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Sonat, Cem; Unluer, Cise

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Development of magnesium-silicate-hydrate (M-S-H) cement with rice husk ash

C. Sonat^a, C. Unluer^{a,*}

^a School of Civil and Environmental Engineering, Nanyang Technological University,
50 Nanyang Avenue, Singapore 639798, Singapore

* Corresponding author. Tel.: +65 91964970, E-mail address: ucise@ntu.edu.sg

Abstract

Rice husk ash (RHA) is a waste material obtained from the combustion of rice hulls. The properties of RHA, such as its crystallinity and reactivity, depend on the combustion conditions. This study investigated the use of RHA as a silica source in MgO-SiO₂ samples. Two different RHA sources (crystalline and amorphous) were used in comparison to microsilica (MS), which is commonly used in MgO-SiO₂ formulations to form magnesium silica hydrate (M-S-H). Isothermal calorimetry and pH measurements were used to analyze the progress of hydration. In addition to compressive strength measurements, microstructural analysis was performed via XRD, TG/DTG, FTIR and FESEM. Samples containing amorphous RHA as the silica source achieved the highest compressive strengths at early ages (34 MPa at 7 days), whereas those containing MS revealed the highest strengths in the long term (47 MPa at 56 days). This was in line with the faster dissolution rate of amorphous RHA in comparison to MS, as observed in pH measurements. The formation of M-S-H was clearly observed in all samples containing amorphous RHA and/or MS. The use of crystalline RHA led to low strengths, which was provided by brucite in the absence of M-S-H. Combination of amorphous RHA with MgO resulted in M-S-H formation, which was accompanied with a notable mechanical performance. Utilization of amorphous RHA in MgO systems could not only lead to strength gain, but also bring environmental and economic benefits.

Keywords: MgO; rice husk ash; M-S-H; hydration; performance; microstructure

1. Introduction

Magnesium based cement systems have been studied in different contexts, ranging from mixes that rely on carbonation for strength gain (Liska and Al-Tabbaa, 2008; Liska et al., 2008) to those involving the formation of magnesium silicate hydrate (M-S-H) within MgO-SiO₂ mixes (Jin and Al-Tabbaa, 2014; Tran and Scott, 2017; Zhang et al., 2014). M-S-H can be obtained via the reaction between a magnesium source and a silica source in the presence of water. Its use in several applications such as waste encapsulation (Zhang et al., 2011), castables (Zhang et al., 2017) and as a cementitious material (Jiangxiong et al., 2006; Zhang et al., 2014) has been reported. MgO-SiO₂ based mixes can present advantages over Portland cement (PC) based mixes due to their lower pH values, which makes them suitable for applications involving waste encapsulation (Walling et al., 2015; Zhang et al., 2011) and cellulose fibers (Mármol et al., 2016; Zhang et al., 2018). MgO-SiO₂ based formulations have also been reported to demonstrate satisfactory mechanical performance and stable hydration products under aggressive environments involving MgCl₂ and MgSO₄ solutions, under which a reduction in the performance of PC based concrete samples was observed (Sonat et al., 2018). The formation and properties of M-S-H within cement-based mixes depend on several parameters such as the chemical composition and physical properties of the raw materials, mix design (i.e. initial Mg/Si ratio), curing conditions and use of admixtures.

The properties of raw materials, such as MgO and SiO₂, are one of the main factors controlling the strength development of M-S-H formulations. Most of the previous studies (Jin and Al-Tabbaa, 2014; Li et al., 2014; Zhang et al., 2014) reported the use of reactive MgO in combination with microsilica (MS) as the main silica source that reacts with Mg-phases to form M-S-H in cementitious mixes. While it is known that MgO sources with a higher reactivity lead to increased reaction degrees (Jin and Al-Tabbaa, 2013, 2014), the effect of different silica sources on the performance of M-S-H based mixes has not been investigated fully until now.

The chemical composition and physical properties of the silica source, which are controlled by its production conditions, determine the extent of M-S-H formation, as well as its final properties. For instance, crystalline silica was reported to have a

limited reaction with MgO, thereby resulting in low strengths (i.e. 4 MPa at 90 days) in MgO-SiO₂ mixes, whereas higher reaction degrees and associated strength development was observed with the use of amorphous silica (Jin and Al-Tabbaa, 2014). The limited strength development in the former case was associated with the lack of interaction between MgO and crystalline silica, which led to even lower strengths than purely MgO-based samples.

In line with the general trend focusing on enhancing the sustainability of cement-based mixes, the use of alternative materials in MgO-SiO₂ systems must be explored for the development of formulations with lower environmental impacts. Other than the commonly used MS, supplementary cementitious materials (SCMs) such as pulverized fuel ash (PFA) can be used as a silica source to react with Mg-phases and result in the formation of M-S-H. However, the use of PFA or similar SCMs can present some challenges as their chemical composition does not only consist of silica but also often includes Al₂O₃, CaO and Fe₂O₃, resulting in the formation of phases other than M-S-H (Zhang et al., 2016). Although the use of PFA can be advantageous from an environmental standpoint, the variations in its composition and properties can limit strength development and result in lower strengths than samples containing MS.

Rice husk ash (RHA), which is a waste material obtained via the burning of rice hulls, is an alternative source that can be considered in the production of M-S-H due to its high SiO₂ content soluble in alkaline conditions and low environmental impact. Previous approaches involved the use of rice hulls as a fuel to power steam engines and disposal of RHA into water streams, which have other environmental implications. To alleviate this problem, many studies (Chao-Lung et al., 2011; Ganesan et al., 2008; Rodríguez de Sensale, 2010; Zain et al., 2011) investigated the use of RHA as a SCM in concrete mixes. In addition to presenting advantages in terms of mechanical performance, RHA enhanced the durability of concrete samples by contributing to the increase in density as a physical filler and via its pozzolanic activity in line with the amorphous silica content. Furthermore, the utilization of RHA in concrete formulations resulted in samples with lower environmental impacts due to the waste nature of RHA. These initiatives also reduced the amount of waste going

to landfills, the contamination of clean water sources from the uncontrolled disposal of RHA.

Within the cement context, the properties of RHA depend on the raw materials and conditions used in its production. The production of RHA involves the burning of rice hulls, which can take place via uncontrolled or controlled combustion. Uncontrolled combustion usually lasts for longer durations and often results in a crystalline product (e.g. cristobalite or tridymite) with a high residual carbon content and a blackish color, which makes the resulting RHA unsuitable for any pozzolanic reaction. Alternatively, controlled combustion leads to the production of a higher quality RHA with a high amorphous SiO_2 content. Hence, the quality (i.e. crystallinity/amorphous phase content) and therefore the suitability of the resulting RHA as a cementitious material depends on the burning conditions and the source of the rice husk (Chao-Lung et al., 2011). In this regard, the use of amorphous RHA improves the performance of cement-based mixes mostly due to its pozzolanic effect, whereas crystalline RHA mainly provides a filler effect (Isaia et al., 2003; Rodríguez de Sensale, 2006).

This study investigated the influence of two different types of RHA (i.e. crystalline and amorphous) as a silica source in MgO-SiO_2 formulations and provided a comparison with corresponding samples containing MS. The overall goal was to assess the potential use of RHA as a silica source in the production of M-S-H and evaluate its role in the strength development of MgO-SiO_2 samples. The mechanical performance of the prepared samples was examined via compressive strength development over a duration of 56 days. The reaction mechanisms were observed via isothermal calorimetry and pH measurements. The hydration products and microstructural development were investigated via x-ray diffraction (XRD), thermogravimetric analysis/derivative thermogravimetry (TG/DTG) and Fourier-transform infrared spectroscopy (FTIR). These results were further supported with an examination of the morphologies of the final phases via field emission scanning electron microscopy (FESEM).

2. Materials and Methodology

2.1. Materials

Reactive MgO (commercial name “calcined magnesite 92/200”) and MS (commercial name “940U”) were obtained from Richard Baker Harrison (UK) and Elkem Materials (Singapore), respectively. Crystalline RHA (RHA-c), having a specific surface area (SSA) of 8.6 m²/g, was obtained from Dinxings (Malaysia), whereas another source of RHA with a significant amorphous SiO₂ content (RHA-a) and a SSA of 24.1 m²/g was obtained from NanoSiltech (Malaysia). RHA-a was burned under controlled calcination conditions (i.e. 700 °C) using a plasma incinerator, while RHA-c was burned under uncontrolled conditions. In line with the particle size of each material, RHA-a was used in the prepared mixes as received, while RHA-c was ground using a ball mill grinder to reach a similar particle size with the other silica sources. The chemical composition and SSA of all raw materials are listed in Table 1. Sodium hexametaphosphate (SHMP), obtained from VWR (Singapore), was used as a superplasticizer in the prepared mixes.

2.2. Mix composition and sample preparation

The details of the mix compositions prepared in this study are presented in Table 2. All mixes included 50% MgO and 50% SiO₂ by mass. While the same MgO source was used as the main binder in all mixes, the rest of the mix composition included three different SiO₂ sources (MS, RHA-a and RHA-c). Samples M, Rc, Ra and Ra-M contained MS, RHA-c, RHA-a, and RHA-a and MS at equal amounts for their SiO₂ source, respectively. In all 4 samples, the water/solid (w/s) ratio was kept constant at 0.55. SHMP was included as a superplasticizer at an amount of 1% (i.e. by mass of solids).

Sample preparation initiated by dissolving SHMP in water, after which MgO was slowly added in during mixing. The silica source (MS, RHA-a and RHA-c) was then gradually added to the mix and the mixing continued for 10 minutes until a thoroughly mixed paste was obtained. The prepared paste was then poured into

50x50x50 mm cubic molds, which were kept in a sealed moist condition for 24 hours before being demolded. The demolded samples were cured in a sealed environment at an ambient temperature of 28 ± 2 °C and RH of $90\pm 5\%$ for up to 56 days until being tested.

2.3. Methodology

2.3.1. Particle size distribution (PSD)

The PSD of the raw materials was determined via a Malvern Mastersizer 2000. Before the analysis, the powders were added into water and mixed thoroughly to prepare a homogenous suspension. A few drops of this suspension were placed in the equipment for the PSD analysis.

2.3.2. Isothermal calorimetry

The heat flow and cumulative heat evolved due to the hydration of each sample were determined under isothermal conditions at 26 °C by an I-Cal 2000 High Precision Calorimeter in accordance with ASTM C1702 – 15a (2015). To initiate the analysis, the dry powders (i.e. 30 grams for each mix) were added to 37.5 grams of water, which was previously heated inside the calorimeter in order to produce mixes at the same temperature as the calorimeter temperature. The prepared mix was instantaneously placed into the isothermal calorimeter channel to measure the heat of hydration at the designated temperature.

2.3.3. pH

The pH values of the raw material and sample suspensions were determined at different ages (i.e. 0, 1, 2, 7, 14 and 28 days) by dispersing the powders in water. The prepared suspensions were continuously mixed until the measurements were taken. The pH was measured by using a Horiba F-52 pH meter with an accuracy of

± 0.01 . All the measurements were conducted in triplicates and the average values were recorded.

2.3.4. Compressive strength

The compressive strengths of the prepared paste samples were measured by uni-axial loading at 3, 7, 28 and 56 days, in accordance with ASTM C109/C109-M13 (ASTM, 2013). The equipment used for this purpose was a Toni Technik Baustoffprüfsysteme machine, operated at a loading rate of 55 kN/min. Four samples were tested for each data point and their average and standard deviation were reported.

2.3.5. XRD, TG/DTG, FTIR and FESEM analyses

Samples extracted from the cubes crushed during compressive strength testing were stored in acetone for at least 3 days to stop hydration, followed by vacuum drying in preparation for XRD, TG/DTG, FTIR and FESEM analyses.

XRD data was collected via a Bruker D8 advance instrument using Cu K α radiation (40 kV, 30 mA) with a scanning rate of 0.02° 2 θ /step from 10 to 80° 2 θ . The Reference Intensity Ratio (RIR) technique (Hubbard and Snyder, 1988; Johnson and Zhou, 2000; Snyder, 1992) was applied for the quantitative analysis of the crystalline phases by making use of a standard phase with a known proportion, whose integrated intensity was compared to that of a phase of interest. The internal standard used for quantification purposes was fluorite (CaF₂) included at 5 wt.% (Klug and Alexander, 1954). Calibration curves for MgO and Mg(OH)₂, the two main components used for quantitative analysis, are straight lines through the origin i.e. $y = kx$, where x is the RIR of the phase analyzed and y is the weight fraction of the component investigated. The value of k is 0.2886 for MgO and 0.3651 for Mg(OH)₂ (Klug and Alexander, 1954). The RIR was acquired by dividing the integrated intensity of the strongest line of the phase with that of the standard.

TG/DTG was conducted on a Perkin Elmer TGA 4000 equipment from 30 to 900 °C with a heating rate of 10 °C/min under nitrogen flow. The quantification of the formed phases within each sample was performed via the deconvolution of the DTG curves and the calculation of the area corresponding to different decomposition reactions under each deconvoluted curve.

FTIR spectra of the samples were obtained by a Perkin Elmer Frontier FTIR Spectrometer. The infrared spectra were the result of averaging 32 scans over a range of 4000–400 cm^{-1} , with a resolution of 4 cm^{-1} .

For the observation of the sample microstructures via FESEM, the vacuum dried samples were coated with platinum. The morphologies of the hydration products within the prepared samples were investigated via FESEM images obtained by a JEOL JSM-7600F equipment.

3. Results and Discussion

3.1. Characterization of raw materials

3.1.1. Particle size distribution (PSD)

Figure 1 shows the PSD of the raw materials MgO, MS, RHA-a and RHA-c. All four raw materials demonstrated compatible particle size distributions that partially overlapped. MgO had the smallest particle size amongst all the raw materials, with a median particle size ($d(50)$) value of 15.0 μm . Amongst the silica sources, RHA-a, which was aimed to substitute MS as a silica source, had a very similar PSD to MS. RHA-a and MS revealed similar $d(50)$ values of 63.3 and 65.9 μm , respectively. The crystalline RHA source, RHA-c, had a slightly smaller PSD compared to RHA-a and MS, with a $d(50)$ value of 28.7 μm .

3.1.2. XRD

Figure 2 shows the XRD diffractograms of the raw materials. MgO displayed high intensity peaks of periclase and minor peaks of magnesite, which was inherited from the parent material due to its incomplete decomposition during the calcination process. Unlike the crystalline peaks observed in MgO, MS revealed a wide hump between 15 and 27° 2 θ , which was attributed to an amorphous silica phase. The composition of RHA-c was composed of crystalline phase of cristobalite, a polymorph of quartz. Differing from RHA-c, RHA-a contained a combination of low intensity crystalline peaks that matched well with the major peaks of cristobalite, as well as an amorphous hump at around 15-27° 2 θ , which corresponded to amorphous silica, as seen earlier in MS. Albeit the presence of some intensity crystalline peaks, the amorphous nature of RHA-a could present an advantage in the formation of hydrate phases involving silica.

3.1.3. FTIR

Figure 3 shows the FTIR spectra of the raw materials. MgO showed main bands at 1424 cm⁻¹ and 459 cm⁻¹, which were ascribed to Mg-O bending and stretching vibrations, respectively (Jin and Al-Tabbaa, 2014; Li et al., 2017). In addition to the sharp band at 3693 cm⁻¹, the small low intensity band at 1620 cm⁻¹ and the broad band at 3420 cm⁻¹, which were ascribed to OH vibrations (Brew and Glasser, 2005), indicated the partial hydration of MgO due to the high ambient humidity. Amongst the silica sources, MS and RHA-a exhibited very similar FTIR spectra. Both materials demonstrated a wide band between 1235 and 1000 cm⁻¹ and an absorption band at 800 cm⁻¹, which were attributed to Si-O stretching vibrations. The absorption band at 475 cm⁻¹ was ascribed to O-Si-O bending vibrations (Walling et al., 2015). Differing from these amorphous silica sources, RHA-c revealed an additional absorption band at 622 cm⁻¹ attributed to Si-O bending vibrations (Brew and Glasser, 2005). Furthermore, the band ascribed to Si-O vibrations had a sharp center at 1085 cm⁻¹ in RHA-c, as opposed to the broad hump at 1235-1000 cm⁻¹ observed in MS and RHA-a.

3.1.4. Microstructure

The microstructural images of the raw materials are shown in Figure 4. The microstructure of MgO (Figure 4 (a)) consisted of aggregated grains of microparticles, which was consistent with those observed in other studies (Alvarado et al., 2000; Mo et al., 2010). MS (Figure 4 (b)) was composed of spherical SiO₂ particles with clearly defined boundaries. Alternatively, the morphology and arrangement of particles within RHA-a (Figure 4 (c)) resembled those of MgO, in which grains of different sizes were stacked together. Unlike RHA-a, the morphology of RHA-c (Figure 4 (d)) was made up of inhomogeneous particles with larger sizes that agglomerated into a dense structure. These variations amongst the microstructures of the silica sources were in line with the differences observed earlier in the XRD patterns (Figure 2) and FTIR spectra (Figure 3).

3.2. Analysis of samples

3.2.1. Isothermal calorimetry

Figure 5 shows the heat flow and the cumulative heat associated with the hydration of MgO-SiO₂ pastes measured for up to 72 hours via isothermal calorimetry. As seen in Figures 5 (a) and (b), variations in the initial hydration peak were recorded depending on the mix composition (i.e. binder component). Ra, Ra-M and M samples, containing amorphous sources of silica, revealed the highest initial heat flow. The lowest initial peak of Rc sample was attributed to the limited reaction of MgO with the crystalline silica. Alternatively, the presence of amorphous silica within Ra, Ra-M and M samples led to peaks with larger intensities, which was an indication of the higher degree of the initial hydration reaction within these samples.

The cumulative heat released during hydration, shown in Figure 5 (c), continued to increase even after 72 hours, indicating the continuation of the hydration process. Out of all samples, M sample revealed the highest cumulative heat throughout the measured period. The higher amount of heat released by M sample could be an indication of the higher degree of reaction of Mg²⁺ with MS, in comparison to RHA-a

and RHA-c that formed the binder composition within the other samples. Albeit its low initial exothermic peak, Rc sample revealed a similar cumulative heat as Ra and Ra-M samples, which was mainly associated with the hydration of MgO. Although the use of RHA-a in Ra and Ra-M samples led to the highest initial peaks at < 1 hour, this trend did not continue over time. The rapid increase in the initial heat flow of these samples could be an indication of the increased rate of hydration at early ages in the presence of RHA-a, which was not sustained at longer durations.

3.2.2. pH

Figures 6 (a) and (b) show the pH values of the raw materials and the samples over 28 days of curing, respectively. The initial pH values of the raw materials, as seen in Figure 6 (a), ranged between 9.5-11.4. MgO had the highest pH values amongst all, which demonstrated an increase in the initial pH to around 11.6 due to the release of OH⁻ ions. This was followed by a decrease and the stabilization of pH at a range of 11.0-11.2 at 28 days. While the pH of a pure MgO suspension usually stabilizes at around ~10.5, the observed higher pH values could be attributed to the presence of impurities. A similar trend to that of MgO was observed in RHA-a and RHA-c, whose similar pH values were levelled at around 9.6 and 10.1 after a few days of measurement, respectively. Differing from the RHA sources, the pH of MS continued to decrease even after 7 days, reaching below 8.0 at 28 days. The continuous reduction in the pH of MS was attributed to the dissolution of silica, which continued for a longer duration than those of RHA-a and RHA-c, whose pH stabilized in a shorter period.

The pH values of MgO-SiO₂ samples during the first 28 days of curing are shown in Figure 6 (b). The initial increase observed in the pH of all samples was associated with the dissolution of MgO, which resulted in the release of OH⁻ ions. A decrease in the pH of Ra, Ra-M and M samples was recorded after 1 day, which could be due to the dissolution of SiO₂ and subsequent formation of M-S-H. Among these 3 samples, Ra and M samples revealed the highest and lowest pH values throughout the entire measurement period, respectively. Ra-M sample, whose silica source was composed of an equal combination of RHA-a and MS, demonstrated intermediate

pH values (i.e. pH of Ra > Ra-M > M), which was an indication of the role of silica in determining the final pH. The lowest pH values of M samples, whose reduction could be an indication of the extent of hydration, were in line with the trend observed in the pH of the raw materials (Figure 6 (a)), where MS revealed the lowest pH amongst all silica sources. Unlike the other samples, the use of RHA-c in Rc sample led to pH values similar to the pH of MgO due to the lack of reaction between Mg-phases and silica.

3.2.3. Compressive strength

Figure 7 shows the compressive strengths of all samples cured for up to 56 days. Ra sample, which contained RHA-a as its silica source, exhibited a rapid strength gain and highest early strengths that reached 22 and 35 MPa at 3 and 7 days, respectively. This fast strength development of Ra sample could be attributed to a combination of physical and chemical effects. In terms of its physical contribution, RHA-a could act as a filler, thereby contributing to strength development via the formation of a dense structure. Furthermore, the reaction between the amorphous SiO₂ in RHA-a and MgO could lead to the formation of M-S-H, which is known to provide strength in MgO-SiO₂ formulations (Sonat et al., 2017; Zhang et al., 2014). The compressive strength of Ra sample remained relatively stable at around 33 MPa at 28 days, while a reduction was observed in the longer durations, resulting in a strength of 26 MPa at 56 days. This unexpected reduction could be associated with the volume instability of Ra sample due to the formation of hydrate phases in the later ages. At early ages (≤ 7 days) the rapid formation of M-S-H may have covered the surface of unreacted MgO particles, resulting in a reduced amount of surface area available for further hydration and hindering access to unhydrated zones. At longer curing durations (≥ 28 days) with the penetration of pore water towards the unhydrated MgO surfaces, further hydration might have taken place, resulting in the initiation of cracks due to the expansive nature of brucite formation.

Alternatively, M sample, which consisted of MS as its silica source, exhibited a consistent strength development over 56 days. This strength gain demonstrated by M sample was an indication of the continuous formation of hydration products even

in the longer periods (e.g. 56 days). The continuation of the hydration reaction within M sample led to the highest strengths amongst all samples at 56 days (47.5 MPa), which was 64% and 84% higher than the corresponding strengths of Ra-M and Ra samples, respectively.

Ra-M sample, which consisted of a combination of RHA-a and MS at equal amounts as its silica source, exhibited a similar compressive strength development to M sample during the first 7 days of curing. Although the strength development of Ra-M sample continued after 7 days, it revealed lower strengths than M sample and equivalent strengths to Ra sample as the duration of curing increased beyond 7 days. This relatively lower rate of strength development of Ra-M sample after 7 days could be attributed to its lower MS content when compared to M sample. The observed strength developments of M and Ra samples revealed the contribution of RHA-a and MS to strength at shorter (i.e. <7 days) and longer durations (i.e. 56 days), respectively. Consisting of both RHA-a and MS, Ra-M sample demonstrated a compressive strength development trend resembling both Ra and M samples; though the trends were not as obvious as in Ra and M samples as the initial RHA-a and MS contents were both halved within Ra-M sample.

Rc sample, which involved the use of RHA-c, revealed the lowest strengths among all samples throughout 56 days. While these samples were too weak for strength testing at 3 days, they could only reach 3 and 12.5 MPa at 7 and 56 days, respectively. This limited strength development was associated with the inability of crystalline silica to react with Mg-phases and result in the formation of any strength providing hydration products. Therefore, any strength, albeit low, was provided by the formation of brucite, which is known to offer limited strength in MgO systems (Liska et al., 2008). These variations in the strength results amongst different samples highlight the role of reactive forms of silica in the strength development of MgO samples.

Overall, the compressive strength results showed that Ra sample, containing RHA-a, revealed the highest strengths at early ages (≤ 7 days); whereas M sample, containing MS, demonstrated a continuous strength gain and led to the best performance amongst all samples in the longer durations (> 7 days). Ra-M sample

exhibited a moderate strength gain, resulting in lower early age (≤ 7 days) strengths than Ra sample and lower strengths than M sample in the longer durations. Although the 56-day strengths of Ra-M could not reach those of M sample, a constant increase in strength was observed throughout the 56 days, unlike Ra sample, which was associated with the partial presence of MS within Ra-M sample.

The strength development was mainly due to the formation of hydrate phases (M-S-H) via the reaction of silica with Mg-phases during the curing process. MS continued to react with MgO and form hydration products in the longer durations, whereas the extent of the reaction between RHA-a and MgO was limited to early ages. These findings were in line with the pH measurements shown in Figure 6 (a), where the pH of the MS solution continued to decrease even after 7 days, while the pH of the RHA-a solution stabilized after a few days. This lack of change in the pH was an indication of the limited dissolution of SiO_2 within the RHA-a solution in the longer periods. A similar outcome was seen in the pH values of the extracted samples shown in Figure 6 (b), where M sample revealed a continuous decrease and the lowest pH results amongst all samples. Despite the comparatively lower strengths of samples containing RHA-a than those containing MS, the high early strength gain and the satisfactory long term strengths of the former indicate the potential of RHA-a to replace MS in MgO- SiO_2 systems.

3.2.4. XRD

Figure 8 shows the XRD diffractograms of all samples cured for 7 and 56 days. Some of the main phases observed were MgO (at 36.9° , 42.9° , 62.3° , 74.7° and 78.6° 2θ) and brucite (at 18.6° , 38.0° , 50.8° , 58.6° and 68.2° 2θ), in addition to fluorite (at 28.3° , 47.0° and 55.8° 2θ), which was used as a reference. Within samples containing amorphous silica (Ra, Ra-M and M), broad peaks indicative of amorphous M-S-H (at $17\text{--}28^\circ$, $32\text{--}39^\circ$ and $58\text{--}62^\circ$ 2θ) were identified. While the amorphous silica peak within these silica sources, located at around $15\text{--}27^\circ$ 2θ as shown earlier in Figure 2, largely disappeared in all mixes, the presence of MgO even after 56 days of curing was an indication of its incomplete dissolution and hydration.

Amongst the samples cured for 7 days (Figure 8 (a)), the presence of amorphous M-S-H peaks (especially at $58-62^{\circ} 2\theta$) were more obvious within Ra and Ra-M samples, which could indicate that RHA-a contributed to M-S-H formation more rapidly compared to MS at early ages. Similarly, while the presence of brucite was minimal within Ra and Ra-M samples, M sample revealed clear peaks of brucite. The formation of M-S-H and lack of brucite within samples containing RHA-a could be an indication of the rapid reaction of Mg-phases with silica, forming M-S-H at early ages. This rapid formation of M-S-H in the presence of RHA-a was also reflected in the high early strengths of Ra sample, as seen in Figure 7. Alternatively, in addition to brucite, the presence of the amorphous silica peak at around $22^{\circ} 2\theta$ within M sample suggested the incomplete dissolution of silica at 7 days. These observations were in line with the pH of the raw materials (Figure 6 (a)), where the pH of the MS solution continued to decrease, as opposed to the stable pH values revealed by the RHA-a solution after 7 days. Rc sample contained high intensity cristobalite peaks, which originated from the raw material RHA-c, in addition to the MgO and brucite peaks. Differing from the other 3 samples, Rc sample did not reveal an observable M-S-H peak, which was due to the lack of the dissolution of silica and the absence of any reaction between silica and Mg-phases. The formation of brucite as the main hydrate phase within this sample could explain its limited early strengths.

The XRD diffractograms of all samples cured for 56 days (Figure 8 (b)) revealed the presence of MgO and brucite, indicating incomplete hydration even after 56 days of curing. Similar to the observations at 7 days, the presence of M-S-H was seen within Ra and Ra-M samples at 56 days without a significant change in the amorphous humps, whereas M sample revealed an obvious increase in the intensity of its M-S-H peaks from 7 to 56 days. This continuous formation of M-S-H could explain the continuous increase in the compressive strength of M sample up to 56 days. The intensity of the brucite peak reduced with an increase in the amount of RHA-a content, almost disappearing in Ra sample, whose silica source was only RHA-a. This observation suggested that the type and properties of the silica source played a role in the extent of the hydration reaction and the formation of different hydrate phases. Rc sample revealed the highest brucite peak amongst all samples. When coupled with the cristobalite peaks, whose intensity did not show any major decrease

over time, the presence of high intensity brucite peaks suggested that RHA-c did not react with Mg-phases to form M-S-H even after 56 days. This lack of reaction corresponded well with the limited compressive strength development revealed by Rc sample.

The amounts of MgO and $\text{Mg}(\text{OH})_2$ present in all samples at 7 and 56 days, as quantified by XRD-RIR, are listed in Table 3. At 7 days, samples that incorporated amorphous silica sources (Ra, Ra-M and M) revealed similar MgO contents (~25%). Ra and Ra-M samples, which included the use of RHA-a, contained ~3% brucite, whereas this value was higher at ~8% for M sample at 7 days. The lowest content of brucite within Ra could be an indication of its increased conversion to M-S-H, which could explain the highest strength results of Ra at early ages. Alternatively, the high MgO content (~38%) of Rc sample was an indication of the lack of hydration and thereby the formation of strength providing hydrate phases (M-S-H) within this sample.

When the phase contents obtained at 56 days were compared, the lowest MgO contents (~10%) were revealed by Ra-M and M samples, which was due to the continuation of the hydration reaction and thereby the utilization of MgO in the longer term. Differing from these samples, Ra sample contained a higher MgO content of ~17%, which could explain the trends observed in the strengths of these samples at 56 days. This relatively higher MgO content of Ra sample could suggest that the rapid formation of hydration products at early ages may have hindered the continuation of the hydration reaction by forming a layer on the surface of unreacted particles (Mo et al., 2010). While the brucite contents of all other samples increased over time from 7 to 56 days, a decrease was observed in M sample. This could be an indication of the utilization of brucite in the formation of M-S-H, which was supported by the obvious increase in the amount of M-S-H observed in the XRD patterns and the increase in the compressive strength of M sample from 7 to 56 days. Alternatively, the increase in the brucite content of Rc sample and its higher MgO content in comparison to other samples (~28% vs. 10-17%) was an indication of the lack of reaction between the crystalline silica and Mg-phases and thereby the inadequate strength development, which mainly relied on the formation of brucite as opposed to M-S-H. The modest increase observed in the brucite content of Ra and

Ra-M samples (2.0-2.9%) was an indication of the continuation of the hydration of MgO, resulting in the formation of brucite; while brucite was consumed (i.e. at a slightly lower rate than MgO) to form M-S-H.

3.2.5. TG/DTG

Figures 9 and 10 show the TG/DTG plots of all samples cured for 7 and 56 days, respectively. When the total mass losses revealed by all samples were compared, Rc sample revealed the lowest mass loss amongst all samples at both curing durations. This difference was more significant at 7 days, after which Rc sample exhibited a notable formation of brucite and revealed closer mass loss values to the rest of the samples at 56 days. The lower mass loss of Rc sample than other samples were in line with its inferior mechanical performance and was attributed to the inert nature of the crystalline silica source, which did not contribute to the hydration reaction. Alternatively, samples with amorphous silica sources (Ra, Ra-M and M) revealed similar total mass loss values at both curing durations. Although the total mass loss values of these samples were similar, the types and contents of the formed hydrated phases exhibited some differences, as inferred from the varying intensities of DTG peaks shown in Figures 9 (b) and 10 (b). Amongst these 3 samples, those that demonstrated the highest compressive strengths (i.e. Ra sample at 7 days and M sample at 56 days) exhibited slightly lower total mass loss values at both curing durations. This observation suggested that mechanical performance was not only correlated to the total mass loss, but was determined by the contents of different types of hydrate phases (M-S-H vs. brucite) that formed. In MgO-SiO₂-H₂O systems, the main steps involved during thermal decomposition can be summarized as below (Lothenbach et al., 2015; Nied et al., 2016; Zhang et al., 2014):

1. 30-300 °C: Loss of interlayer water of M-S-H
2. 300-750 °C: Decomposition of brucite and separation of hydroxyl groups in M-S-H (i.e. separation of Mg-OH in M-S-H (Lothenbach et al., 2015))
3. 750-900 °C: Dehydroxylation of silanol groups

In addition to these decomposition reactions, additional mass loss associated with adsorbed water could be seen in the 30-300 °C range. Although all samples were dried before TGA, it is common to observe some mass loss below 150 °C due to the dehydration of adsorbed water. Furthermore, the contribution of the loss on ignition (LOI) associated with the impurities within the raw materials, was also considered in the quantification of hydrate phases within each sample. For instance, the decomposition of undecomposed magnesite (i.e. used as a raw material during the production of MgO) within MgO, whose presence was shown earlier in Figure 2, also contributed to the total mass loss within the 300-750 °C range, as observed from the 2 small peaks at ~550 °C and ~650 °C on the DTG plots (Figures 9 (b) and 10 (b)). Accordingly, the LOI of MgO, MS, RHA-a and RHA-c were measured as 6.3%, 2.2%, 5.2% and 1.3%, respectively. These decomposition temperatures and corresponding mass loss values revealed by the TG/DTG analysis were used to quantify the hydrate phases within each sample, whose details are provided in the following section.

3.2.6. Phase quantifications from DTG

Figures 11 and 12 show the deconvoluted DTG curves for all samples cured for 7 and 56 days, respectively. The plots included the original data (represented by the black dots) as well as the cumulative fit (represented by the solid lines) for each sample. In addition to these two sets, the deconvoluted curves, whose combination formed the cumulative fit, were presented. Each sample consisted of a series of curves, which represented different decomposition reactions. For instance, two curves were used to represent the dehydration of adsorbed water and loss of interlayer water of M-S-H below 300 °C within Ra, Ra-M and M samples. A peak centered at ~400 °C, was used to represent the dehydroxylation of brucite in all samples. To represent the LOI of the raw materials and the dehydroxylation of M-S-H, a combination of two wide curves were used. For Rc sample at 56 days (Figure 12 (d)), three curves represented the dehydration of adsorbed water, dehydroxylation of brucite and LOI of raw materials. The lower number of curves for Rc sample was due to the lack of M-S-H formation within this sample.

Table 4 shows the mass loss values based on the deconvoluted DTG curves for all samples cured for 7 and 56 days. Rc sample revealed the lowest mass loss values between 30-300 °C than the rest of the samples at both curing durations, which could be attributed to the lack of M-S-H formation in the presence of crystalline silica. Other samples containing amorphous silica (Ra, Ra-M and M) demonstrated higher mass loss values within this initial temperature range, which included the dehydration of adsorbed water and the loss of interlayer water from M-S-H. The mass loss due to brucite dehydroxylation was the lowest for Ra sample at 7 days, which was in line with the XRD observations. Alternatively, Rc sample demonstrated the highest mass loss from brucite dehydroxylation at 56 days (5.6% vs. 2.2-2.5% of other samples), which could be attributed to the lack of reaction between brucite and crystalline silica, as was also shown earlier in XRD and strength results. Similar to the phase quantifications obtained via XRD-RIR (Table 3), the mass loss associated with brucite increased from 7 to 56 days for all samples except for M sample, whose reduced brucite content could indicate the formation of M-S-H over time.

The last two columns in Table 4 show the mass loss due to the dehydroxylation of M-S-H within all samples at 7 and 56 days. These values also involved the mass loss from the LOI of the raw materials. This was obvious from the mass loss values of Rc sample, for which LOI was the main contributor to mass loss within this range as M-S-H formation was not observed in the presence of crystalline silica. Amongst the other 3 samples, the highest increase in the mass loss associated with M-S-H dehydroxylation from 7 to 56 days was revealed by M sample. This increase could refer to the continuous formation of M-S-H within M sample, which was consistent with the XRD patterns and strength results.

3.2.7. FTIR

Figures 13 (a) and (b) show the FTIR spectra of all samples cured for 7 and 56 days, respectively. At 7 days, all samples exhibited structural OH⁻ bands at ~1640 and ~3400 cm⁻¹ (Jin and Al-Tabbaa, 2014), which had higher intensities than those seen in the raw materials (Figure 3). This could indicate the formation of new OH⁻ bonds,

which could explain the strength development at 7 days. The Mg-OH stretching band at 3693 cm^{-1} (Brew and Glasser, 2005), indicating the presence of brucite, was more pronounced in Rc sample in comparison to others at 7 days. The band at $\sim 1430\text{ cm}^{-1}$, which could be ascribed to Mg-O bending vibration, was present in all samples at 7 days. This band was associated with unreacted MgO, in line with the XRD observations. The absorption bands at ~ 800 and $\sim 475\text{ cm}^{-1}$, which were also observed in the silica sources (MS, RHA-a and RHA-c), were present in all samples, albeit at lower intensities than the raw materials. This suggested that silica was not fully consumed in any of the samples at 7 days. All samples exhibited bands that were ascribed to Si-O bands between the wide range of $\sim 980\text{-}1120\text{ cm}^{-1}$ with slight shifts amongst the samples. These bands could refer to the silica sources or the newly formed Si-O chains in M-S-H. Within the $980\text{-}1120\text{ cm}^{-1}$ range, two shoulders were observed in all samples except for Ra-M sample, in which three shoulders were observed. The additional shoulder could be due to the two different silica sources (RHA-a and MS) included in Ra-M sample. A small peak at $\sim 890\text{ cm}^{-1}$ attributed to the Si-OH group of layered M-S-H (Jin and Al-Tabbaa, 2014; Li et al., 2017), which was not present in any of the raw materials, appeared in all samples, indicating the formation of a new phase.

The FTIR spectra of all samples at 56 days (Figure 13 (b)) exhibited similar bands as those observed at 7 days, with some minor changes. The intensities of the OH bonds at ~ 1640 and $\sim 3400\text{ cm}^{-1}$ increased for all samples when compared to 7 days, indicating the continuation of hydration from 7 to 56 days. The intensity of the band at 3693 cm^{-1} was higher for Rc sample than all other samples at 56 days. This was an indication of the higher brucite content within Rc sample in comparison to other samples at 56 days, which was in line with the XRD and TG/DTG observations. The absorption band at $\sim 800\text{ cm}^{-1}$, attributed to Si-O stretching vibrations in the silica sources, diminished for M sample. These changes were an indication of the utilization of MS within M sample after 56 days of curing. This absorption band ($\sim 800\text{ cm}^{-1}$) could still be observed in Ra sample, whereas it had a prominent presence in Rc sample, indicating that silica sources were not fully utilized even after 56 days. The existence of the adsorption band at $\sim 800\text{ cm}^{-1}$, which was fully diminished in M sample, within Ra sample, indicated that MS dissolved at a higher extent in comparison to RHA-a at longer durations. The lack of any significant change in the

intensity of the same absorption band ($\sim 800\text{ cm}^{-1}$) between 7 and 56 days in Ra sample was in line with the stability of the pH of the RHA-a suspension after 7 days. Ra, Ra-M and M samples demonstrated similar patterns within the ~ 980 to 1120 cm^{-1} range that was ascribed to Si-O stretching vibrations, which suggested that RHA-a and MS resulted in final hydrate phases (M-S-H) with similar structures.

3.2.8. Microstructure

Figure 14 shows the FESEM images of all samples after 7 days of curing. Ra sample (Figure 14 (a)) demonstrated a homogenous microstructure composed of particles that were more densely packed together when compared to other samples, which could explain its high early strengths. In Ra-M sample (Figure 14 (b)), the partial formation of hydration products could be seen surrounding other particles, in addition to the SiO_2 spheres that resembled the microstructures of both MS and RHA-a. The presence of loose, unreacted spherical SiO_2 particles was more clearly observed in M sample (Figure 14 (c)) in comparison to Ra-M sample. Other than the unreacted spherical silica particles, a cloudy, gel-like structure, which could be attributed to the partial formation of M-S-H, was observed. The existence of SiO_2 particles within Ra-M and M samples was an indication of the incomplete utilization of silica. In addition to unreacted silica particles, the less abundant formation of hydration products was the main reason for the lower compressive strengths of these samples when compared to Ra sample at 7 days. Unlike Ra-M and M, Ra sample showed the well-distributed formation of M-S-H gel, whereas the presence of unreacted silica particles was less abundant. Alternatively, Rc sample (Figure 14 (d)) did not indicate the formation of any gel-like hydration products, but instead exhibited brucite and unreacted MgO particles, which were loosely arranged into clusters with rough and inhomogeneous surfaces. These findings were in line with the XRD and TGA results, also explaining the variations in the performance of each sample.

Figure 15 shows the FESEM images of all samples after 56 days of curing. Ra sample (Figure 15 (a)) exhibited a microstructure consisting of particles of different size and shape stacked together. Differing from the well-packed and dense microstructure it had demonstrated at 7 days, Ra sample revealed a loosely packed

structure at 56 days. This change over time could explain the reduction in the strength of Ra sample from 7 to 56 days. Alternatively, M sample (Figure 15 (c)) exhibited a dense structure composed of a well-connected network without many loose particles of unreacted brucite/MgO. This network was mainly established via the dense formation of M-S-H throughout the structure, which could explain the continuous strength development of M sample until 56 days. Unreacted spherical silica particles were much less abundant compared to the microstructure observed at 7 days, indicating that the formation of M-S-H proceeded over time. The continuous formation of M-S-H gel corresponded well with the highest strengths obtained by M sample, which outperformed all other samples at 56 days. Ra-M sample resembled the microstructures of both Ra and M samples at different locations, revealing a continuous layer on the left hand-side and a rough morphology consisting of loosely packed small particles on the right hand-side of Figure 15 (b). The partial formation of M-S-H gel was accompanied with a cluster of unhydrated particles as well as brucite within Ra-M sample, which indicated that different SiO₂ sources may have led to the formation of different hydrate phases. The increase in the compressive strength of Ra-M sample from 7 to 56 days could be attributed to the partial formation of M-S-H observed in its microstructure. Rc sample (Figure 15 (d)) presented the formation of brucite along with unreacted MgO and silica particles, resulting in a rough and discontinuous microstructure. The absence of a well-connected M-S-H network was the main reason for the lower strengths of Rc sample even after 56 days of curing.

3.3 Environmental and economic aspects

Over 740 million tonnes of rice paddies were produced worldwide in 2016 (FAO, (2016)). About 22% of this amount constituted of rice hulls, which led to the production of RHA after being burned. This significant amount of ash is treated as a waste, thereby creating environmental concerns as it does not decompose and occupies large areas of landfills. However, this material has a great potential to be utilized in alternative applications within the building industry as a majority of its composition is made up of amorphous silica, which can participate in the formation of strength providing phases in cement-based mixes. A recent study (Gursel et al.,

2016) that provided a detailed life-cycle assessment (LCA) suggested that the global warming potential (GWP) of PC mixes could be lowered with the use of SCMs such as RHA, without jeopardizing mechanical and durability properties. Furthermore, microsilica, which is commonly used in MgO-SiO₂ formulations, is a relatively expensive material when compared to PC and other SCMs (Agarwal and Gulati, 2006). Therefore, considering the environmental concerns associated with the disposal of large volumes of RHA and the high market price of microsilica, RHA containing amorphous sources of silica, has a large potential to be used in MgO-SiO₂ based binders, as revealed by this study.

4. Conclusions

This study investigated the performance and microstructural development of MgO-SiO₂ based samples over a 56-day period. Each sample included MgO and a different source of SiO₂, namely microsilica, amorphous RHA and crystalline RHA. The isothermal calorimetry, pH and strength results were supported with microstructural analyses involving XRD, TG/DTG, FTIR and FESEM. In addition to the evolution of sample microstructure, the data corresponding to the quantification of hydrate phases within each formulation, obtained via thermal analysis and XRD-RIR, was used to explain the variations in sample performance.

Samples with crystalline RHA revealed the lowest strengths amongst all samples due to the lack of any reaction between crystalline silica and Mg-phases. Based on the microstructural analyses performed, the only hydrate phase that formed within these samples was brucite, which did not provide any major binding strength. A different scenario was observed in samples with amorphous silica sources, which achieved higher strengths due to the formation of M-S-H, whose formation was clearly detected via XRD, TG/DTG and FESEM observations. Samples incorporating amorphous RHA exhibited a rapid early compressive strength development reaching 22 and 34 MPa at 3 and 7 days, respectively. Although the formation of M-S-H initially took place at a slower rate in the presence of microsilica, these samples achieved the highest strength, 47 MPa, amongst all samples at 56 days due to the continuous formation of M-S-H. This difference between the formation rate of M-S-H

within different samples could be attributed to the variations in the properties and the dissolution rates of various silica sources.

The results of this study clearly demonstrated the potential of amorphous RHA to be utilized as a silica source in MgO-SiO₂ formulations. Samples containing amorphous silica sources reached promising strengths, which were attributed to the development of a dense microstructure enabled by the formation of M-S-H. Amorphous RHA, which is considered as a waste material, can effectively replace microsilica in MgO-SiO₂ formulations, presenting environmental and economic benefits in the production of MgO-based samples. While amorphous RHA sources can be utilized in MgO-SiO₂ formulations to form M-S-H, crystalline RHA sources do not have the same effect. Further studies on the determination of ideal conditions for the production of fully amorphous RHA and the optimization of mix designs involving its use can further improve the mechanical performance and environmental impacts of MgO-SiO₂ formulations.

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References

- Agarwal, S.K., Gulati, D., 2006. Utilization of industrial wastes and unprocessed micro-fillers for making cost effective mortars. *Constr. Build. Mater.* 20(10), 999-1004.
- Alvarado, E., Torres-Martinez, L.M., Fuentes, A.F., Quintana, P., 2000. Preparation and characterization of MgO powders obtained from different magnesium salts and the mineral dolomite. *Polyhedron* 19(22), 2345-2351.
- ASTM, 2013. Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (using 2-in. Or [50-mm] Cube Specimens). ASTM International.

ASTM C1702 – 15a, 2015. Standard Test Method for Measurement of Heat of Hydration of Hydraulic Cementitious Materials Using Isothermal Conduction Calorimetry. ASTM Committee C01, West Conshohocken, PA 19428-2959, United States, p. 8.

Brew, D., Glasser, F., 2005. Synthesis and characterisation of magnesium silicate hydrate gels. *Cement and Concrete Research* 35(1), 85-98.

Chao-Lung, H., Anh-Tuan, B.L., Chun-Tsun, C., 2011. Effect of rice husk ash on the strength and durability characteristics of concrete. *Constr. Build. Mater.* 25(9), 3768-3772.

FAO, (2016). <<http://www.fao.org/faostat/en/#data/QC>>. (Accessed 26/12/2017).

Ganesan, K., Rajagopal, K., Thangavel, K., 2008. Rice husk ash blended cement: assessment of optimal level of replacement for strength and permeability properties of concrete. *Constr. Build. Mater.* 22(8), 1675-1683.

Gursel, A.P., Maryman, H., Ostertag, C., 2016. A life-cycle approach to environmental, mechanical, and durability properties of “green” concrete mixes with rice husk ash. *Journal of Cleaner Production* 112, 823-836.

Hubbard, C.R., Snyder, R.L., 1988. RIR-measurement and use in quantitative XRD. *Powder Diffraction* 3(02), 74-77.

Isaia, G.C., Gastaldini, A.L.G., Moraes, R., 2003. Physical and pozzolanic action of mineral additions on the mechanical strength of high-performance concrete. *Cement and Concrete Composites* 25(1), 69-76.

Jiangxiong, W., Yimin, C., Yongxin, L., 2006. The reaction mechanism between MgO and microsilica at room temperature. *J. Wuhan. Univ. Technol. Mat. Sci. Edit.* 21(2), 88-91.

Jin, F., Al-Tabbaa, A., 2013. Thermogravimetric study on the hydration of reactive magnesia and silica mixture at room temperature. *Thermochim. Acta* 566, 162-168.

Jin, F., Al-Tabbaa, A., 2014. Strength and hydration products of reactive MgO–silica pastes. *Cement and Concrete Composites* 52, 27-33.

Johnson, Q., Zhou, R., 2000. Checking and estimating RIR values. *Advances in X-ray Analysis* 42, 287-296.

Klug, H.P., Alexander, L.E., 1954. X-ray diffraction procedures. NY : Wiley, New York.

- Li, Z., Yu, Q., Chen, X., Liu, H., Zhang, J., Zhang, J., Yang, Y., Wei, J., 2017. The role of MgO in the thermal behavior of MgO–silica fume pastes. *Journal of Thermal Analysis and Calorimetry* 127(3), 1897-1909.
- Li, Z., Zhang, T., Hu, J., Tang, Y., Niu, Y., Wei, J., Yu, Q., 2014. Characterization of reaction products and reaction process of MgO–SiO₂–H₂O system at room temperature. *Constr. Build. Mater.*(61), 252-259.
- Liska, M., Al-Tabbaa, A., 2008. Performance of magnesia cements in pressed masonry units with natural aggregates: Production parameters optimisation. *Constr. Build. Mater.* 22(8), 1789-1797.
- Liska, M., Vandeperre, L., Al-Tabbaa, A., 2008. Influence of carbonation on the properties of reactive magnesia cement-based pressed masonry units. *Advances in cement research* 20(2), 53-64.
- Lothenbach, B., Nied, D., L'Hôpital, E., Achiedo, G., Dauzères, A., 2015. Magnesium and calcium silicate hydrates. *Cem. Concr. Res.* 77, 60-68.
- Mármol, G., Savastano, H., Tashima, M.M., Provis, J.L., 2016. Optimization of the MgO SiO₂ binding system for fiber-cement production with cellulosic reinforcing elements. *Mater. Des.* 105, 251-261.
- Mo, L., Deng, M., Tang, M., 2010. Effects of calcination condition on expansion property of MgO-type expansive agent used in cement-based materials. *Cem. Concr. Res.* 40(3), 437-446.
- Nied, D., Enemark-Rasmussen, K., L'Hopital, E., Skibsted, J., Lothenbach, B., 2016. Properties of magnesium silicate hydrates (MSH). *Cem. Concr. Res.* 79, 323-332.
- Rodríguez de Sensale, G., 2006. Strength development of concrete with rice-husk ash. *Cem. Concr. Compos.* 28(2), 158-160.
- Rodríguez de Sensale, G., 2010. Effect of rice-husk ash on durability of cementitious materials. *Cem. Concr. Compos.* 32(9), 718-725.
- Snyder, R.L., 1992. The use of reference intensity ratios in X-ray quantitative analysis. *Powder Diffraction* 7(04), 186-193.
- Sonat, C., Dung, N., Unluer, C., 2017. Performance and microstructural development of MgO–SiO₂ binders under different curing conditions. *Constr. Build. Mater.* 154, 945-955.
- Sonat, C., Teo, W.W., Unluer, C., 2018. Performance and microstructure of MgO–SiO₂ concrete under different environments. *Construction and Building Materials* 184, 549-564.

- Tran, H., Scott, A., 2017. Strength and workability of magnesium silicate hydrate binder systems. *Construction and Building Materials* 131, 526-535.
- Walling, S.A., Kinoshita, H., Bernal, S.A., Collier, N.C., Provis, J.L., 2015. Structure and properties of binder gels formed in the system $\text{Mg}(\text{OH})_2\text{-SiO}_2\text{-H}_2\text{O}$ for immobilisation of Magnox sludge. *Dalton Trans*, 44(17), 8126-8137.
- Zain, M.F.M., Islam, M., Mahmud, F., Jamil, M., 2011. Production of rice husk ash for use in concrete as a supplementary cementitious material. *Constr. Build. Mater.* 25(2), 798-805.
- Zhang, T., Cheeseman, C., Vandeperre, L., 2011. Development of low pH cement systems forming magnesium silicate hydrate (MSH). *Cement and Concrete Research* 41(4), 439-442.
- Zhang, T., Dieckmann, E., Song, S., Xie, J., Yu, Z., Cheeseman, C., 2018. Properties of magnesium silicate hydrate (MSH) cement mortars containing chicken feather fibres. *Constr. Build. Mater.* 180, 692-697.
- Zhang, T., Du, Y.N., Sun, Y.J., He, Z.M., Wu, Z.L., 2016. Development of magnesium-silicate-hydrate cement by pulverized fuel ash, *Key Eng. Mater. Trans Tech Publ*, pp. 61-65.
- Zhang, T., Vandeperre, L.J., Cheeseman, C.R., 2014. Formation of magnesium silicate hydrate (MSH) cement pastes using sodium hexametaphosphate. *Cement and Concrete Research* 65, 8-14.
- Zhang, Y., Li, Y., Xu, Y., Sang, S., Jin, S., 2017. Enhanced formation of magnesium silica hydrates (MSH) using sodium metasilicate and caustic magnesia in magnesia castables. *Ceramics International* 43(12), 9110-9116.

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Table 1 Chemical composition and physical properties of the raw materials.

Component/ Content (%)	MgO	MS	RHA-a	RHA-c
MgO	>91.5	-	0.7	0.5
CaO	1.6	-	0.5	0.4
SiO ₂	2.0	>90.0	>79.0	>75.0
Al ₂ O ₃	<0.7	-	0.1	0.06
C	-	-	15.3	18.3
P ₂ O ₅	-	-	1.4	0.6
Fe ₂ O ₃	-	-	0.1	0.09
K ₂ O	-	-	2.4	2.3
SO ₃	-	-	0.3	0.03
Specific surface area (m ² /g)	35.7	17.0	24.1	8.6
LOI (%)	6.3	2.2	5.2	1.3

Table 2 Mix compositions used in this study.

Sample	Composition (wt.%)			
	MgO	RHA-a	MS	RHA-c
Ra	50	50	0	0
Ra-M	50	25	25	0
M	50	0	50	0
Rc	50	0	0	50

Table 3 MgO and Mg(OH)₂ contents obtained by XRD-RIR after 7 and 56 days of curing.

Sample	Content (%)			
	7 days		56 days	
	MgO	Mg(OH) ₂	MgO	Mg(OH) ₂
Ra	25.6	2.7	17.4	4.7
Ra-M	24.8	3.0	10.2	5.9
M	25.4	8.2	10.8	7.3
Rc	37.6	6.3	28.3	15.2

Table 4 Mass loss values based on the deconvoluted DTG curves for all samples cured for 7 and 56 days.

Sample	Mass loss (% of original weight)					
	Adsorbed water dehydration		Brucite dehydroxylation		M-S-H dehydroxylation + LOI of raw materials	
	7 days	56 days	7 days	56 days	7 days	56 days
Ra	6.6	6.7	1.2	2.5	12.6	13.9
Ra-M	7.7	7.9	1.8	2.2	12.1	13.5
M	8.2	5.5	2.7	2.2	10.0	13.2
Rc	2.1	3.0	2.7	5.6	7.4	9.9

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(a)

(b)

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(a)

(b)

(c)

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(a)

(b)

(c)

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