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MAXIMIZING VOLUME OF SPENT BLEACHING EARTH ASH (SBEA) POZZOLAN USED AS CEMENT REPLACEMENT IN MORTAR THROUGH MECHANICAL ACTIVATION

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Graphical abstract

Abstract

Spent bleaching earth ash (SBEA) is harmful waste from the oil refining industry that has previously exhibited pozzolanic properties and potential for use as cement replacement. Conventional pozzolanic replacements in cements are typically limited to 30 % only as excessive amounts have detrimental on cement strength. This research aimed to investigate the feasibility of increasing the level of replacement past 30 % through mechanical activation. Preliminary investigations revealed that SBEA contains sufficient silica and alumina oxides to be classified as Class N pozzolan in accordance with ASTM C618. As expected with pozzolans, the use of SBEA in cement mortar improved the 28 and 56-day compressive strengths up to 30 % substitution but at the same time also increased the water requirement. Mechanical activation was able to improve the level of substitution to 50 % through a mix of increasing pozzolanic reactivity of SBEA as well as increasing the specific surface area of its particles.

Keywords: Spent bleaching earth ash (SBEA), natural pozzolan, pozzolanic reactivity, mechanical activation, grinding

Abstrak

Spent bleaching earth ash (SBEA) adalah sisa berbahaya daripada industri penapisan minyak yang sebelum ini mempamerkan sifat pozzolanic dan berpotensi untuk digunakan sebagai pengganti simen. Penggantian pozzolanic konvensional dalam simen biasanya dihadkan kepada 30% sahaja kerana jumlah yang berlebihan boleh menjejaskan kekuatan simen. Penyelidikan ini bertujuan untuk menyiasat kemungkinan meningkatkan tahap penggantian melepasi 30% melalui pengaktifan mekanikal. Siasatan awal mendedahkan bahawa SBEA mengandungi silika dan alumina oksida yang mencukupi untuk dikelaskan sebagai pozzolan Kelas N mengikut ASTM C618. Seperti yang dijangkakan dengan pozzolan, penggunaan SBEA dalam mortar simen meningkatkan kekuatan mampatan 28 dan 56 hari sehingga 30% penggantian tetapi pada masa yang sama juga meningkatkan keperluan air. Pengaktifan mekanikal dapat meningkatkan tahap penggantian kepada 50% melalui campuran peningkatan kereaktifan pozzolanik SBEA serta meningkatkan keluasan permukaan khususnya.

Kata kunci: Spent bleaching earth ash (SBEA), natural pozzolan, kereaktifan pozzolanik, pengaktifan mekanikal, pengisaran

1.0 INTRODUCTION

Spent bleaching earth ash (SBEA), or also known by its commercial name eco-processed pozzolan (EPP), is a waste by-product from the oils refining industry such as in the production of edible or mineral oils. It originates from Fuller's earth, which is a type of high absorbent montmorillonite clayey soil such as bentonite clay which is used to remove pigmentation and trace contaminants in oil products. These bentonite clays are typically layered silicates with exchangeable cations and reactive OH groups (Othman *et al.*, 2006). The by-product resulting from this process is spent bleaching earth (SBE) waste which has high residual oil content in excess of 40 % (Aziz *et al.*, 2001). SBEs are typically recycled for use as fuel briquettes, as clay replacement in the production of fired bricks and clay tiles as well as composted as bio-organic fertilizer. However, by using the Soxhlet extraction method, the residual oil trapped within SBE could also be extracted as bio-diesel, leaving the de-oiled SBE to be used as fuel to power boilers. The resulting ash from the burning of SBE in this fashion results in spent bleaching earth ash (SBEA) which is a fine powdery waste containing very minimal residual oil (<1 %). Because of its fineness and oil content, SBEA waste is very difficult and costly to dispose off properly (Aziz *et al.*, 2001). The large volume of SBEA being generated globally makes the handling of SBEA waste a major issue. Globally, production of edible oils reached an annual high of 575 million tonnes in 2020 (*Vegetable Oil Prices on an Upward Trend*, 2020) which yielded approximately 5.75 million tonnes of SBEA waste that needed disposal every year.

Currently there are research that looked into recycling SBEA for use as partial cement replacement. Part of these research include assessing the pozzolanic properties of SBEA (Rahman *et al*., 2019) as well as using incorporating it as partial cement replacement in mortar (Rahman *et al*., 2020), foamed concrete (Rokiah *et al*., 2019) and road pavement (Kusaimi *et al.*, 2020). These research have shown that SBEA exhibits sufficient pozzolanic properties for use as cement replacement up to 30 %. It has been well documented that use of pozzolans exceeding 30 % typically starts compromising the properties of cement and concrete especially its strength and workability. Considering the amount of SBEA waste being produced each year, it would be beneficial to investigate the possibility of increasing the level of SBEA replacement past 30 % but not at the expense of its engineering properties such as compressive strength.

Past research has demonstrated that the compressive strength performance of blended cements containing pozzolan can be improved through mechanical activation (Al-Swaidani *et al.*, 2017). Mechanical activation is usually achieved through grinding of the pozzolan into finer particles. Grinding has been shown in the past to increase amorphousness of pozzolans (Mota dos Santos & Cordeiro, 2021) and in turn the amorphousness of pozzolans was found to be the main contributor to its reactivity (Walker & Pavía, 2011). Besides increasing its pozzolanic reactivity, grinding also physically reduces the size of the particles themselves (Yao *et al*., 2020). Finer particles typically have larger surface area available for reaction for the consumption of portlandite (Barbosa *et al.*, 2019). Finally, there is also the physical 'filler effect' offered by finer particles to achieve a more compact and less porous cement mortar matrix (Jaturapitakkul *et al.*, 2011) which contributes to enhanced strength of the mortar (da Silva Andrade *et al.*, 2019).

Hence, this research was commissioned with an aim to investigate the possibility of using mechanical activation to increase the level of allowable SBEA replacement in cement mortar. The objectives of carried out to fulfil this aim are: i) to characterize the pozzolanic properties of SBEA itself, ii) to assess pozzolanic reactivity of both untreated and ground SBEA and iii) to determine the maximum level of replacements achieved by both untreated and ground SBEA in cement mortar.

The pozzolanic reactivity will be assessed using two methods; the first based on the SBEA material itself using X-ray diffraction (XRD) to study its crystalline phases and second, by measuring the amount of residual portlandite content in cement mortars containing SBEA using thermogravimetric methods (TGA). Portlandite, or calcium hydroxide (CH), is a deleterious by-product from the hydration process between cement and water that does not contribute to strength development but is an important prerequisite for pozzolanic reaction. At the same time, calcium silicate hydrates (C-S-H) and calcium alumina silicate hydrates (C-A-S-H) that contributes to the strength of mortar and concrete (Boateng & Skeete, 1990) were also estimated from the TGA test.

The effect of untreated and ground SBEA on compressive and flexural strength were assessed using cement mortar cube and prisms. The level of SBEA replacement investigated range from 10 to 70 % of the weight of cement.

2.0 METHODOLOGY

The experimental regime involved testing of cement mortar prepared consisting Ordinary Portland cement (OPC), fine aggregates, water and SBEA as partial replacement of the OPC. For the OPC, CEM II 32.5 N conforming to BS EN 197:2014 was purchased commercially in bags of 50 kg from Cement Industries Sabah in Sabah, Malaysia. The SBEA used in the experimental regime was supplied by Eco Oils Sdn. Bhd. based at Lahad Datu, Sabah in Malaysia. The untreated SBEA (SU) powder was packed in thick polyethylene bags of 10 kg each. Washed river sand from Kota Belud in Sabah was used as fine aggregates.

Both SBEA and fine aggregates were used in their oven-dried (OD) condition by heating it for 24 hours at 105 °C, and the water content in the mix adjusted based on their respective rates of absorption and moisture content.

Figure 1 Planetary grinding ball mill (left) and sieve to separate SBEA from balls (right)

This study includes investigation on the effect of mechanical activation of SBEA powder by grinding at three different durations; namely 30 mins (SG30), 60 mins (SG60) and 120 mins (SG120) and to investigate its ability to improve the mechanical properties of cement mortar. The mechanical activation was carried out by dry grinding the samples in a planetary grinding ball mill (

Figure 1) which comprises four stainless steel jars with ball bearings inside. The ball mill operates at the rate of 300 hz and changes grinding directions at fixed intervals. Each jar was filled with approximately 150 g of oven dried untreated SBEA powder for grinding, yielding about 600 g of ground SBEA samples per grinding cycle.

The chemical composition of all three main component materials (OPC, untreated SBEA and fine aggregates) were analyzed using X-ray fluorescence (XRF) techniques to identify the amount of silicate and alumina oxides (SiO_2 and Al_2O_3) that contributes to strength as well as the unwanted sulfur trioxide (SO_3) that can compromise the performance of cement through by causing expansion in its lime and sulfate content. A loss of ignition test was also carried out to determine the amount of unburnt carbon contained within.

To further investigate the impact of mechanical grinding treatment, x-ray diffraction (XRD) analysis was also carried out for all untreated as well as ground SBEA samples to study the mineralogy phases it underwent as well as the resulting level of crystallization or amorphization. This was carried out on the Rigaku Smartlab X-ray Diffractometer operated at wavelengths of k1 = 1.54059 and k2 = 1.54441, scanning mode of 2 theta from 3 to 90 °. The materials for each peak were then identified using the diffraction pattern from ICDD card database. The level of crystallinity was estimated by evaluating the areas under the respective peaks. This amorphousness of the material allowed an initial assessment of the reactivity of the pozzolan.

Further pozzolanic reactivity was assessed by measuring the residual portlandite (CH) in mortar samples after 28 days of curing. Thermogravimetric analysis method was adopted for this purpose. The equipment used was a TA Instruments TGA Q500 thermogravimetric analyser. The result from this test was typically provided as a function of weight loss against temperature but re-plotted to show derivative of weight loss against temperature to better highlight the changes in phase. The weight loss due to decomposition of CH was estimated based on the methodology proposed by (Roychand *et al.*, 2016). The combined XRD-TGA has shown versatility in the past in gauging amorphous content of pozzolans (Taylor-Lange *et al.*, 2015).

Both the SBEA and OPC powders also underwent particle size analysis using laser diffraction method to determine its sizes and specific area. For the fine aggregates which are generally coarser than 75 microns, mechanical sieving method was used instead. The microstructure of the samples were observed under a scanning electron microscope (SEM) to identify any physical changes to the particles.

In terms of the mechanical properties, both untreated and ground SBEA were assessed based on its effect on:

i) water requirement of fresh mortar and,
ii) compressive and flexural strength of cement mortar at ages 7, 28 and 56-day.

To achieve this, samples of cement mortar cubes measuring 50 x 50 x 50 mm were produced using cast iron moulds. The mix design for the mortar cubes based off ('ASTM C109/C109M-02 Standard Test Method for Compressive Strength of Hydraulic Cement Mortars', 2002) and summarized in Table 1. The mix allows six cubes to prepared and for this experiment, the mix was re-proportioned for nine cubes so that there are three cubes for 7-, 28- and 56-day compressive strength testing. All materials used in the casting were in oven dried condition and the weight adjusted to account for it. Right after casting the specimens allowed to harden for 24 hours under plastic sheeting cover to prevent moisture loss. After that the specimens were moved into a tank containing saturated lime water for curing.

Table 1 Mix design for six no. control mortar cubes

Material	Amount
OPC	500 g
Graded sand	1375 g
Water	242 mL (w/c 0.485)

The control mix was prepared based on a fixed amount of water based on w/c of 0.485, taking into account for the absorption rate of the sand, as shown on Table 1. Workability of fresh cement mortar was assessed using the flow table test in accordance with (*ASTM C1437 –07 Standard Test Method for Flow of Hydraulic Cement Mortar*, 2009). In this instance, the control mix achieved a flow of 95 %. The test mixes were then prepared using the same w/c of 0.485 but with additional water required to achieve similar flow of that for control mix (± 5) to account for the absorption of the oven-dried SBEA. Superplasticizers have not been used in this research as the previous trial runs have deemed it impractical.

For the compressive strength test, a total of 29 different test mixes were prepared; one control mix utilizing only OPC (MCTRL series), seven test mixes using untreated SBEA (MSU series) to replace OPC from 10 to 70 % replacement and another 21 test mixes using ground SBEA of three different grinding durations, namely 30 (MSG30 series), 60 (MSG60 series) and 120-min (MSG120 series) to replace OPC from 10 to 70 % replacement as well. These nomenclatures are summarized in **Error! Reference source not found.**.

Table 2 Code for specimens used in tests

Code	Specimen
SU	Untreated SBEA
SG30	Ground SBEA (30 mins)
SG60	Ground SBEA (60 mins)
SG120	Ground SBEA (120 mins)
MCTRL	Control mortar containing OPC
MSUxx	Test mortar containing untreated SBEA
MSG30xx	Test mortar containing ground SBEA (30 mins)
MSG60xx	Test mortar containing ground SBEA (60 mins)
MSG12xx	Test mortar containing ground SBEA (120 mins)

('xx' succeeding the specimen codes refer to the level of replacement of SBEAs in % weight of cement)

Similar batching mix were also used to prepare 40 x 40 x 160 mm prisms for flexural strength tests. The flexural strength test consisted of a set of control mix (MCTRLF), one set of test mix with untreated SBEA (MSU series) and three sets of test mixes incorporating ground SBEA at 30, 60 and 120-min respectively (MSG30, MSG60 and MSG120). In contrast to the compressive strength testing, only replacement levels of 20 and 50 % were prepared and tested.

Both the compressive and flexural strength of the cement mortar samples were determined using a universal testing machine (

Figure **2**) for an average strength of three replicates per test sample mix.

Figure 2 Flexural strength testing using the universal testing machine

3.0 RESULTS AND DISCUSSION

Chemical Properties

The chemical composition of the SBEA, OPC and fine aggregates are summarized in Table 3. It can be seen that SBEA contains total oxides of 71 %, with a sulfur trioxide content of 1 % and LOI of 3 %, all meeting the chemical requirements of Class N pozzolan as defined by (*ASTM C618–05 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*, 2005). It would appear the oxide content varies according to the SBEA stock as past research has shown that it could be both much higher (Rokiah *et al.*, 2019) or lower amount (Rahman *et al.*, 2020).

Table 3 Chemical properties of materials used (in % weight)

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	LOI
SBEA	49	11	10	11	1	3
OPC	16	4	3	69	3	2
Sand	65	12	5	4	0	3

Morphology and Phase Analysis

The XRD pattern of both untreated (SU) and ground SBEA can be seen in Figure 3. The diffraction patterns for all samples were marked by various sharp peaks. The highest of these occur at 2θ = 26.62° where major crystalline phase, quartz (Q), comprising SiO_2, was detected. Significant peaks of quartz were also detected at 2θ of 20.88°, 36.58 and 50.1° and these very much corresponds to previous findings (Rahman *et al.*, 2020). The minor constituents detected were corundum, hematite, and quicklime.

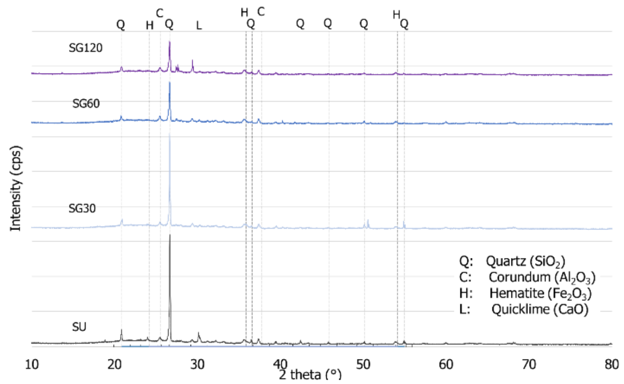


Figure 3 X-ray diffraction (XRD) pattern for SU, SG30, SG60 and SG120

After being subjected to grinding, most of the peak intensity experienced a reduction (26.6, 42.5, 54.9 °), with some peaks disappearing completely, especially in sample SG120 (24.2, 30.2, 42.5, 45.8 °). This reduction in the peak intensities indicates that amorphization had occurred and brought about reduced crystallinity and a loss of structural order, as explained by (Cheng *et al.*, 2021). The phenomenon was also confirmed quantitatively through an evaluation of the overall level of crystallinity which saw a reduction from 37.5 % down to 35.1 % for SG30, 34.0 % for SG60 and 32.9 % for SG120 (Table 4). The maximum peak heights of the quartz and alumina (Corundum) had also seen corresponding reduction as a result of the ground SBEA, as had been previously observed (Cordeiro *et al.*, 2016). However, it appeared that iron oxides (Hematite) contents retained its crystallinity. As such it can be surmised that grinding the subsequent reduction of material particle sizes can cause it to lose crystallinity. Grinding duration also plays a role in the magnitude of loss in crystallinity. In this instance, however, the grinding period was probably insufficient for full amorphization to take place, which could be in excess of 20 hours (Ilić *et al.*, 2016).

Table 4 Degrees of crystallinity and peak intensities

Level of treatment	No. of peaks	Degree of crystallinity	Maximum peak height/intensity
SU	39	37.5 %	16,464
SG30	39	35.1 %	14,440
SG60	34	34.0 %	6,800
SG120	33	32.9 %	5,520

Physical Properties

SBEA particle sizes are typically coarser compared to OPC particles, with the mean particle size about twice as large (Table 5). Due to this, SBEA particles have just under half the specific surface area of OPC particles. SBEA is about two-thirds the weight of OPC, whilst having only half of its specific surface area.

SBEA, as explained earlier in the Introduction section, typically originates from highly absorbent bentonite-type clays and hence this is reflected through its high water absorption rate of 35 %. Bentonite are well known for its high absorption capability and these can range anything from 10 % to 100 % depending in the relative humidity (RH) at the time of mixing.

Table 5 Physical characteristics of materials

Material	Particle size (μm)			Absorption	Specific
	d_{10}	d_{50}	d_{90}	(%)	gravity
SBEA	8	36	100	35.0	2.3
OPC	3	16	48	-	3.1
Sand	272	345	1202	5.0	-

Grinding of the SBEA powders appear to have significant effect on reducing its overall particle sizes (PS) (Figure 4) as well as its specific surface areas (SSA) whereby 30-minute grinding had reduced the mean particle size by 29.6 %. It can also be observed that magnitude of reduction increases with grinding time, but this increase is not linear (Figure 5). Instead, the trend gradually flattened out and the benefit gained from extended grinding time began diminishing. This is evident where doubling the grinding time to 60 minutes did not yield a two-fold reduction in particle size but rather only a reduction of 50 % over the original size. The change in PS was also more evident in the upper percentile, d_{90}, than the mean sizes or the lower end of the PS spectrum, d_{10}. Coincidentally 60-minute grinding brought the particle size distribution to similar trend as that of the OPC used in this experiment. Further doubling the grinding time to 120 minutes sees only 62 % reduction in overall particle size. Identical phenomenon has been observed in other research (Yao *et al.*, 2020) as well involving other pozzolanic materials.

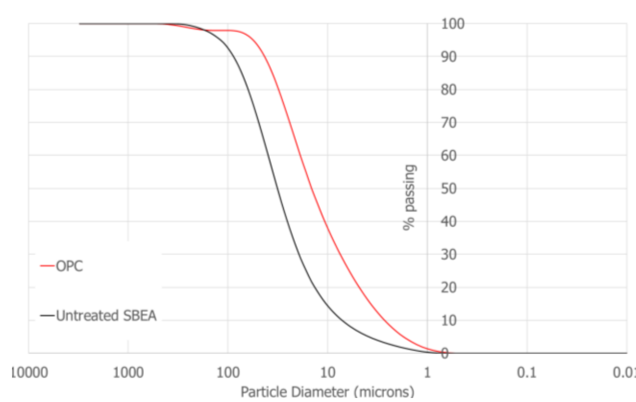


Figure 4 Particle size distribution of untreated vs. ground SBEA and OPC

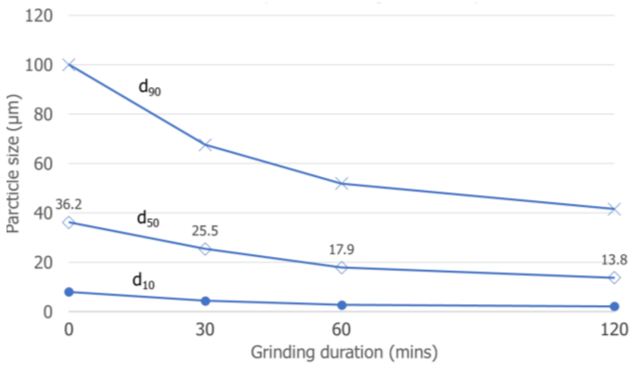


Figure 5 Mean particle size vs grinding duration with mean (d_{50}) particle sizes shown

The reduction in particle sizes from grinding is also reflected in the increase in the SSA of the particles. In this instance the trend is more linear where 30-minute grinding increased this by 58 % whilst 60-minute grinding doubled the surface area to 127 % (Figure 6). Finally, 120 minutes of grinding further increased the surface area by 186 %. As with the PS, the gain in SSA with grinding duration appeared non-linear especially past the 60 min mark. Other researchers (Vizcayno *et al.*, 2010) have also observed similar trends where SSA increases linearly with grinding duration.

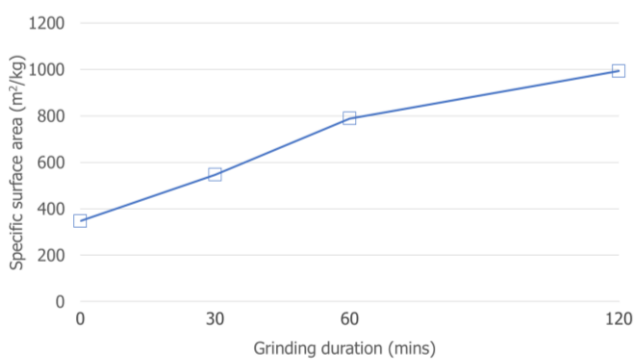
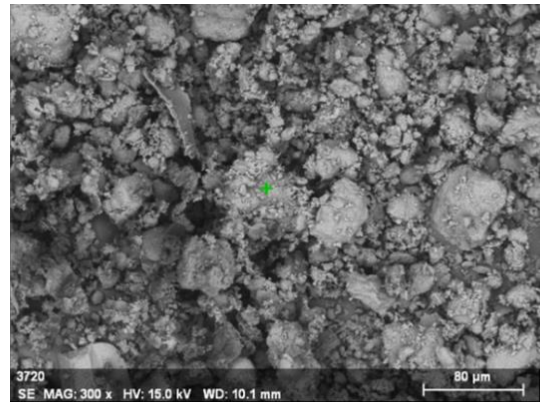


Figure 6 Specific surface area vs grinding duration

The overall reduction in particle size from grinding was also evident from the SEM images (Figure 7). Much more fines were observed after grinding that resulted in greater packing density.



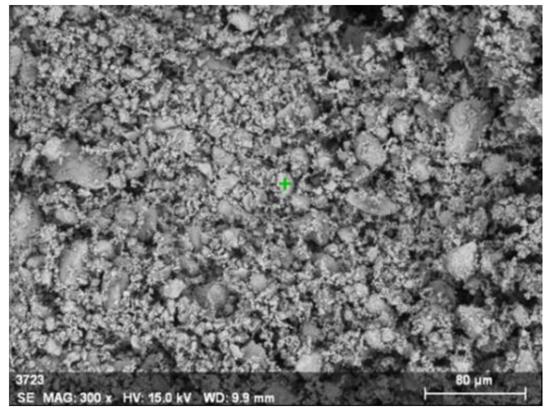


Figure 7 Microstructure of untreated (top) and ground SBEA (bottom) at 300x

At 2500x magnification, the pores in the untreated SBEA particles became visible in Figure 8 (top). The width of these pores appeared vary from 2 μm to less than 1 μm and were scattered randomly all across the surface of the particles. These pores are likely the product of SBE being ignited when used as boiler fuel. In addition to the pores, agglomeration of the particles, especially the smaller ones on the surfaces of the larger ones were observed as well.

The magnified image of ground SBEA particle can be seen in Figure 8 (bottom). In the image, the pores originally observed in the untreated particles are all but gone. In this instance, grinding appeared to have eliminated these pores whilst at the same time reducing the size of the particles itself. Agglomeration was still clearly visible within the sample.

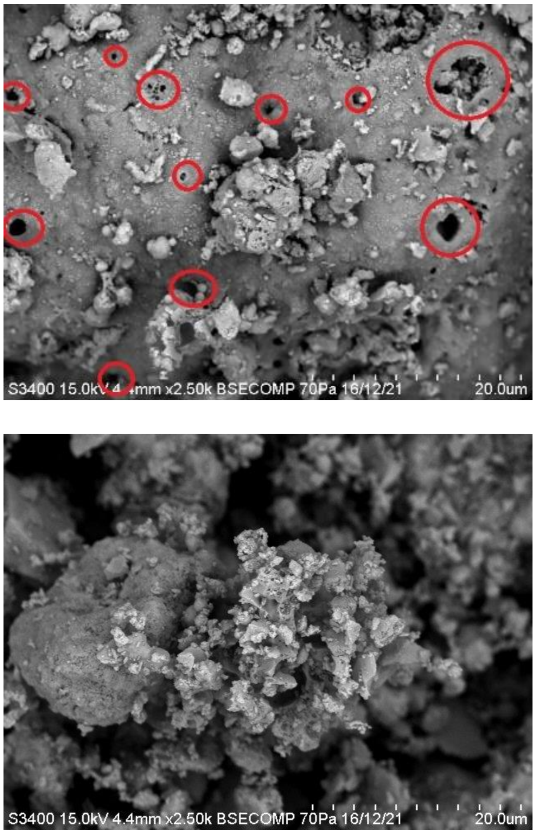


Figure 8 Pores as seen on untreated (top) vs ground (bottom) SBEA particle at 2500x

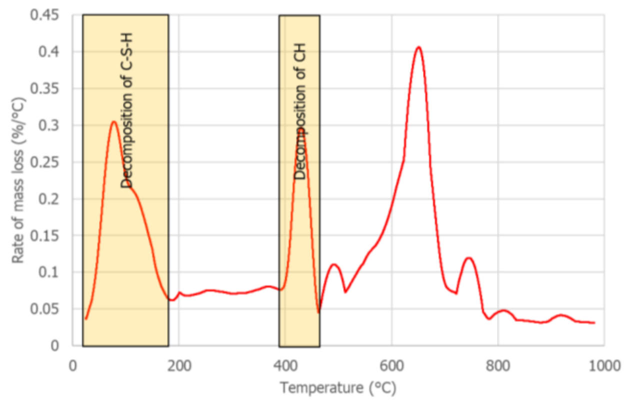


Figure 9 DTG of control sample, MCTRL showing decomposition zones of CH and C-S-H

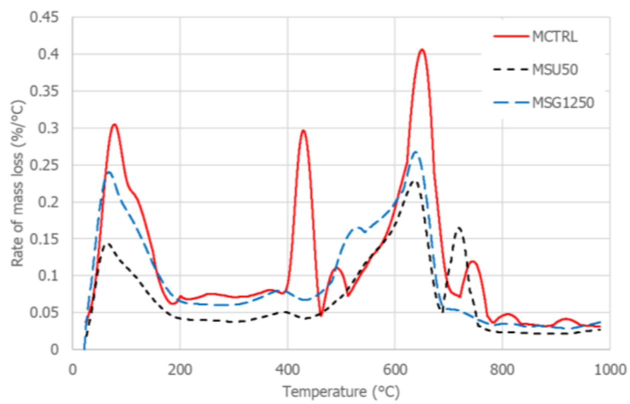


Figure 10 DTG of test samples, MSU50 and MSG1250, overlaid over MCTRL

Pozzolanic Reactivity

The pozzolanic reactivity of SBEA in mortar samples was assessed by measuring the residual CH and C-S-H contents in the control and test mortar samples. The decomposition zones for both materials can be distinguished by the spike/peak in the DTG curve around this temperature range. Based on past research, the decomposition of C-S-H could occur anywhere between 30 to 350 °C whilst for CH, this could range from 400 to 550 °C. These temperatures were material dependent and could be lower (Asim & Mohamed Sutan, 2016) or higher (Samadi *et al.*, 2020). The DTG curve is a derivative of TGA curve and provides a simpler way for identifying changes in the mass of the sample than TGA curves. The DTG curves for the control, MCTRL and test samples are shown in Figure 9 and Figure 10 respectively. It can be seen that whilst the C-S-H decomposition zone for both MCTRL and test samples (MSU50 and MSG1250) were similar (circa 40 to 185 °C), it was noticeably different for the decomposition of the CH contents. The MCTRL sample had a higher CH decomposition temperature than the test samples by approximately 35 °C.

In terms of residual CH content, on the DTG curve for MCTRL (Figure 9), a large spike in the rate of mass reduction of 0.3 %/°C can be seen at the CH decomposition temperature range, but this spike was almost non-existent in the curves for both the test samples (Figure 10).

The percentage CH mass loss was quantified from the DTG graph to enable a more accurate comparison. This is presented in (Figure 11). It can be seen that the control sample, MCTRL, with no pozzolans had the highest residual CH content, followed by the sample containing untreated SBEA, MSU50, which had less than half of the CH content. This clearly demonstrated that SBEA consumed the CH in the mortar samples, albeit a small amount still remained, which probably explains why pozzolanic cements tend to continue developing strength past 28 days. The lowest CH content came from sample containing ground SBEA, MSG1250, with about half of that of sample MSU50, proving that grinding SBEA was able to further improve its pozzolanic reactivity, albeit with limited effect.

These findings correlate well with the assessment of pozzolanic reactivity of SBEA using XRD analysis earlier in Chemical Properties section which showed that SBEA became more amorphous and as a result also more pozzolanic due to mechanical activation via grinding.

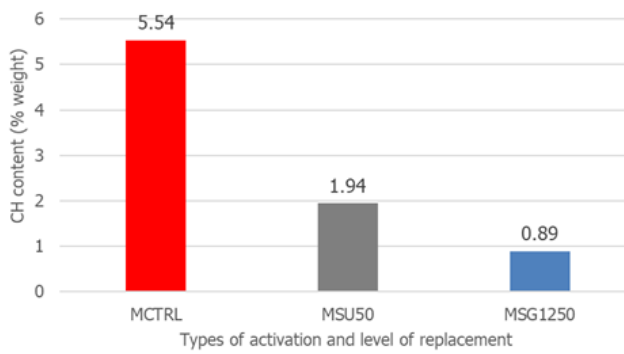


Figure 11 Summary of residual CH content in mortar samples

Similar observations had been noted in the past where the residual CH content in mortar containing ground fly ash had reduced compared to both the control and the unground fly ash samples (Feng *et al.*, 2018). In that instance, the magnitude of reduction was lower, owing to a lower level of fly ash replacement.

The C-S-H content, which is primarily responsible for strength development in the mortar samples were also compared in the Figure 10 and also quantified in Figure 12. From the DTG graph, it could be seen that the MCTRL had the highest rate of mass loss, followed by the test mortar sample containing ground SBEA (MSG1250) and the lowest being test sample containing untreated SBEA (MSU50). When this C-S-H content was quantified as a percentage total weight, it could be seen that both MCTRL and MSG1250 had almost identical amounts of C-S-H present, whilst sample MSU had only about half of this C-S-H content. This result showed that grinding of SBEA does bring about improvement to C-S-H content which should ultimately be reflected in its mortar strength later in this paper as well.

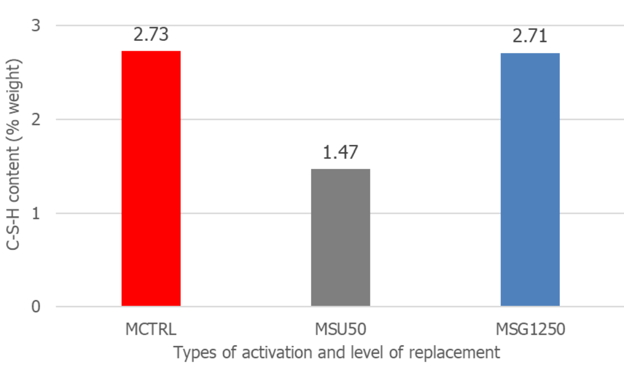


Figure 12 Summary of C-S-H content in mortar samples @ 28 days

Water Requirement

The water requirement in mixes containing SBEA is shown in Figure 13. From the findings, it can be seen that increasing amounts of additional water was required to maintain the same level of workability as levels of replacement untreated SBEA (MSU) increases. As soon as SBEA was introduced into the mix, the water demand began to increase and remained relatively linear up until 50 % replacement whereafter it spiked sharply. The findings is consistent with past research where replacement of OPC with natural pozzolans was characterized by reduction in workability and increase in water demand of cement mortars (Ghasemi *et al.*, 2019).

This increase in water requirement can be explained by the high water absorption rate of 35 % tested in Table 5 As the SBEA were being used in their oven dried condition as mentioned in Methodology, it caused the SBEA particles to absorb and trap water in its porous microstructure as shown in Figure 8 (top), resulting in additional water being required to bring it to the same flow as the control sample. Similar explanation to describe the increase in water demand porous due nature of the untreated SBEA particles was also explained by past research (Zhang & Lu, 2019).

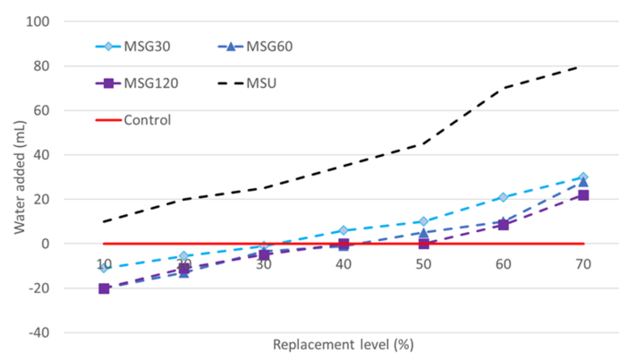


Figure 13 Water requirement for untreated vs. ground SBEA

However, once subjected to grinding, the mechanically activated SBEA (MSG30, MSG60 and MSG120) has shown potential in reducing the water demand at all levels of replacement (Figure 13). The magnitude of reduction was seen to be increasing with the amount of replacement. Grinding duration also played a role in reducing water demand where 60-minute grinding was shown to be more effective than 30-min grinding. However, 120-min grinding samples showed very similar water demand as 60-min grinding, indicating that there may be a threshold whereafter grinding no longer improves the water demand. This reduction in water requirement was mainly due to the elimination of the pores in the ground SBEA particles that could hold water within Figure 8 (bottom), hence reducing the water absorption rate of the particles and reducing the need for additional water to achieve the target flow. Similar findings in the past had also shown ground POFA improved the workability of concrete mixes and reducing its water demand (Megat Johari *et al.*, 2012).

Early Age Compressive Strength

As expected, inclusion of pozzolans tend to have detrimental effect on the early age strength of cement mortars (Abdelli *et al.*, 2017) due to insufficient portlandite available to trigger pozzolanic reaction. This is evident where the 7-day compressive strength results of MSU samples were consistently below that of the control and lies on a linear downward trajectory with increasing levels of replacement (Figure 14). Mechanical activation of SBEA was able to improve this early age strength, especially mixes MSG60 and MSG120 which were able to maintain strength close to the control samples up until 40 % replacement. MSG30 underperforms when compared to MSG60 and MSG120 but still improved strength of untreated SBEA (MSU). It was also observed the peak strength was achieved by mix MSG60 at 30% replacement which just barely exceeded the control strength. The enhancement of early age strength brought about by grinding of pozzolans has also been corroborated by past research (Day & Shi, 1994).

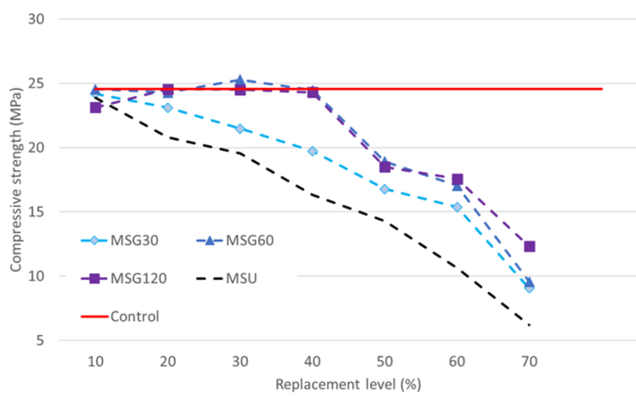


Figure 14 Compressive strength of cement mortar for untreated vs. ground SBEA at 7 days

Compressive Strength at 28 and 56 days

At 28 days (Figure 15), untreated SBEA (MSU) mix was able to improve the strength of cement mortars up to a peak of 30 % replacement, whereafter the strength started dropping sharply below that of the control sample. Ground SBEA, on the other hand, allowed this peak strength to be pushed further along to 40 % and allowable level of replacement to be pushed close to 50 % before compromising on the strength. It is also worth noting that the peak strength was achieved by mix MSG120 at 40 % replacement, with an improvement of 24.6 % over the control sample. As with the 7-day strength tests, mechanical activation generally improved the 28-day strength over untreated SBEA (MSU) mixes, but the duration of grinding now plays a more pronounced role, with extended grinding periods conferring significant improvement to compressive strength. This is evident where strength trend for MSG60 and MSG120 no longer overlaps.

This huge improvement in strength can be attributed to both the amorphization of the silica and alumina contents in SBEA brought about by grinding (Yao *et al.*, 2019) as well as the increase in specific surface area of its particles that allowed for more effective pozzolanic reaction (Cordeiro *et al.*, 2009).

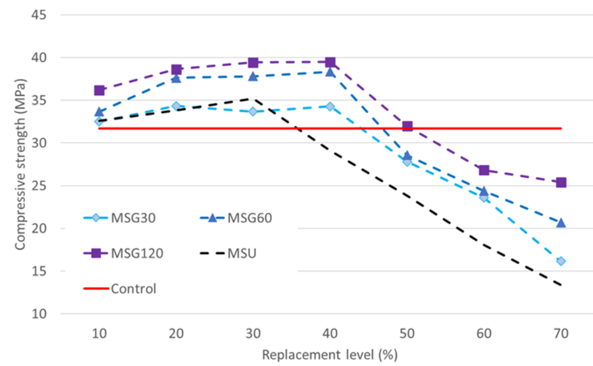


Figure 15 Compressive strength of cement mortar for untreated vs. ground SBEA at 28 days

These findings support previous research where ground sugarcane bagasse ash in mortar exhibited superior strength to Portland cement mortars (Cordeiro *et al.*, 2019). Past research involving ultra-fine palm oil fuel ash (POFA) with a mean particle sizes of 2.06 µm were able to achieve levels of replacement up to 60 % could be attained (Megat Johari *et al.*, 2012). However, 2.06 µm is a fraction of the mean particle size of the 120-min ground SBEA and there was no mention regarding the grinding duration needed to achieve that ultra-fine particle size.

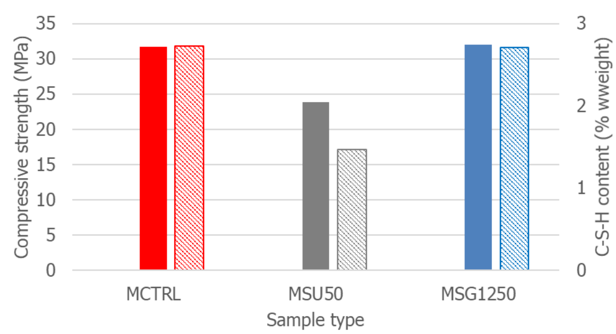


Figure 16 Comparison between compressive strength (solid fill) and C-S-H content (hatched) of cement mortar at 28 days

A correlation between the mortar compressive strength and its C-S-H content could also be drawn, as shown on Figure 16. It can be seen that both MCTRL and MSG1250 (ground SBEA) had similar strengths, as well as near identical C-S-H contents. This showed that most of the compressive strength from sample MSG1250 had been derived from formation of the C-S-H paste. Sample MSU50 containing untreated SBEA which had much less strength compressive strength showed correspondingly less C-S-H contents too. This

this showed that despite having finer particles, sample MSG1250 with ground SBEA particles hardly benefitted from the 'filler' effect. This is alluding that a majority of the mortar compressive strength appear to be derived directly from its C-S-H content.

The 56-day strength profile (Figure 17) is similar to the 28-day equivalent. Test mix MSU achieved peak strength at 20 % replacement. As with the 28-day strength, mechanical activation of SBEA managed to push the allowable level of replacement to 50 % prior to losing strength. Meanwhile, the peak strength for ground SBEA at this stage is at 40 % replacement level for all activated mixes, with mix MSG60 being the best performing sample, offering an improvement of 26.8 % over that of the control sample. This is closely followed by mix MSG120.

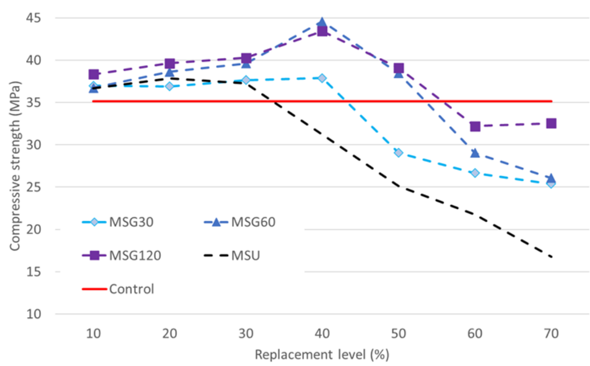


Figure 17 Compressive strength of cement mortar for untreated vs. ground SBEA at 56 days

Flexural Strength at 28 days

The flexural strength at 28 days is shown in Figure 18. As with compressive strength, use of untreated and ground SBEA at lower percentages (20 %) confers improvement to its flexural strength with sample MSG60 being the best performing of the set. This is in contrast to the findings for compressive strength tests where MSG120 was the best performing sample. The implication of this is that whilst extended grinding periods may seem to benefit compressive strength of the samples, the same may not necessarily be true for flexural strength. To prove this point further, at 20% replacement level, MSG30 had lower flexural strength than MSU.

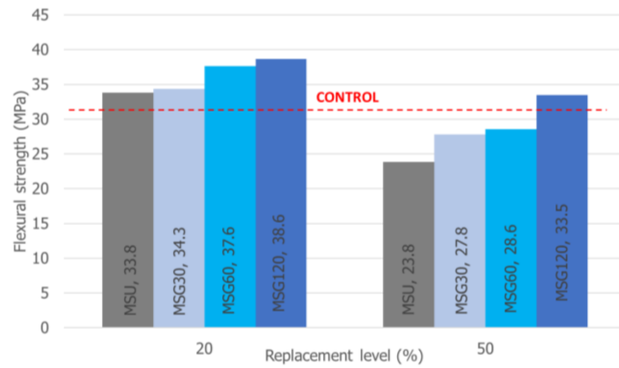


Figure 18 Flexural strength of cement mortar at 28 days

At higher levels of replacement (50 %), the samples see a more significant loss of flexural strength compared to the compressive strength, where none of the samples could match the control sample strength. This corresponds to previous findings where increased amounts of pozzolans, be it perlite, fly ash and ground granulated blast furnace slag, had a detrimental effect on flexural strengths (Sičáková *et al.*, 2020). However the benefit from grinding is clearer in this instance as it could seen to be consistently improving the strength with increased grinding duration.

The flexural strength also did not correlate well with the compressive strength results as sample MSG120 at 50 % replacement had failed to match the control sample strength.

The flexural strength results from tested mortar prisms were also compared against the theoretical values derived from the tested compressive strength using prediction formulas from past research. These comparisons were carried out using the ratio of flexural strength/ compressive strength (f_{cuf}/f_{cu}). The theoretical flexural strengths were obtained from various such as (Kubica & Galman, 2022), (*IS 456:2000 Plain Concrete and Reinforced - Code of Practice*, 2000), (*IS 456:2000 Plain Concrete and Reinforced - Code of Practice*, 2000) and (Croney & Croney, 1997). The comparison is presented in Figure 19.

Whilst the strength ratios from all four theoretical predictions showed good match with one another, the empirical testing from this research clearly bucked the trend. The flexural strength ratio from test results (red curve) exhibited much higher overall strength against all the theoretical models except for sample MSU with 50 % replacement. Thus there may be a need to further improve upon the theoretical prediction model that takes into account use of different types of pozzolans.

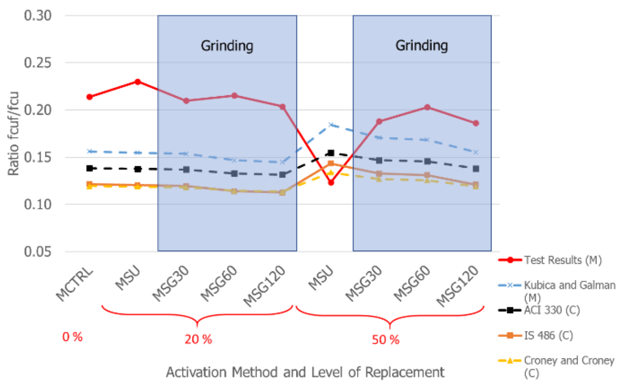


Figure 19 f_{cuf}/f_{cu} ratio comparison between testing results and theoretical prediction

4.0 CONCLUSION

SBEA, in its untreated form, contains sufficient oxides (> 70 %) to be classified Class N pozzolan. It can be used to replace up to 30 % Portland cement without loss of strength. Incorporating untreated SBEA in cement mortar increases water requirement but grinding SBEA allowed water demand to be reduced significantly.

Mechanical activation via grinding was able to significantly reduce overall particle sizes and at the same time increase its specific surface area. Grinding duration also played a role in these physical changes to the particles. Grinding the SBEA samples also causes it to lose crystallinity, rendering it more amorphous and improving its pozzolanic reactivity. This was shown in both the XRD and TGA study of SBEA. Optimal grinding duration in this study appears to be the longest one, 120-min. This grinding duration allowed the highest level of replacement of 50 % to be achieved due to its maximum level of amorphization, as well as the one that yielded the finest particle sizes and hence largest specific surface area available for reaction.

At early ages (7-day), compressive strength, untreated SBEA under-performs against control mix. However, mechanical activation especially SBEA ground for at least 60 minutes was able to maintain strength close to the control sample up until 40% replacement. At 28 and 56-day, replacement of OPC with untreated SBEA improved the compressive strength of cement mortar up to 30% dosage, and ground SBEA allowed the level of replacement to be increased further to 50%.

The improvement in compressive strength appeared to be derived mainly from the C-S-H content, based on information from TGA tests. 'Filler' effect due to the fineness of the ground SBEA particles appeared to be minimal.

The benefits of grinding became less apparent when assessing its benefit on the flexural strength of cement mortar, with minor improvements observed only at low levels of replacement. The level of improvement attained in the compressive strength tests could not be replicated in the flexural tests.

FUTURE STUDIES

This research covered grinding durations of 30, 60 and 120 minutes. The results indicate that extended grinding time can confer increased benefits such as increased strength, it may be beneficial to investigate grinding times longer than 120 minutes.

However, grinding is an energy intensive activity. The cost benefit of grinding should be assessed to determine if the benefits gained can outweigh the additional costs and effort incurred.

The filler effect of offered by ground SBEA, whilst appearing to be minimal, could investigated to establish its contribution to strength improvement.

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References

[1] Abdelli, K. *et al.* 2017. Influence of the Pozzolanic Reactivity of the Blast Furnace Slag (BFS) and Metakaolin on Mortars. *Energy Procedia*. 139: 224-229.

[2] Al-Swaidani, A. M., Aliyan, S. D. and Adarnaly, N. 2017. Mechanical Strength Development of Mortars Containing Volcanic Scoria-based Binders with Different Fineness. *Collection of Engineering Science and Technology*.

[3] Asim, F. Z. A. and Mohamed Sutan, N. 2016. Thermal Characterization of Pozzolanic Activity of Hydrated Cement System Modified by Silica Based Industrial Waste. *Journal of Applied Science & Process Engineering*. 2(1): 1-7.

[4] ASTM C109/C109M-02. 2002. Standard Test Method for Compressive Strength of Hydraulic Cement Mortars. *ASTM International*. 1-6.

[5] ASTM C1437 –07. 2009. Standard Test Method for Flow of Hydraulic Cement Mortar ASTM International.

[6] ASTM C618–05. 2005. Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. ASTM International.

[7] Raman, A. A. A . *et al.* 2001. Feasibility Study of Oil Recovery from Used Bleaching Earth Using Waste Solvents. *Chemistry & Technology Conference, 2001 PIPOC International Palm Oil Congress*. 126-133.

[8] Barbosa, J. M. *et al.* 2019. Influence of Grinding on the Pozzolanic Activity of Granite Residue, *Revista Escola de Minas*. 72(3): 395-404.

[9] Boateng, A. A. and Skeete, D. A. 1990. Incineration of Rice Hull for Use as a Cementitious Material: The Guyana Experience. *Cement and Concrete Research*. 20(5): 795-802.

[10] Cheng, S. *et al.* 2021. Pozzolanic Activity of Mechanochemically and Thermally Activated Coal-

series Kaolin in Cement-based Materials. *Construction and Building Materials*. 299: 123972.

[11] Cordeiro, G. C. *et al.* 2009. Ultrafine Grinding of Sugar Cane Bagasse Ash for Application as Pozzolanic Admixture in Concrete. *Cement and Concrete Research*. 39(2): 110-115.

[12] Cordeiro, G. C., Andreão, P. V. and Tavares, L. M. 2019. Pozzolanic Properties of Ultrafine Sugar Cane Bagasse Ash Produced by Controlled Burning. *Heliyon*. 5(10): 0-5.

[13] Cordeiro, G. C., Tavares, L. M. and Toledo Filho, R. D. 2016. Improved Pozzolanic Activity of Sugar Cane Bagasse Ash by Selective Grinding and Classification. *Cement and Concrete Research*. 89: 269-275.

[14] Croney, D. and Croney, P. 1997 *Design and Performance of Road Pavements*. 3rd Edition. McGraw-Hill Professional.

[15] Day, R. L. and Shi, C. 1994. Influence of the Fineness of Pozzolan on the Strength of lime Natural-pozzolan Cement Pastes. *Cement and Concrete Research*. 24(8): 1485-1491.

[16] Feng, J., Sun, J. and Yan, P. 2018. The Influence of Ground Fly Ash on Cement Hydration and Mechanical Property of Mortar. *Advances in Civil Engineering*. 2018.

[17] Ghasemi, M. *et al.* 2019. Dealing with Workability Loss Challenge in SCC Mixtures Incorporating Natural Pozzolans: A Study of Natural Zeolite and Pumice. *Construction and Building Materials*. 222: 424-436.

[18] Ilić, B. *et al.* 2016. Effects of Mechanical and Thermal Activation on Pozzolanic Activity of Kaolin Containing Mica. *Applied Clay Science*. 123: 173-181.

[19] IS 456: 2000. Plain Concrete and Reinforced - Code of Practice 2000 Bureau of Indian Standards, New Dehli.

[20] Jaturapitakkul, C. *et al.* 2011. Filler Effect and Pozzolanic Reaction of Ground Palm Oil Fuel Ash. *Construction and Building Materials*. 25(11): 4287-4293.

[21] Kubica, J. and Galman, I. 2022. Investigations on Flexural and Compressive Strengths of Mortar Dedicated to Clinker Units—Influence of Mixing Water Content and Curing Time. *Materials*. 15(1).

[22] Kusaimi, N. F. M. *et al.* 2020. Compressive Strength and Water Absorption of Pavement Derived from Palm Oil Eco Processed Pozzolan (Epp) Material as Partial Cement Replacement. *ASEAN Journal of Chemical Engineering*. 20(2): 205-215.

[23] Megat Johari, M. A. *et al.* 2012. Engineering and Transport Properties of High-strength Green Concrete Containing High Volume of Ultrafine Palm Oil Fuel Ash. *Construction and Building Materials*. 30: 281-288.

[24] Mota dos Santos, A. A. and Cordeiro, G. C. 2021 Investigation of Particle Characteristics and Enhancing the Pozzolanic Activity of Diatomite by Grinding. *Materials Chemistry and Physics*. 270(September 2020).

[25] Othman, N., Ismail, H. and Mariatti, M. 2006. Effect of Compatibilisers on Mechanical and Thermal Properties of Bentonite Filled Polypropylene Composites. *Polymer Degradation and Stability*. 91(8): 1761-1774.

[26] Rahman, R. F. A. *et al.* 2020. Study of Eco-processed Pozzolan Characterization as Partial Replacement of Cement. *Journal of Environmental Treatment Techniques*. 8(3): 967-970.

[27] Rokiah, O. *et al.* 2019. Effect of Processed Spent Bleaching Earth Content on the Compressive Strength of Foamed Concrete. *IOP Conference Series: Earth and Environmental Science*. 244(1).

[28] Roychand, R. *et al.* 2016. High Volume Fly Ash Cement Composite Modified with Nano Silica, Hydrated Lime and Set Accelerator. *Materials and Structures/Materiaux et Constructions*. 49(5): 1997-2008.

[29] Samadi, M. *et al.* 2020. Enhanced Performance of Nano-palm Oil Ash-based Green Mortar against Sulphate Environment. *Journal of Building Engineering*. 32(March): 101640.

[30] Sičáková, A., Figmigová, E. and Špak, M. 2020. Comparison of the Strength Development of Binary and ternary Cements Containing Perlite Powder. *Selected Scientific Papers - Journal of Civil Engineering*. 15(1): 47-57.

[31] da Silva Andrade, D. *et al.* 2019. Investigation of C-S-H in Ternary Cement Pastes Containing Nanosilica and Highly-reactive Supplementary Cementitious Materials (SCMs): Microstructure and Strength. *Construction and Building Materials*. 198: 445-455.

[32] Taylor-Lange, S. C. *et al.* 2015. Calcined Kaolinite-bentonite Clay Blends as Supplementary Cementitious Materials. *Applied Clay Science*. 108: 84-93.

[33] Vegetable Oil Prices on an Upward Trend 2020 Oil Seeds: World Markets and Trade.

[34] Vizcayno, C. *et al.* 2010. Pozzolan Obtained by Mechanochemical and Thermal Treatments of Kaolin. *Applied Clay Science*. 49(4): 405-413.

[35] Walker, R. and Pavía, S. 2011. Physical Properties and Reactivity of Pozzolans, and Their Influence on the Properties of Lime-pozzolan Pastes. *Materials and Structures/Materiaux et Constructions*. 44(6): 1139-1150.

[36] Yao, G. *et al.* 2019. Effect of Mechanical Grinding on Pozzolanic Activity and Hydration Properties of Siliceous Gold Ore Tailings. *Journal of Cleaner Production*. 217: 12-21.

[37] Yao, G. *et al.* 2020. Effects of Mechanical Grinding on Pozzolanic Activity and Hydration Properties of Quartz. *Advanced Powder Technology*. 31(11): 4500-4509.

[38] Zhang, C. and Lu, N. 2019 *Peering into Pores: What Happens When Water Meets Soil?* EOS.