## ORIGINAL ARTICLE

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# Hydration behavior and compressive strength of cement mixed with exploded wood fiber strand obtained by the water-vapor explosion process

**Abstract** Poor compatibility was found between exploded wood fiber strand (WFS) and cement due to the excessive presence of water-soluble degraded polysaccharides in extractives of exploded WFS obtained from weathered wood waste treated by the water-vapor explosion process (WVEP). This study presents some comparative results from a continuing investigation on the compressive strengths of exploded WFS–cement mixtures. Based on results previously obtained with the hydration test, the relation between hydration behavior and compressive strength of the mixture was explored. In addition, the effect of the curing age on compressive strength development of the mixture with selected additive chemicals was examined. The results supported the results of early studies with hydration tests indicating that adding $MgCl_2$ to the mixtures of exploded WFS mixed with quick-curing cement or ordinary Portland cement and a composite of $MgCl_2 + CaO$ added to the mixture of exploded WFS and furnace-slag cement effectively improved the hydration behaviors; it greatly enhanced the compressive strengths of mixtures as well. Compressive strengths were strongly correlated to maximum hydration temperatures ($T_{max}$) of wood–cement mixtures influenced by the cement type, wood wastes (treated or not with WVEP), additive chemicals, and their content levels. The results also indicated that adding selected chemicals had no significant effect on compressive strength among the mixtures of exploded WFS mixed, respectively, with three types of cement at a curing age of 180 days. X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray spectroscopy were used to identify the hydration products and to probe the element distribution of the mixture in the wood–cement interface zone from a fractured surface.

**Key words** Wood–cement mixture · Compressive strength · Cement hydration reaction · Additive chemical · Water-vapor explosion of wood

## Introduction

The utilization of wood wastes (forest wastes, construction wastes) when developing new wood-based products has become of paramount importance in recent years as one of the potential ways to overcome resource reduction and environmental problems. Wood–cement mixtures (WCMs) have the potential and well-known advantages of providing diversified products for building applications using a wide range of recycled wood wastes. The value-added and potential application of these products could be further improved through a better understanding of the hydration behaviors and mechanical properties of WCM.[1-3]

The water-vapor explosion process (WVEP) is a valuable method for separating wood wastes into wood fiber strands (WFS), which subsequently can be used in many areas such as the production of wood-based panels and composites. This pretreatment is conducted under severe conditions of high temperatures and high pressures, so some chemical reactions take place in the main components of the wood. The cellulose, hemicellulose, and pectin are partially degraded to low-molecular-weight and water-soluble polysaccharides.[4-6]

To produce WCM using exploded WFS as an expedient reinforcement material, prior assessment was undertaken based on the investigation of two main issues: (1) the compatibility of exploded WFS and cement; and (2) the selection of suitable additive chemicals and additive contents to modify the compatibility. Previous approaches that evalu-

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ated the hydration behaviors of exploded WFS–cement mixtures led to the main conclusions that: (1) the degraded polysaccharides in the extractives of exploded WFS seriously inhibited cement hydration and hence caused the least compatibility between exploded WFS and cement; and (2) with addition of suitable additive chemicals and additive contents, the hydration behaviors of exploded WFS–cement mixtures could be significantly improved.[7]

In this study, based on the results obtained with the hydration tests, compressive strength tests paralleling the hydration tests were designed. Thus, the focus shifted to an investigation of the influence of hydration behavior on the mechanical performance of the mixture that would benefit such mixtures so they become acceptable engineered building materials.

The work outlined herein had four main objectives: (1) to investigate the influence of cement types, wood wastes (treated or not treated with WVEP), additive chemicals, and additive contents on the compressive strength of mixtures; (2) to correlate the relation between the hydration characteristics and the compressive strength of the mixture; (3) to examine the compressive strength development of the mixture at various curing ages; and (4) to characterize the hydration products and the chemical element distribution at the interface of the wood and cement using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS), as these characteristics are assumed to be directly related to wood–cement bonding and to the mechanical performances of the wood–cement mixtures.

## Materials and methods

### Materials

Weathered wood wastes were used in this study: sugi (*Cryptomerica japonica* D. Don) with various moisture contents (MCs) in air-dried (MC 15%–20%) and water-soaked (MC 150%–200%) conditions and with dimensions of 900mm (L), 150mm (W), and 25mm (T). They were treated by WVEP under explosion conditions: temperature 300°C; pressure 2.5MPa; time 4.0min. The actions of high temperature and high pressure caused the weathered wood wastes in a specially designed hot press to collapse and soften. Then, after sudden decompression followed by rapid expansion of water vapor (explosion), the weathered wood wastes were exploded into fibers and fiber strands (WFSs) with irregular lengths (100–250mm) and diameters ($\phi$ 1–4mm). In a previous study, the exploded WFSs proved to be extremely inhibitory to cement hydration owing to the excessive presence of water-soluble degraded polysaccharides in its extractives.[4,7,8]

Three commercial cements were used throughout this study: quick-curing cement (QC), ordinary Portland cement (OC), and B-type furnace-slag cement (FC) (Taiheiyo Cement). Their main compositions are given in Table 1. Six additive chemicals ($AlCl_3$, $CaCl_2$, $MgCl_2$, $Al_2(SO_4)_3$,

**Table 1.** Main compositions of the cements used in this study

| Composition | QC | OC | FC (B-type) |
|---|---|---|---|
| Oxides | | | |
| Silicon dioxide ($SiO_2$) | 20.4 | 20.7 | 25.6 |
| Aluminum oxide ($Al_2O_3$) | 5.1 | 5.1 | 8.6 |
| Ferric oxide ($Fe_2O_3$) | 2.5 | 2.9 | 1.6 |
| Calcium oxide (CaO) | 65.1 | 64.6 | 56.0 |
| Magnesium oxide (MgO) | 1.3 | 1.2 | 3.2 |
| Sulfur oxide ($SO_3$) | 3.0 | 2.0 | 2.2 |
| Sodium oxide ($Na_2O$) | 0.2 | 0.3 | 0.3 |
| Potassium oxide ($K_2O$) | 0.5 | 0.4 | 0.4 |
| Compounds | | | |
| Tricalcium silicate ($C_3S$) | 64 | 53 | – |
| Dicalcium silicate ($C_2S$) | 11 | 21 | – |
| Tricalcium aluminate ($C_3A$) | 9 | 9 | – |
| Tetracalcium aluminoferrite ($C_4AF$) | 8 | 9 | – |
| Clinker | – | – | 55 |
| Furnace slag | – | – | 45 |

Results are given as the weight (percent)
QC, quick-curing cement; OC, ordinary Portland cement; FC, B-type furnace slag cement

$Na_2SiO_3$, CaO) were selected either as a single or a composite accelerator to determine the greatest potential for enhancing the compatibility and compressive strength of exploded WFS–cement mixtures.

### Sample preparation and the hydration test

The apparatus and method used for measuring hydration characteristics [maximum hydration temperature ($T_{max}$) and time ($t_{max}$) required to reach $T_{max}$] were described in a previous study.[7] The exploded WFS and unexploded wood (weathered wood waste) were reduced to wood powders (20–40 mesh), dried, and then stored in polyethylene bags to avoid quality changes due to moisture problems. All samples were mixed with a mass ratio of cement (200g)/ wood (15g, oven-dried)/distilled water (100ml, including the water in wood powder).

Three groups (A–C) of samples were designed for the hydration test. Group A was prepared to investigate the retarding influence of exploded WFS on cement hydration. Group B was used to assess six additive chemicals with respect to the hydration behavior of the mixture at 4% additive content based on cement weight. Group C was prepared to determine the influence of the content of the selected additive chemicals on the hydration characteristics of the mixtures. Based on comparisons in group B, the contents of the selected additive chemicals were examined at six levels (1%–6%). Three replications for each sample were prepared. The ambient temperature was 20°–23°C throughout the experiment.

### Sample preparation and measurement of compressive strength test

The compression test was designed to parallel the hydration test, investigating the effect of hydration behavior on the

mechanical performance of the mixture and the relations between the hydration characteristics and the compressive strength of the mixtures. Samples (groups A–C) for the compression tests were prepared with the same mass ratios and set up like those used for the hydration test. In addition, group D was designed to examine the compressive strength development of the mixtures as a function of curing age when suitable chemicals were added to the mixtures as well as the additive content levels, which were based on the results of the hydration tests in groups B and C. In group D, the samples were prepared using the same mass ratios and were set up similar to the samples in groups A–C.

After the cement and wood powder were mixed, the mixtures were tamped into a cylinder mold with dimensions of 80 mm height and 56 mm diameter. After curing for 24 h, the molded samples were carefully removed from the molds. The group A–C samples were cured at an ambient temperature of 20°–23°C for 28 days; group D samples were cured at ambient temperature for 3, 7, 14, 28, 90, and 180 days. The cured samples were tested in compression (loading speed 1.0 mm/min) at the desired curing age. The compressive strength was calculated from the maximum loads and the cross-sectional areas of the cylindrical samples. Three replications were prepared for each sample.

Sample preparation for X-ray diffraction, scanning electronic microscopy, and energy-dispersive spectroscopy

The samples for XRD, SEM, and EDS analyses were selected from fractured parts of four mixtures (neat OC, OC + unexploded wood, OC + exploded WFS, and OC + exploded WFS + 4% MgCl$_2$). To obtain a significant and distinct interface between wood and cement for SEM and EDS analysis, the samples were prepared using short fiber strands of exploded WFS (sugi, water-soaked) and wood strands of unexploded wood (sugi, water-soaked) instead of wood powder mixed with cement. The exploded WFS and unexploded wood were reduced to short fiber strands or wood strands ($\phi$ 1.0–3.5 mm diameter, 20 mm length), dried, and stored in polyethylene bags. The samples were mixed with the same mass ratios as for the hydration and compression tests and then were cured at an ambient temperature for 28 days.

The fractured portions of the samples (cured at 28 days) were subcarbonized in an oven at certain treatment conditions (temperature 200°C; time 60 min; gas flow nitrogen) with which the mixture could be easily broken to obtain a smooth surface (cross section) that included the interface zone of the cement and the adjacent wood tissue, which is good for SEM observation and EDS spectrum and mapping.[9,10]

The XRD analysis was carried out in a JEOL JDX 8200 X-ray diffractometer with Cu-K$\alpha$ radiation and $2\theta$ scanning ranging between 10° and 60°. A JEOL model JXA-840A SEM equipped with a JEOL model JED-2110 EDS analyzer was used.

Calculations and data analysis

Duncan's new multiple comparison procedure and analysis of variance (ANOVA) was conducted on the means at the 5% significance level. Linear regressions were also fitted to the data for evaluating the variation in compressive strength with the hydration characteristics of the mixtures.[11]

## Results and discussion

Correlation between compressive strength and maximum hydration temperature of WCMs mixed with wood wastes (treated or not with WVEP)

With respect to the three types of cement, a comparison of the effect of wood (before and after WVEP treatment) on the compressive strength, and the relation between the compressive strength and maximum hydration temperature ($T_{max}$) of mixtures without addition of chemicals are shown in Fig. 1. The strength values could be distinctly divided into three groups representing the compressive strength of neat cement (group A), cement + unexploded wood (air-dried or water-soaked) (group B), and cement + exploded WFS (air-dried or water-soaked) (group C).
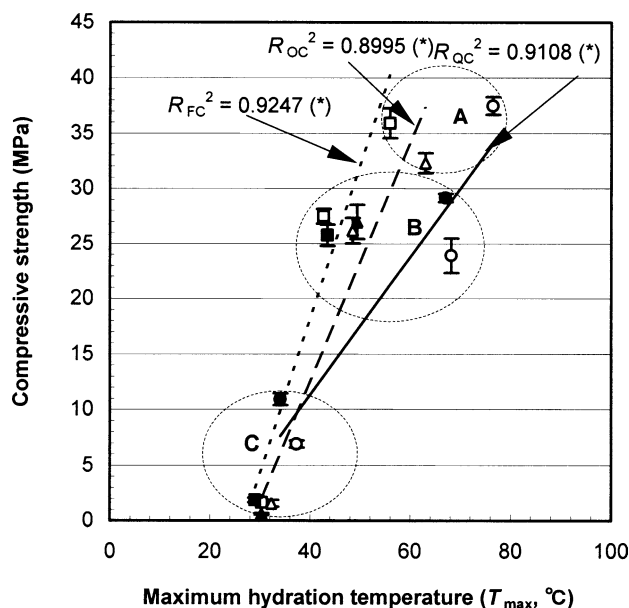


Fig. 1. Relation between compressive strength and maximum hydration temperature ($T_{max}$) of a wood–cement mixture without additive chemicals. *Group A*: *Open circles, triangles,* and *squares* represent three types of neat cement: quick-curing cement (*QC*), ordinary Portland cement (*OC*), and B-type furnace slag cement (*FC*) respectively. *Group B*: *Open circles, triangles,* and *squares* represent QC, OC, and FC, respectively, mixed with unexploded wood (sugi, air-dried). *Filled circles, triangles,* and *squares* represent QC, OC, and FC, respectively, mixed with unexploded wood (sugi, water-soaked). *Group C*: *Open circles, triangles,* and *squares* represent QC, OC, and FC, respectively, mixed with exploded wood (sugi, air-dried). *Filled circles, triangles,* and *squares* represent QC, OC, and FC, respectively, mixed with exploded wood (sugi, water-soaked). Compressive strengths of mixtures were measured after curing at 28 days. *Means are significantly different at the 5% significance level

The mixtures of different types of cements (QC, OC, FC) mixed with unexploded wood (water-soaked), for example, produced relatively high compressive strengths that reached, respectively, about 80%, 83%, and 75% those of neat QC, OC, and FC even though there were no additive chemicals in the mixtures. However, the exploded WFS obtained by WVEP demonstrated a strong retarding influence on cement hydration and resulted in the least compatibility when mixed with cement; the presence of excessive low-molecular-weight and water-soluble degraded polysaccharides in its extractives, reported in previous report, was confirmed.[7] It became evident that there was a violent reduction in compressive strength of the mixtures after addition of exploded WFS (air-dried or water-soaked). It could therefore be concluded that without pretreatment with suitable additive chemicals to increase the compatibility with cement mixtures of exploded WFS could not be used as an acceptable reinforcement material in WCMs for building applications. In addition, when QC was mixed with unexploded wood (air-dried or water-soaked) or exploded WFS wood (air-dried or water-

soaked), relatively larger differences in the compressive strength of the mixtures were found in groups B and C, respectively. This might be attributed to the fact that the compressive strengths of the mixtures appeared to be more sensitive to the amounts and compositions of extractable inhibitory components of the wood, probably due to a higher $C_3S$ content in QC than in OC and FC.

Furthermore, good linear correlations between compressive strength and the $T_{max}$ of mixtures were observed owing to the fact that the compressive strength reductions were proportional to the reductions in $T_{max}$ of mixtures corresponding to the three cements (QC, OC, FC).

### Effects of additive chemicals and additive contents on compressive strengths and hydration characteristics of exploded WFS–cement mixtures

Using three types of cement (QC, OC, FC), six additive chemicals were respectively added to the exploded WFS–cement mixtures to investigate their ability to enhance the compressive strength. Table 2 summarizes the influence of

**Table 2.** Effects of additive chemicals on hydration characteristics and compressive strength of cement mixed with exploded WFS (sugi, water-soaked)

| Composites | $T_{max}$[a] | | $t_{max}$[a] | | Compressive strength[c] | |
|---|---|---|---|---|---|---|
| | °C | Grouping[b] | Hours | Grouping | MPa | Grouping |
| Neat quick-curing cement (QC) | 76.5 (1.7)[d] | B | 9.0 (0.2)[d] | B | 37.5 (2.4)[d] | A |
| QC + exploded WFS | 34.1 (0.3) | D | 0.5 (0.1) | –[e] | 10.9 (1.6) | C |
| QC + exploded WFS + CaCl$_2$[f] | 76.8 (0.7) | B | 3.6 (0.1) | A | 33.6 (6.5) | A |
| QC + exploded WFS + AlCl$_3$ | 62.7 (0.8) | C | 13.7 (1.0) | B | 13.7 (1.8) | C |
| QC + exploded WFS + MgCl$_2$ | 87.2 (1.1) | A | 5.2 (0.3) | A | 36.9 (1.2) | A |
| QC + exploded WFS + Al$_2$(SO$_4$)$_3$ | 56.4 (0.5) | C | 6.4 (0.1) | A | 28.1 (4.1) | B |
| QC + exploded WFS + Na$_2$SiO$_3$ | 24.9 (0.1) | D | 0.6 (0.1) | – | 15.1 (1.5) | C |
| QC + exploded WFS + CaO | 29.9 (1.9) | D | 23.8 (0.3) | C | 10.0 (6.2) | C |
| Correlation coefficients | | | $R = 0.8839$ ($T_{max}$ – Compressive strength) | | | |
| | | | $R = 0.3733$ ($T_{max}$ – Compressive strength) | | | |
| Neat ordinary Portland cement (OC) | 63.0 (1.4) | A | 11.3 (0.2) | B | 32.3 (2.7) | A |
| OC + exploded WFS | 30.3 (0.3) | C | 0.9 (0.1) | – | 0.6 (0.3) | C |
| OC + exploded WFS + CaCl$_2$ | 36.5 (0.4) | C | 0.6 (0.3) | – | 27.6 (5.2) | A |
| OC + exploded WFS + AlCl$_3$ | 47.6 (1.1) | B | 22.6 (0.4) | C | 28.1 (2.3) | A |
| OC + exploded WFS + MgCl$_2$ | 64.2 (0.8) | A | 15.7 (0.2) | B | 30.0 (4.5) | A |
| OC + exploded WFS + Al$_2$(SO$_4$)$_3$ | 61.5 (1.9) | A | 0.7 (0.1) | – | 11.7 (3.0) | B |
| OC + exploded WFS + Na$_2$SiO$_3$ | 25.0 (0.3) | C | 2.7 (0.4) | A | 6.2 (2.6) | C |
| OC + exploded WFS + CaO | 33.5 (0.6) | C | 2.2 (0.2) | A | 0.6 (0.1) | C |
| Correlation coefficients | | | $R = 0.8695$ ($T_{max}$ – compressive strength) | | | |
| | | | $R = 0.5117$ ($T_{max}$ – compressive strength) | | | |
| Neat furnace-slag cement (FC) | 56.0 (1.8) | A | 13.7 (0.7) | B | 34.6 (1.8) | A |
| FC + exploded WFS | 29.0 (0.1) | C | 0.7 (0.2) | – | 1.9 (0.6) | C |
| FC + exploded WFS + CaCl$_2$ | 34.4 (1.8) | C | 0.5 (0.7) | – | 30.4 (2.3) | A |
| FC + exploded WFS + AlCl$_3$ | 63.1 (0.9) | A | 0.3 (0.1) | – | 27.6 (3.1) | B |
| FC + exploded WFS + MgCl$_2$ | 45.6 (1.1) | B | 24.0 (0.2) | C | 30.6 (2.5) | A |
| FC + exploded WFS + Al$_2$(SO$_4$)$_3$ | 48.8 (0.6) | B | 2.5 (0.1) | A | 9.6 (1.0) | C |
| FC + exploded WFS + Na$_2$SiO$_3$ | 25.6 (0.2) | C | 4.5 (0.2) | A | 2.8 (0.6) | C |
| FC + exploded WFS + CaO | 32.8 (0.2) | C | 0.5 (0.1) | – | 8.5 (1.1) | C |
| FC + exploded WFS + MgCl$_2$ + CaO (1%) | 54.8 (0.4) | A | 20.5 (0.6) | C | 32.5 (2.4) | A |
| FC + exploded WFS + MgCl$_2$ + CaO (2%) | 60.6 (0.3) | A | 13.1 (0.5) | B | 37.4 (1.3) | A |
| Correlation coefficients | | | $R = 0.9110$ ($T_{max}$ – Compressive strength) | | | |
| | | | $R = 0.4845$ ($T_{max}$ – Compressive strength) | | | |

[a] Each value is the average of three replications
[b] Means with the same capital letter are not significantly different at the 5% significance level (based on a Duncan grouping analysis)
[c] Compressive strengths of mixtures were measured after curing for 28 days
[d] Data in parentheses are standard deviations
[e] Only one peak appeared within 1 h during a 24-h observation period
[f] Chemicals were added at 4% of cement weight; CaO was added at 1% and 2% of cement weight

these additives on the compressive strength and hydration characteristics of the mixtures. The results indicated that these chemicals were considerably different in terms of their ability to improve the compressive strength or the hydration characteristics ($T_{max}$ and $t_{max}$) of exploded WFS–cement mixtures.

Three additives [$CaCl_2$, $MgCl_2$, $Al_2(SO_4)_3$] exerted a strong influence on increasing the compressive strength of the QC–exploded WFS mixtures. Among them, $MgCl_2$ was considered the best because of its high strength value and proper $t_{max}$. Lower compressive strength was found after adding 4% $AlCl_3$ to the mixture. The $AlCl_3$ reacted violently with cement and resulted in rapid loss of the fluidity and workability of the mixture, making it difficult to obtain a perfect cylindrical sample for a strength test. $Na_2SiO_3$ and CaO did not show any significant positive effect on the compressive strength of mixtures.

For the OC–exploded WFS mixtures, there were no significant differences in compressive strength when $CaCl_2$, $MgCl_2$, or $AlCl_3$ was added. Among them, $MgCl_2$ appeared to be the most effective, with a highest strength and an appropriate $t_{max}$ value. Addition of $Al_2(SO_4)_3$, $Na_2SiO_3$, or CaO was not effective, and consequently the compressive strengths of the mixtures were low.

Although adding $CaCl_2$, $MgCl_2$, or $AlCl_3$ to the FC–exploded WFS mixture produced relatively high strength values, the $t_{max}$ of the mixtures was considered undesirable because the hydration of $C_3S$ was markedly delayed. In fact, with the addition of $CaCl_2$ or $AlCl_3$, the $t_{max}$ of mixtures appeared, respectively, at 34.5 and 40.2 h (based on the results of duplicate experiments). $Al_2(SO_4)_3$, $Na_2SiO_3$, and CaO showed lower strength values. The highest compressive strength (35.6 MPa) of a mixture was achieved after adding 4% $MgCl_2$ + 2% CaO as a composite to the mixture. The $t_{max}$ was also adjusted to 13.1 h, which was considered appropriate compared with that of neat FC. A mixture of Portland cement clinker and furnace slag, FC has latent hydraulic reactivity. The activation of furnace slag is mainly

based on the generation of calcium hydroxide [$Ca(OH)_2$]. The calcium hydroxide, liberated mostly during hydration of tricalcium silicate, provides hydroxyl ions, which attack slag grain surfaces. However, the quantity of calcium hydroxide, being produced in the furnace slag cement, is relatively decreased because of the lesser amount of clinker, compared to that in OC. A small addition of CaO might provide more hydroxyl ions to accelerate the hydration reaction and form more hydration products, which improve the early-stage strength of FC.

Thus, after adding available chemicals, the compressive strengths of the three cement–exploded WFS mixtures were, respectively, close to those of neat cement and could be grouped into the same group (A) based on Duncan's grouping analysis. Moreover, using correlation analysis, high coefficients (R value) were found between compressive strength and the $T_{max}$ of exploded WFS–cement mixtures corresponding to the three types of cement. However, low correlations between compressive strength and $t_{max}$ were found with the lower coefficients. These results were consistent with those from previous studies and indicated that either mechanical properties or the $T_{max}$ of mixtures could, at a certain content, be used to evaluate the compatibility of mixtures with different wood properties.[12–14]

In accordance with the comparisons conducted on hydration characteristics ($T_{max}$, $t_{max}$) and the compressive strength of mixtures, a single additive ($MgCl_2$) for QC and OC and a composite additive ($MgCl_2$ + CaO) for FC were selected as suitable additive chemicals. The results indicated that with modification of these selected additives the compatibility and the compressive strength of exploded WFS–cement mixtures could be improved, and the exploded WFS could be considered acceptable wood material in WCMs.

The influence of the content of the selected additive chemicals on the compressive strength of mixtures was also examined. As shown in Fig. 2, the compressive strength of exploded WFS–QC mixtures was enhanced with increasing
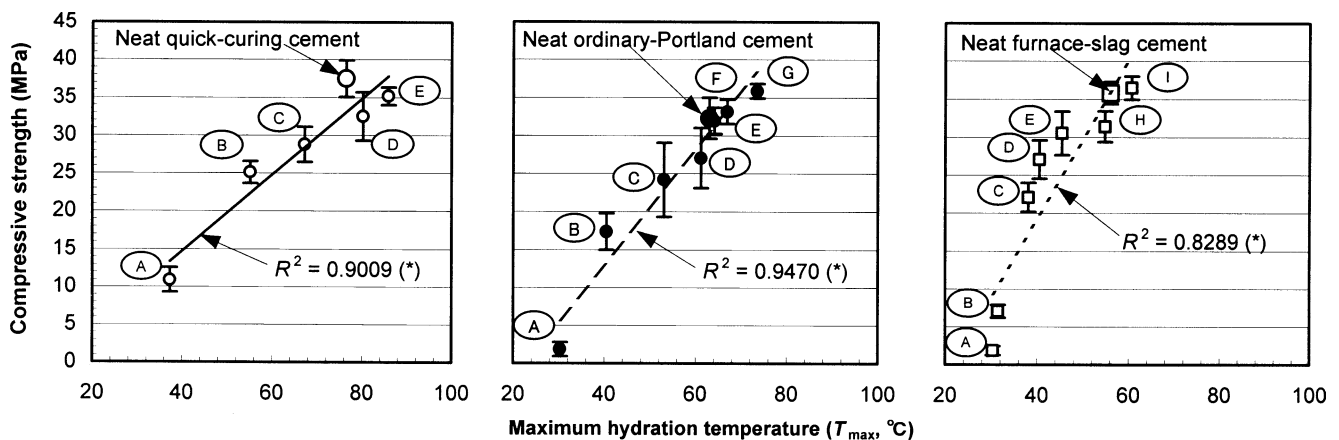


**Fig. 2.** Influence of selected additive chemicals on compressive strength and maximum hydration temperature ($T_{max}$) of cement mixed with exploded wood fiber strand (WFS) (sugi, water-soaked). *A*, 0% $MgCl_2$; *B*, 1% $MgCl_2$; *C*, 2% $MgCl_2$; *D*, 3% $MgCl_2$; *E*, 4% $MgCl_2$; *F*, 5% $MgCl_2$; *G*, 6% $MgCl_2$; *H*, 4% $MgCl_2$ + % CaO; *I*, 4% $MgCl_2$ + 2% CaO. Compressive strengths of mixtures were measured after curing at 28 days. *Means are significantly different at the 5% significance level

MgCl$_2$ content (ranging from 1% to 4%). With 2%–3% additive content, the compressive strength of mixtures, respectively, reached 28.8 and 32.5 MPa, which corresponds to about 77% and 87% compared to that of neat QC. They therefore were considered acceptable additive contents. The determination of an available additive's content would not only depend on the strength value but also on a consideration of the workability of mixtures, as more chemical added to the mixtures would lead to a rapid reduction in fluidity, causing incremental operational difficulties during the manufacture of products. Similarly, 4%–5% additive content was appropriate for OC. The compressive strength of mixtures reached 32.0 and 32.2 MPa, which were, respectively, about 96% and 105% of that of the neat OC. In the case of FC, by adding 4% MgCl$_2$ + 2% CaO as a composite the compressive strength of mixtures reached 36.5 MPa, which was about 101% that of neat FC.

By increasing the additive content, the compressive strength of mixtures was linearly proportional to the $T_{max}$ with the high coefficients ($R$ value) shown in Fig. 2. In addition, ANOVA revealed that the differences in compressive strength of mixtures were statistically significant at the 5% level.

### Influence of curing age on compressive strength development of exploded WFS–cement mixtures

Understanding the pattern of strength development would be beneficial to the product design, production, and application of exploded WFS–cement mixtures. In Fig. 3 are three curves representing the changes in compressive strength development of three types of cement (QC, OC, FC) and
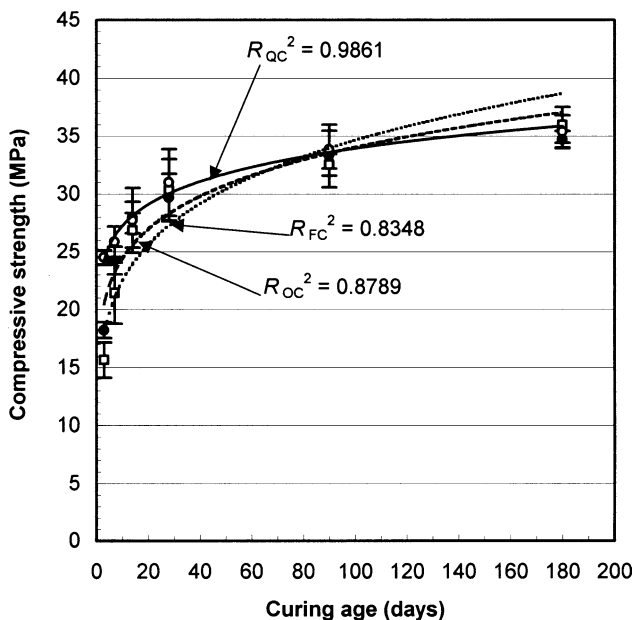


**Fig. 3.** Effect of curing age on compressive strength development of cement mixed with exploded WFS (sugi, water-soaked). *Open circles,* exploded WFS–QC mixture with added MgCl$_2$ (2%); *filled circles,* exploded WFS–OC mixture with added MgCl$_2$ (4%); *Squares,* exploded WFS–FC mixture with added MgCl$_2$ (4%) + CaO (2%)

exploded WFS mixtures. The additive chemicals and their contents in these mixtures were 2% MgCl$_2$ (QC), and 4% MgCl$_2$ (OC), and 4% MgCl$_2$ + 2% CaO (FC), which were considered acceptable and suitable based on the results of hydration and compressive strength tests.[7] Continuous curing and increasing compressive strength (up to 180 days) of the mixtures were observed throughout the experiment. Several conclusions could be drawn. There are two stages of strength development during the 180-day period. During the first stage the strength development of mixtures progressed rapidly (up to about 28 days), although the strength development of mixtures with different types of cement were significantly different. The mixtures containing QC showed higher early strength because QC has a higher content of C$_3$S than OC or FC. The mixtures with FC that contained furnace slag and a lower content of clinker than QC and OC showed the lowest early strength at this stage. It was also noted especially that with the relatively high rates of strength development, the compressive strengths of exploded WFS–cement mixtures (cured at 28 days) reached about 91% (QC), 87% (OC), and 85% (FC) compared with the 180-day values. Thereafter, during the second stage, the growth in strength gradually slowed. When approaching 180 days, the increase in compressive strength toward stabilization was evident. Furthermore, by adding selected chemicals the QC–exploded WFS mixture had higher early-stage compressive strength at curing ages of 3, 7, and 14 days. It was also evident that although the FC–exploded WFS mixture had lower early-stage compressive strength at curing ages of 3, 7, and 14 days it had a considerably high compressive strength at 90 and 180 days, although these figures were not significantly different from those of mixtures of exploded WFS and QC or OC.[12,15]

### X-ray diffraction analysis results

Some comparative results from XRD analysis of WCM with respect to the different compositions (samples A–D, cured at 28 days) are shown in Fig. 4. The neat cement (OC, sample A) provided a typical diffraction pattern of well-hydrated cement in which several major characterized peaks could be detected and used to evaluate cement hydration. The peak corresponding to cement hydration product CH [Ca(OH)$_2$] appeared at $d$ (Å) = 4.900 ($2\theta$ = 17.8°), and the peaks corresponding to C$_3$S (3CaO·SiO$_2$) and C$_2$S (2CaO·SiO$_2$), located respectively at $d$ (Å) = 3.022, 2.776, 2.764, 2.602, 2.185, 1.771, and 1.632 ($2\theta$ = 29.2°, 32.3°, 32.7°, 34.5°, 41.1°, 51.5°, and 56.4°), are discussed in this study. Among them, the most prominent peaks that appeared at $2\theta$ = 32.3°, 32.7°, and 34.5° conformed with the amount of unhydrated cement clinker according to previous studies.[15–17] Note that with the addition of unexploded wood (sample B) the mixture presented an XRD pattern that was similar to that of neat cement. Although a small decrease in the CH peak was detected, the unexploded wood proved to be least inhibitory to cement hydration.[7] However, in the case of a mixture with exploded WFS (sample C), the CH peak could not be detected, whereas the C$_3$S and C$_2$S peaks
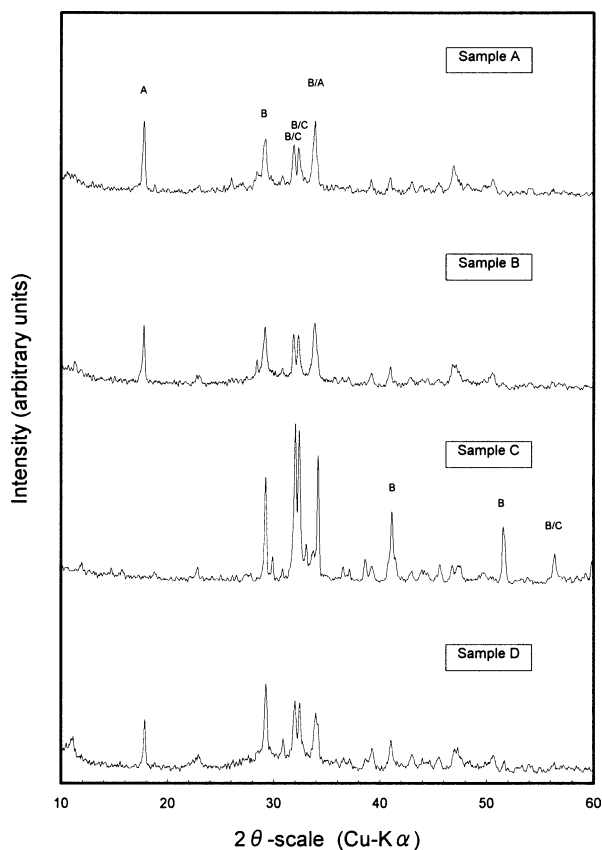
**Fig. 4.** Comparison on results of X-ray diffraction (XRD) analysis of wood–cement mixtures with various compositions (the fractured surfaces of mixtures, cured for 28 days, obtained after the compression test). *A*, CH [Ca(OH)$_2$]; *B*, C$_3$S (3CaO·SiO$_2$); *C*, C$_2$S (2CaO·SiO$_2$). *Sample A*: neat ordinary-Portland cement (OC). *Sample B*: OC–unexploded wood mixture (sugi, water-soaked). *Sample C*: OC–exploded WFS mixture (sugi, water-soaked). *Sample D*: OC–exploded WFS (sugi, water-soaked) mixture with added MgCl$_2$ (4%)

at $2\theta = 29.2°$, $32.3°$, $32.7°$, and $34.5°$ had greatly increased. Moreover, some characterized peaks of C$_3$S and C$_2$S at $2\theta = 41.1°$, $51.5°$, and $56.4°$ were also observed. The results were attributed to the fact that the strong retarding influence of degraded polysaccharides in the extractives of exploded WFS caused an incomplete cement hydration process, and a considerable amount of unhydrated cement clinker remained in the cured mixtures. It resulted in the least compatibility and poor strength performance of the mixture. However, it was also obvious that by adding 4% MgCl$_2$ to the exploded WFS–cement mixture (sample D) the intensity of the CH peak significantly increased, and that of the peaks representing C$_3$S and C$_2$S decreased, even disappearing.

These results from diffractograms were in good agreement with our previous results obtained with the hydration and strength tests. It was believed that the compatibility and strength development of mixtures were directly related to the amount of hydration product and unhydrated cement clinker that remained in the cured mixtures.[16,17]

## SEM observations

To gain a better understanding of cement hydration and the morphology of the hydration products affected by the different mixture compositions, SEM observations were undertaken. The results are shown in Fig. 5. Figure 5A shows an SEM micrograph of the fractured surface of neat cement (OC), in which the typically well-developed crystals of hydration products, including mainly the large laminated hexagonal plates of calcium hydroxide (CH) and bloom-shaped structures of calcium silicate hydrate (CSH), could be identified. Similar crystalline structures of CH and CSH, as well as a few needle-like crystals of ettringite (ET), were observed in the unexploded wood–cement mixture (Fig. 5B) as well. In addition, the growth of CH crystals appeared to be hindered, as relatively fewer CH crystals were detected in comparison with the neat cement. Figure 5C revealed a completely different crystalline state and poor hydration products in the mixture corresponding to the presence of exploded WFS. The unhydrated cement particles seemed to be covered with a smooth, film-like layer; and the conventional crystalline structures of CH and CSH were not found. Furthermore, some small, rod-like crystals were observed in the fractured surface. These crystals were probably incomplete ET crystals that were initially formed during hydration of C$_3$A (3CaO·Al$_2$O$_3$) but the growth ceased due to rapid inhibition during the hydration process.[18,19] This anomalous crystalline state appeared to make no contribution to strength development and could be related to the low strength of the exploded WFS–cement mixtures.

With addition of 4% MgCl$_2$ to the exploded WFS–cement mixture, as shown in Fig. 5D, the crystalline state of the products formed during cement hydration significantly improved, as indicated by the reappearance of a well-developed CH and CSH crystalline structure; thus, faster strength development of the mixture was achieved. In this case, few ET crystals were found, probably due to the fact that during the late stage of the accelerated hydration reaction, accompanied by consumption of gypsum (CaSO$_4$) and reduction of SO$_4^{2-}$ ions, the ET partially transformed to monosulfoalminate (AFm), which resulted in the formation of denser crystalline structures.

## Energy-dispersive spectroscopy analysis

To identify the element distribution at the wood–cement interface from a fractured surface of the mixture, EDS analysis was performed in this microregion (Fig. 6A). The results (Fig. 6, B1 to B3) indicated that in this microregion the intensity profiles of element distribution across the interface from cement paste to wood surface varied, influenced by the composition of the WCM. Examining the fractured surface of the unexploded wood and cement mixture (Fig. 6, B1) showed that elements such as Ca and Si were detected at the wood surface. This phenomenon implies that there was a gradient increase in deposits of the main hydration products (e.g., CH, CSH, and ET crystals) close to the wood surface.[20–22] The local increases of these
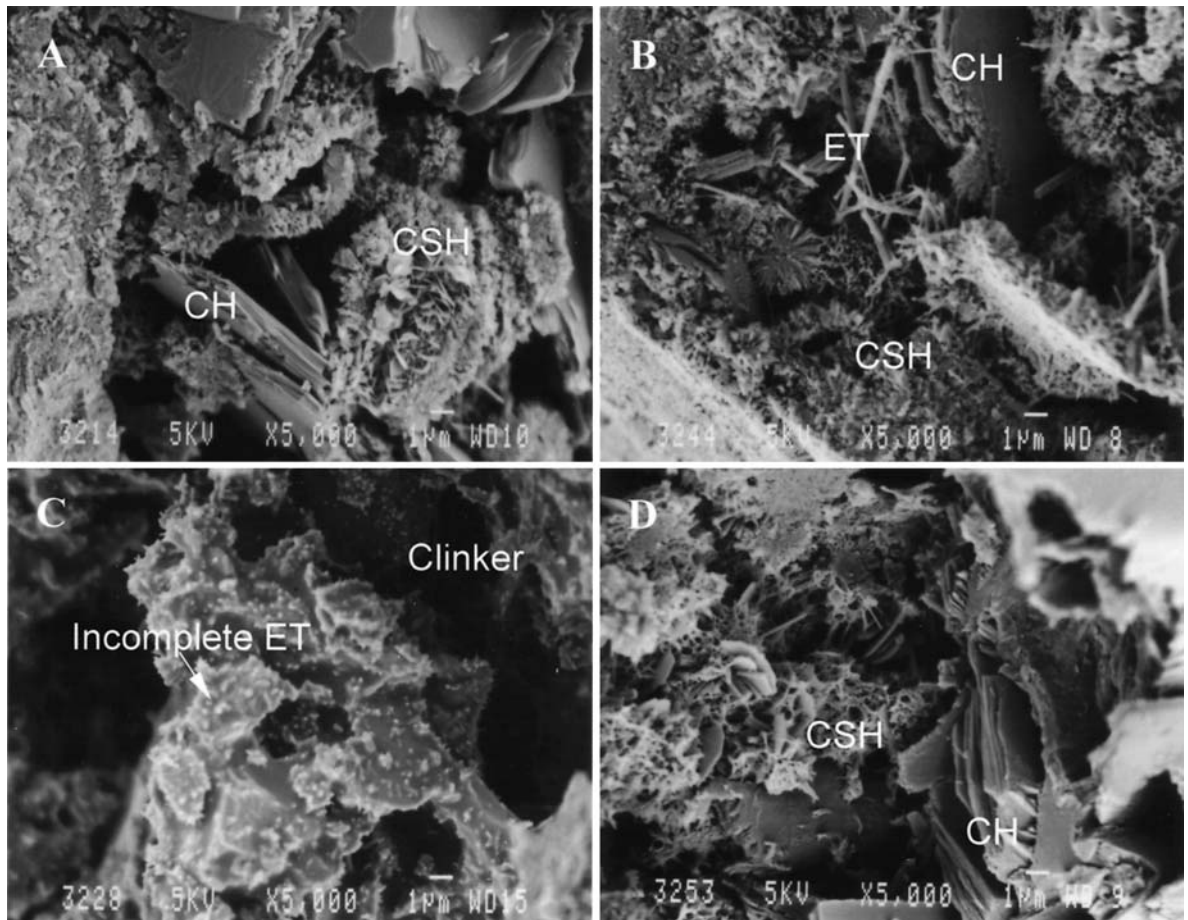
**Fig. 5.** Scanning electron microscopic (SEM) photographs of fractured surfaces of wood–cement mixtures in various compositions. *CH*, calcium hydroxide; *CSH*, calcium silicate hydrate; *ET*, Ettringite. **A** Neat ordinary Portland cement (OC). **B** OC–unexploded wood mixture (sugi, water-soaked). **C** OC–exploded WFS mixture (sugi, water-soaked). **D** OC–exploded WFS (sugi, water-soaked) mixture with added MgCl$_2$ (4%)

crystals near the wood surface may be attributed to the fact that there was a large capacity for water attraction on the wood surface, resulting in a strong water flow and better mobility of ions such as Ca$^{2+}$ and Si$^{4+}$ toward the wood surface in a desirable hydration environment. The presence of these crystals could be expected to produce higher wood–cement bonding strength due to the formation of more mechanical interlocking on the porous wood surface.[23,24]

In the presence of exploded WFS in the mixture, however, there were no similar high concentrations of these elements near the wood surface (Fig. 6, B2). This could be due to existence of excessive polysaccharides, resulting in an incomplete cement hydration process, consequently hindering the crystallization of hydration products. In contrast, with the acceleration of cement hydration by the addition of 4% MgCl$_2$ to the exploded WFS–cement mixture, a higher concentration of these elements close to the wood surface appeared in their distribution profiles (Fig. 6, B3).

The results obtained in the EDS analysis were apparently consistent with the results of the XRD, SEM analysis, and strength tests. These results led to the conclusion that the characteristics of the wood–cement interface are influ-

enced by the composition of the mixtures and are thus directly related to wood–cement bonding and the mechanical performance of the mixture.

## Conclusions

The exploded WFS obtained by the WVEP had a strong inhibitory effect on cement hydration, resulting in poor compressive strength of the exploded WFS–cement mixture. Without addition of a suitable chemical, it could not be considered an acceptable wood reinforcement material. MgCl$_2$ proved to be a suitable additive chemical. By adding 2%–3% and 4%–5% of MgCl$_2$ as the single additive in mixtures with QC and OC, respectively, and 4% of MgCl$_2$ + 2% of CaO as the composite additive in mixtures with FC, the compressive strength could be greatly enhanced. Good correlations were found between $T_{max}$ and the compressive strength of WCMs of various fiber–cement compositions. However, the correlations were low between $t_{max}$ and the compressive strength.
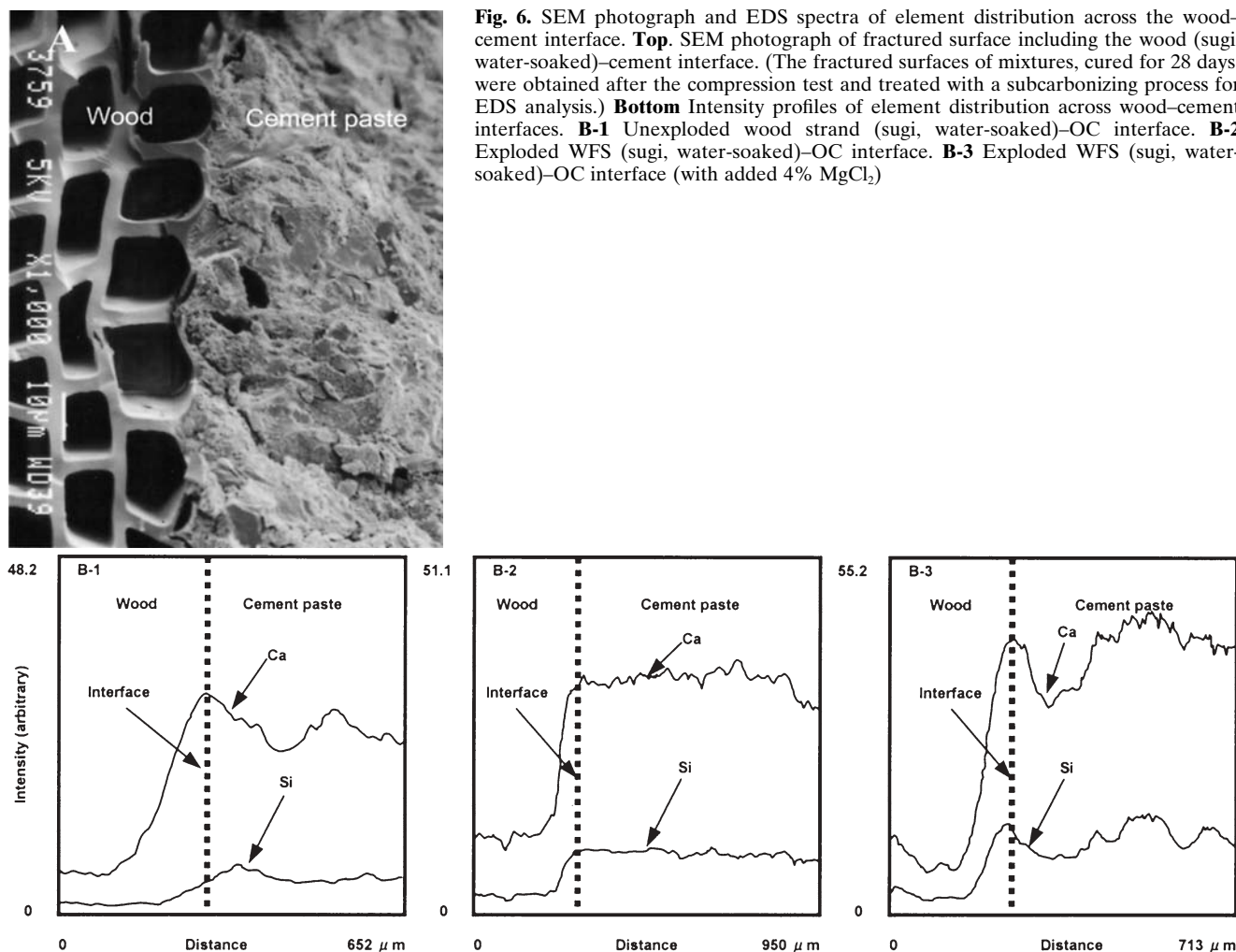
**Fig. 6.** SEM photograph and EDS spectra of element distribution across the wood–cement interface. **Top**. SEM photograph of fractured surface including the wood (sugi, water-soaked)–cement interface. (The fractured surfaces of mixtures, cured for 28 days, were obtained after the compression test and treated with a subcarbonizing process for EDS analysis.) **Bottom** Intensity profiles of element distribution across wood–cement interfaces. **B-1** Unexploded wood strand (sugi, water-soaked)–OC interface. **B-2** Exploded WFS (sugi, water-soaked)–OC interface. **B-3** Exploded WFS (sugi, water-soaked)–OC interface (with added 4% MgCl$_2$).

With the addition of the selected chemicals, the exploded WFS–QC mixture showed higher early-stage compressive strength than exploded WFS mixed, respectively, with OC or FC at curing ages of 3, 7, or 14 days. However, there were no significant differences in the compressive strength among the QC, OC, and FC mixtures with exploded WFS at curing ages of 180 days.

According to the results of XRD analysis, the poor formation of hydration products and the existence of large quantities of unhydrated cement clinker were thought to be the main causes of the low compatibility and low compressive strength of the exploded WFS–cement mixtures. The results of SEM revealed that the crystalline state of the hydration products was significantly influenced by the mixtures' compositions. The exploded WFS seriously hindered the formation of CH and CSH crystals and had a significant negative impact on the strength performance of the mixture. The EDS analysis performed at the wood–cement interface from a fractured surface showed that the element distributions near the wood surface appeared to be influenced by the mixture's composition and were related to the strength performance of the mixture as well.

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