 | 0.01 | | 2.38 | 0.004 | 0.005 |
| | cv% | | 11.7 | 1.9 | 3.7 | | | 30.1 | 21.7 | | 45.5 | 11.8 | 15.2 |
| Pine sapwood | n | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 |
| | Ave | 373.6 | 205.9 | 1.07 | 12.67 | 1.05 | 1.67 | 0.11 | 0.01 | < 0.10 | 5.61 | 0.47 | 0.02 |
| | Stdev | | 19.8 | 0.171 | 0.496 | | 0.43 | 0.005 | 0.001 | | 0.8 | 0.081 | 0.004 |
| | cv% | | 9.6 | 16.0 | 3.9 | | 25.7 | 4.5 | 10.0 | | 14.3 | 17.2 | 20.0 |
| Pine heartwood | n | 1 | 4 | 2 | 2 | 1 | 4 | 2 | 2 | 1 | 4 | 2 | 2 |
| | Ave | 556.8 | 288.8 | 0.48 | 10.78 | <1.5 | <1.5 | 0.005 | 0.009 | 4.48 | 3.47 | 0.024 | 0.032 |
| | Stdev | 22010 | 21.2 | 0.012 | 0.324 | | | 0.001 | 0.003 | | 0.54 | 0.004 | 0.003 |
| | cv% | | 7.4 | 2.5 | 3.0 | | | 20.0 | 33.3 | | 15.6 | 16.7 | 9.4 |

Table 2. Concentrations of calcium, sodium, and potassium, in solution and in the lignocellulosic substrates (eucalypt and pine, sapwood and heartwood, and cork), before and after mixing with aqueous $Ca(OH)_2$

adsorbed by the woods and cork as indicated by the increase in concentration in the substrates. This increase was accompanied by a decrease of the same cation in the solution. For Na and K the most noticeable feature is the decrease of these cations in cork, and in blue gum and pine sapwoods. For these same substrates, a noticeable increase in solution was measured for K, but was not significant for Na. This means that as the starting concentrations of Na and K are very low in the initial solution of reagent grade $Ca(OH)_2$ solution that there is diffusion of these cations from the substrates to the liquid phase, due to a concentration gradient. The lower concentrations measured in the cases of blue gum and pine heartwoods is probably attributable to comparatively lower concentrations of Na and K in the bulk of these substrates.

Table 3 presents the same kind of results presented in Table 2, but for cement water 0.35 kg/L. The same trend is evident for Ca; it increases in the solid lignocellulosic particles and decreases in the solutions. However, for Na and K, the feature is different compared with the case of the Ca(OH)₂ solution. All the substrates present a positive variation in their Na and K contents. This suggests that the substrates were able to withdraw Na and K cations from the solution. However, this hypothesis could not be unambiguously confirmed because of the small variation in the before and after concentrations of the Na and K cations in the less concentrated cement water solution. A more definitive relationship between the amounts adsorbed by the substrates and those remaining in the solution was observed in the case of the more concentrated cement water (2.22 kg/L), as Table 4 shows. In fact, an increasing concentration of Ca, Na and K in the substrates is clearly accompanied by a decrease of these cations in the solutions.

It was of interest to evaluate whether the adsorption of cations by the substrates could be reversed by leaching with acid. Substrates that had been in contact with the less concentrated cement water (0.35 kg/L) were leached with 1.2 M HCl, and the results before and after leaching were compared with those of fresh substrates. Table 5 confirms that, besides reversing the sorption process, acid leaching also removed some cations that existed in the starting substrates. The acid leaching caused a big decrease in the cation contents of the substrates, to levels of nearly zero. The one exception was the calcium in cork. Although the calcium in cork decreased substantially with acid leaching, the remaining level was only slightly lower than that of the starting cork, probably because the calcium in the fresh cork might be in a tightly bound, non-leachable form.

The data from this study suggest that the woods and the cork behave as cation exchange substrates when mixed with aqueous $Ca(OH)_2$ or with cement water. In fact, when the substrates were mixed with the calcium hydroxide solution, calcium was adsorbed, while sodium and potassium were released to the solution. When the substrates were mixed with cement water, the three cations were adsorbed, because their concentrations in the initial solution were higher compared with the respective substrate contents. When the substrates

| | | | Ca | | | | Na | | | К | | | |
|--------------------|-------|----------|-----------------|--------|----------|------------------|-------|------------------|-------|----------|--------|------------------|-------|
| | | Solution | Solution (mg/L) | | e (mg/g) | ng/g) Solution (| | (mg/L) Substrate | | Solution | (mg/L) | Substrate (mg/g) | |
| | | Before | After | Before | After | Before | After | Before | After | Before | After | Before | After |
| Cork | n | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 |
| | Ave | 1030 | 721 | 3.43 | 23.61 | 230 | 234 | 0.25 | 1.07 | 1841 | 1897 | 1.22 | 5.02 |
| | Stdev | | 13 | 0.035 | 1.159 | | 2 | 0.084 | 0.039 | | 25 | 0.002 | 1.16 |
| | cv% | | 1.8 | 1.0 | 4.9 | | 0.9 | 33.6 | 3.6 | | 1.3 | 0.2 | 23.1 |
| Blue gum sapwood | n | 1 | 3.6 | 4 | 2 | 1 | 2 | 4 | 2 | 1 | 2 | 4 | 2 |
| | Ave | 1013 | 801 | 0.43 | 17.81 | 247 | 247 | 0.14 | 0.27 | 1957 | 1987 | 0.53 | 1.3 |
| | Stdev | | 47 | 0.011 | 0.812 | | 1 | 0.019 | 0.021 | | 21 | 0.12 | 0.167 |
| | cv% | | 5.9 | 2.6 | 4.6 | | 0.4 | 13.6 | 7.8 | | 1.1 | 22.6 | 12.1 |
| Blue gum heartwood | n | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 |
| 0 | Ave | 914.3 | 525.7 | 0.52 | 23.92 | 204.4 | 215.7 | 0.073 | 0.673 | 1763 | 1773 | 0.034 | 3.94 |
| | Stdev | | 25.7 | 0.01 | 0.024 | | 2.3 | 0.022 | 0.066 | | 43.1 | 0.004 | 0.074 |
| | cv% | | 4.9 | 1.9 | 0.1 | | 1.1 | 30.1 | 9.8 | | 2.4 | 11.8 | 1.9 |
| Pine sapwood | n | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 |
| T T | Ave | 1003 | 720 | 1.07 | 19.22 | 229 | 236 | 0.11 | 0.33 | 1903 | 1916 | 0.47 | 1.79 |
| | Stdev | | 121 | 0.171 | 0.779 | | 3 | 0.005 | 0.017 | | 15 | 0.081 | 0.202 |
| | cv% | | 16.8 | 16.0 | 4.1 | | 1.3 | 4.5 | 5.2 | | 0.8 | 17.2 | 11.3 |
| Pine heartwood | n | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 |
| | Ave | 973.7 | 697.3 | 0.48 | 15.9 | 205.7 | 213.8 | 0.005 | 0.548 | 1736 | 1760 | 0.024 | 2.60 |
| | Stdev | | 26.7 | 0.012 | 0.719 | | 2.8 | 0.001 | 0.005 | | 25.44 | 0.004 | 0.405 |
| | cv% | | 3.8 | 2.5 | 4.5 | | 1.3 | 20.0 | 0.9 | | 1.4 | 16.7 | 15.6 |

Table 3. Concentrations of calcium, sodium, and potassium in solution and in the lignocellulosic substrates (eucalypt and pine, sapwood and heartwood, and cork) before and after mixing with cement water (0.35 kg/L)

| | | | Ca | | | | N | la | | Κ | | | |
|-----------------|-------|-----------------|-------|-----------|--------|-----------------|-------|------------------|-------|-----------------|-------|------------------|-------|
| | | Solution (mg/L) | | Substrate | (mg/g) | Solution (mg/L) | | Substrate (mg/g) | | Solution (mg/L) | | Substrate (mg/g) | |
| | | Before | After | Before | After | Before | After | Before | After | Before | After | Before | After |
| Cork | n | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 |
| | Ave | 586.5 | 123.8 | 3.43 | 8.969 | 1110 | 1019 | 0.25 | 2.763 | 9090 | 8420 | 1.22 | 22.62 |
| | Stdev | | 37.7 | 0.035 | 0.152 | | 136.9 | 0.084 | 0.16 | | 886.8 | 0.002 | 0.958 |
| | cv% | | 30.5 | 1.0 | 1.7 | | 13.4 | 33.6 | 5.8 | | 10.5 | 0.2 | 4.2 |
| Blue gum | n | 1 | 2 | 4 | 2 | 1 | 2 | 4 | 2 | 1 | 2 | 4 | 2 |
| sapwood | Ave | 643 | 124.3 | 0.43 | 4.796 | 1071 | 1029 | 0.14 | 1.762 | 8790 | 8501 | 0.53 | 12.64 |
| | Stdev | | 9.97 | 0.011 | 0.054 | | 107.1 | 0.019 | 0.011 | | 965.2 | 0.12 | 0.403 |
| | cv% | | 8.0 | 2.6 | 1.1 | | 10.4 | 13.6 | 0.6 | | 11.4 | 22.6 | 3.2 |
| Blue gum | n | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 |
| heartwood | Ave | 680 | 91.2 | 0.52 | 5.258 | 1151 | 928.8 | 0.073 | 1.942 | 9523 | 7552 | 0.034 | 14.4 |
| | Stdev | | 35.1 | 0.01 | 0.064 | | 26.23 | 0.022 | 0.078 | | 256.5 | 0.004 | 1.77 |
| | cv% | | 38.6 | 1.9 | 1.2 | | 2.8 | 30.1 | 4.0 | | 3.4 | 11.8 | 12.3 |
| Pine sapwood | n | 1 | 2 | 2 | 4 | 1 | 2 | 2 | 4 | 1 | 2 | 2 | 4 |
| | Ave | 625.3 | 117.9 | 1.07 | 6.376 | 1128 | 861.7 | 0.11 | 1.857 | 9265 | 7171 | 0.47 | 13.59 |
| | Stdev | | 42.8 | 0.171 | 0.646 | | 296 | 0.005 | 0.154 | | 2313 | 0.081 | 0.86 |
| | cv% | | 36 | 16.0 | 10.1 | | 34 | 4.5 | 8.3 | | 32 | 17.2 | 6.3 |

Table 4. Concentrations of calcium, sodium, and potassium in solution and in the lignocellulosic substrates (eucalypt and pine, sapwood and heartwood, and cork) before and after mixing with cement water (2.22 kg/L)

(continued)

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Table 4. Continued

| | | | Ca | | | | Ν | la | | К | | | |
|-------------------|--------------------------|-----------------|---------------------------|---------------------------|-----------------------------|-----------|----------------------------|-----------------------------|----------------------------|-----------|---------------------------|-----------------------------|----------------------------|
| | | Solution (mg/L) | | Substrate | e (mg/g) | Solution | (mg/L) | Substrate | e (mg/g) | Solution | (mg/L) | Substrat | e (mg/g) |
| | | Before | After | Before | After | Before | After | Before | After | Before | After | Before | After |
| Pine heartwood | n Ave Stdev cv% | 1 680 | 2 51.7 19.3 37.4 | 2 0.48 0.012 2.5 | 2 5.706 0.992 17.4 | 1 1151 | 2 928.8 18.24 2.0 | 2 0.005 0.001 20.0 | 2 1.705 0.023 1.3 | 1 9523 | 2 7740 153.3 2.0 | 2 0.024 0.004 16.7 | 2 11.56 0.978 8.5 |

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| | | _ | Ca (mg/g) | | | Na (mg/g) | | K (mg/g) | | | |
|----------|-------|-------------------|--------------------------------------|--------------------------------|-------------------|--------------------------------------|--------------------------------|-------------------|--------------------------------------|--------------------------------|--|
| | | Starting material | After mixing with cement water | After leaching with acid | Starting material | After mixing with cement water | After leaching with acid | Starting material | After mixing with cement water | After leaching with acid | |
| Cork | n | 2 | 1 | 1 | 2 | 1 | 1 | 2 | 1 | 1 | |
| | Ave | 3.43 | 18.16 | 2.98 | 0.25 | 0.38 | 0.01 | 1.22 | 1.55 | 0.05 | |
| | Stdev | 0.035 | | | 0.084 | | | 0.002 | | | |
| | cv% | 1.0 | | | 33.6 | | | 0.2 | | | |
| Blue gum | n | 4 | 1 | 1 | 4 | 1 | 1 | 4 | 1 | 1 | |
| sapwood | Ave | 0.43 | 10.46 | 0.08 | 0.14 | 0.27 | 0.004 | 0.53 | 1.03 | 0.01 | |
| | Stdev | 0.011 | | | 0.019 | | | 0.12 | | | |
| | cv% | 2.6 | | | 13.6 | | | 22.6 | | | |
| Pine | n | 2 | 1 | 1 | 2 | 1 | 1 | 2 | 1 | 1 | |
| sapwood | Ave | 1.07 | 12.99 | 0.29 | 0.11 | 0.32 | 0.01 | 0.47 | 1.42 | 0.04 | |
| | Stdev | 0.171 | | | 0.005 | | | 0.081 | | | |
| | cv% | 16.0 | | | 4.5 | | | 17.2 | | | |

Table 5. Concentration of calcium, sodium, and potassium in cork and blue gum and pine sapwoods; originally, after mixing with cement water (0.35 kg/L), and after leaching with 1.2 M HCl

were immersed in an acid solution their Ca, Na, and K contents decreased because of the competition of the H^+ ion for functional groups in the solid phase. Under acidic conditions protons are dominant and displace the metal cations.

The main question is how these phenomena, adsorption of cations from solution, can influence cement hardening reactions. When cement is mixed with water, part of the material undergoes dissolution giving rise to new crystalline forms that "set," conferring to the hardened cement its well-known physical properties. A new system of hydrated inorganic compounds develops. Supposing that the inorganic species originated from cement reaction with water undertook full hydration, the set of reactions that took place can be summarized as follows:^[16]

- I. $2(3CaO \cdot SiO_2) + 6H_2O \leftrightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2$
- II. $2(2CaO \cdot SiO_2) + 4H_2O \leftrightarrow 3.3CaO \cdot 2SiO_2 \cdot 3.3H_2O + 0.7Ca(OH)_2$
- III. $3CaO \cdot Al_2O_3 + Ca(OH)_2 + 12H_2O \leftrightarrow 4CaO \cdot Al_2O_3 \cdot 13H_2O$
- $Fe_2O_3 \cdot H_2O$
- $V. \quad CaO \cdot Fe_2O_3 \cdot H_2O + 2Ca(OH)_2 + nH_2O \longleftrightarrow 3CaO \cdot Fe_2O_3 \cdot mH_2O$
- VI. $3CaO \cdot Fe_2O_3 \cdot mH_2O + 3CaO \cdot Al_2O_3 \cdot 6H_2O \longrightarrow$ solid solutions
- VII. $3CaO \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 26H_2O \iff 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$

This complex system of reactions, which do not include all the reactions that can happen, is influenced by, among other parameters, the concentration of Ca(OH)₂, (calcium plays a key role in cement hydration reactions), pH, and temperature of the reacting medium. Different conditions determine different yields for the reactions and different stabilities for the final products.

Thus, the data presented in this article suggest that when woods, or lignocellulosic materials in general, are mixed with cement and water in order to manufacture wood-cement composites, some cations, especially calcium, will be adsorbed onto wood particles and, as a consequence, will be partially depleted from solution. This change in calcium concentration could affect the inorganic reactions that are taking place, maybe impairing the full hydration of cement, or retarding it. Accordingly, the adsorption of cations by the lignocellulosic substrates suggests a new potential contributor to the explanation of why the compatibility of woods with cement can vary.

The effects that pine, blue gum, and cork, and also their extractives, can have on cement hydration is the subject of future research. Neat cement with water, wood, or cork-cement-water systems, and these same mixtures but with extracted wood or cork, will be monitored to obtain the thermal plots of cement hardening. Measurements of maximum temperature, time to reach maximum temperature, and of the heat evolved in the process, will indicate the extent cement hardening is impaired by the presence of the lignocellulosic substrates and if removal of extractives confers any advantage.

CONCLUSIONS

Blue gum, maritime pine, and cork acted as cation exchange substrates, and adsorbed several cations present in solution in a cement suspension. Under the alkaline conditions of a cement suspension, acidic functional groups in the lignocellulosic substrates ionize and cations like Ca^{++} , Na^+ , and K^+ , and maybe others are adsorbed. The adsorption of these cations, particularly calcium, and the concomitant reduction of their concentrations in the water of the cement suspension, can potentially adversely influence the inorganic reactions that lead to cement hardening. With the possible exception of some of the calcium in cork the cations can be leached from the lignocellulosic substrates with acid.

Results presented in this article potentially contribute to a better understanding of the well-known hindrance of cement hardening that occurs when attempting to prepare lignocellulosic–cement composites from some species.

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