

# Assessment of Pozzolanic Reactivity for Calcined Spent Bleaching Earth Ash (SBEA) using Strength Activity Index (SAI), Frattini Test and X-Ray Diffraction (XRD)

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**Abstract.** This research briefly investigates and compares three different and distinct methods of assessing the pozzolanic reactivity of a cementitious replacement material, Spent Bleaching Earth Ash (SBEA). SBEA is waste by-product of the edible oils refining industry and has some pozzolanic properties that could possibly be enhanced through calcination. Many methods have been developed to assess the reactivity of pozzolans and three of the most common ones were employed in this research; namely the Strength Activity Index (SAI), Frattini Test and X-Ray Diffraction (XRD) methods. These three methods were chosen as they measured reactivity based on fundamentally different methods; the SAI method relies on the mechanical strength of mortar cubes, XRD based it on the morphology of the material whilst the Frattini test looks into consumption of artificially-introduced calcium hydroxide by the pozzolan. This investigation allows correlation to be drawn between the three methods and at the same time, the effectiveness of calcination on SBEA can also be evaluated. The calcined SBEA was obtained through a 700°C heating process in the furnace at the for 4 hours. Both the SAI and Frattini tests were in good agreement and showed that the calcined SBEA consistently under-performed compared to uncalcined SBEA at both testing ages. This was, however, disputed by the XRD result which showed that SBEA benefitted from the calcination process as it lost over 7 % in crystallinity, hence making it more reactive. This outcome tells us that the selection of testing methods for pozzolanic reactivity must be done carefully and ideally several methods be used concurrently in order to correlate the results.

## 1 Introduction

Spent bleaching earth ash (SBEA) is a solid waste product of the palm oil industry's bleaching process. This solid waste is commonly disposed of without treatment in landfills, resulting in significant water and air pollution. The direct disposal of SBEA might also pose a logistical nightmare as the annual production volume of SBEA is huge. Therefore, if SBEA

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could be re-purposed or recycled it would reduce the burden on the disposal. In the past, SBEA has been adapted or incorporated in the production ceramics, bricks and fuel briquettes amongst others. SBEA has also been shown to contain sufficient amount of  $\text{SiO}_2$  for it to be considered pozzolanic in nature. This meant it can react with calcium hydroxide (CH) contents of a cement mix to produce additional C-S-H which will impart additional strength to the concrete. There have been numerous past studies looking into the partial substitution of cement with SBEA with success. This can be further improved through activation of SBEA through various means such as mechanical grinding, or thermal methods through calcination of the pozzolan. Mechanical activation of pozzolans have been well established whereby grinding of the pozzolans to make it finer would create more surface area to promote more effective reactivity [1]. On the other hand, thermal activation typically involves subjecting the SBEA to high temperature of around 400 to 900 °C in a furnace for a certain duration to break down its atomic structure and making it more amorphous/less crystalline. The target or ideal calcination temperature has been an area of contention, however, as it depended on the material itself and sometimes its source. Kaolinitic clays, for example, benefitted the most from 700 °C calcination [2] whereas raw clays saw better performance when calcined to 850 °C [3]. Calcination at excessive temperatures, however, cause decarbonation of the pozzolan and new phases caused by crystallization may start to appear [4]. SBEA is a pozzolan that has very similar properties to kaolinitic clays [5] and thus may benefit from calcination based on similar parameters.

To assess the improvement in reactivity of pozzolans such as SBEA, there are many methods which have been developed. The most common of these is the Strength Activity Index (SAI) bases the reactivity on the mechanical strength of mortar cubes containing 20 % pozzolanic replacements. A SAI of 75 % indicates the material has sufficient reactivity to qualify as pozzolan whilst values exceeding 100 % indicates performance exceeding the cement strength itself.

On the other hand, the XRD method looks at the relative crystallinity of pozzolans to assess reactivity. XRD is a versatile, non-destructive method which analyzes the phase or morphology change of material based on its crystalline structure. It works by beaming a laser at the material, and the beam may get diffracted upon impacting crystals or may just pass through if there were no obstructions. By studying the intensity of the peaks in the diffractogram, one can get indication about the level of crystallinity of the material tested. This technique is suitable for assessment of calcined pozzolans as the high heat treatment causes its crystalline arrangement to disintegrate and should show up as less intense peaks in the diffractogram. This loss of crystallinity renders the pozzolan more amorphous and hence more reactive [6]. For testing pozzolans the XRD test can be conducted on the pozzolanic material itself or on mortars containing the pozzolan.

Finally, there is also a method which measures the consumption of CH in the presence of cement called the Frattini test. The Frattini test assesses pozzolanic reactivity by measuring the consumption/loss of calcium hydroxide from the hydration of Portland cement after 8 or 15 days of reaction. The loss of calcium hydroxide is carried out by using chemical titration to measure the contents of OH<sup>-</sup> (hydroxyl ions) and CaO (calcium oxide) ions remaining. This method has been known to be reliable and offers a fast way of testing pozzolanic reactivity [7] and has shown good correlation to SAI test [8].

All these methods rely on principally different method to assess reactivity of pozzolans and past studies have been shown that results from one test do not necessarily correlate with the other. This study was commissioned to conduct a more comprehensive investigation into comparing the three most common methods of assessing reactivity using the relatively new pozzolan called SBEA as well as using calcination to introduce variety into the reactivity of the SBEA.

## 2 Experimental methodology

This section discusses the research framework as well as the methodology adopted in the laboratory work.

### 2.1 Materials preparation

CEM II 32.5 R Ordinary Portland Cement (OPC) was used as control and supplied in 50 kg bags. The fine aggregates used was sand sourced from the river and prior to use, it was oven-dried in 100 °C for 24 hours before the testing to remove any trapped moisture. The pozzolan used was spent bleaching earth ash (SBEA) obtained locally then oven dried at 100 °C prior to use as uncalcined SBEA whilst to produce calcined SBEA, the oven dried SBEA was further subjected to 700 °C heat treatment for 4 hours (Fig. 1). Water source used was tap water from the public water system.



**Fig. 1.** Uncalcined SBEA (left) and Calcined SBEA (right)

### 2.2 Strength Activity Index (SAI)

The mortar cubes prepared for SAI test conformed with ASTM C109. Three sets of mortar mixes were produced for the control specimens as well as two test specimens containing uncalcined SBEA and calcined SBEA. For the control specimen only OPC was used whilst for the test specimens 20 % of the OPC was substituted with uncalcined and calcined SBEA respectively. e the two assess the control mortar, uncalcined SBEA, and calcined SBEA. For all the specimen mortars, 6 cubes were produced so that 3 were available for 7-day strength test and another 3 for the 28-day strength test.

**Table 1.** Mortar mix design for six mortar cubes.

Material	Specimens		
	Control	Uncalcined SBEA	Calcined SBEA
OPC	500 g	400 g	400 g
SBEA	0 g	100 g	100 g
Sand	1330 g	1330 g	1330 g
Water	401 g	461 g	456 g

The flow table test was done to adjust the water/binder ratio to obtain a flow of within  $110 \pm 5$  mm in accordance with guidance from ASTM C109. Then, the mixtures were remixed for 30 seconds and casted into 50mm cubes with the aid of vibrating table. All blocks were demoulded after 24 hours and placed in a water bath for curing until the day of testing.

The SAI was obtained thus as a percentage of the compressive strength of test specimen against that of the control specimen.

### 2.3 X-Ray Diffraction (XRD)

The XRD test utilizes cut samples from the mortar specimens cast for the SAI test. To ensure that the hydration process does not continue whilst the cut samples were in storage, they were immersed in an alcohol solution for 7 days before being stored in a vacuum container until the day of testing. XRD analysis was carried out on the Rigaku Smartlab X-ray Diffractometer operated at wavelengths of  $k_1 = 1.54059$  and  $k_2 = 1.54441$ , scanning mode of 2 theta from 3 to 90°. From the diffractogram, the ratio of area under each peak against the overall area would give the percentage crystallinity of the material. As explained earlier, the lower the level of crystallinity meant higher reactivity.

### 2.4 Frattini test

The Frattini test assesses pozzolanic reactivity by measuring the consumption/loss of calcium hydroxide from the hydration of Portland cement after 8 or 15 days of reaction. To do this, 20 g of the SBEA was prepared by sieving through 2.7 $\mu$ m nominal size filter and then immersed and mixed in distilled water. These were mixed well and left for 8 and 15 days in a sealed glass bottle in an oven at 40°C until the testing day. Two testing solutions were prepared for the assessment of residual of CH concentrations in the filtrate. The first of these is the preparation of diluted 0.1 mol/L hydrochloric acid using sodium carbonate, water and methyl orange indicator (Fig. 2). This will be used to titrated to evaluate OH<sup>-</sup> (hydroxyl ions) concentrations. The second is CaO concentration prepared using Patton and Reeder's reagent and 0.03 mol/L EDTA solution and adjusted to a pH of 12.5. The filtrate was analysed for two types of observation which are OH<sup>-</sup> and CaO.

The loss of calcium hydroxide is carried out by using chemical titration to measure the contents of OH<sup>-</sup> (hydroxyl ions) and CaO (calcium oxide) ions remaining. Results are plotted onto a calcium ion (y-axis) vs hydroxyl ion (x-axis) graph and compared against curve for a control sample of 100% CEM-I cement. Results that lie beneath this curve show positive loss of calcium ions, indicating pozzolanic activity whilst those that lie on or above the curve correspond to no pozzolanic activity.



**Fig. 2.** Titration to dilute HCl using methyl orange indicator

### 3 Results and discussion

The SAI test results in Fig. 3 show that all samples exhibited considerable pozzolanic reactivity, having achieved minimum ASTM C618-05 requirement of 75 % to qualify as pozzolanic material. Of notable mention was how the uncalcined SBEAs was the best performing amongst all the specimens, better than both the control and calcined specimens at both testing ages. In fact, this result was expected because it was observed during mixing of the mortar that the calcined SBEA required much more water to achieve the same flow workability. This finding was further corroborated by tests on the SBEA samples itself which showed a much higher absorption rate of up to 30 % for calcined SBEA compared to 18 % for uncalcined SBEA. Naturally, as cement:water ratio reduces in a mortar, it was expected that this will be reflected in the reduction in strength. thus, this is one limitations of the SAI method where reliant on mechanical strength of mortar specimens resulted in a drawback.

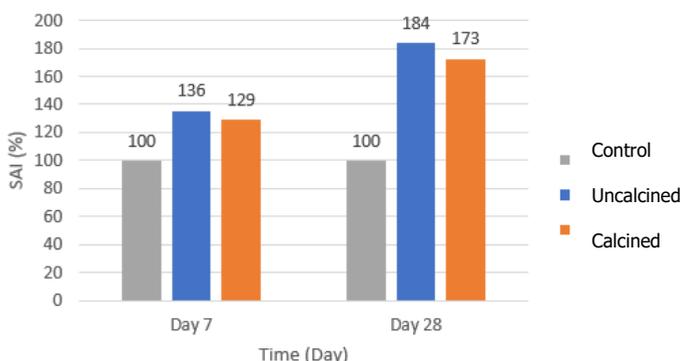


Fig. 3. Strength activity index of mortar specimens

When the same mortar samples used in SAI tests were analysed using XRD, the reverse was observed instead whereby the calcined SBEA displayed improved reactivity due to the loss of crystallinity from 28 % prior to calcination to 21 % afterward. This 7 % reduction in crystallinity can be observed visually in the drop of the peak intensities at 18.1° and 21.8 ° (Fig. 4) after calcination whilst the peak at 26.3 ° has also diminished quite drastically. The loss in crystallinity in these major peaks directly led to the loss of crystalline structure in the pozzolan and rendering it more amorphous.

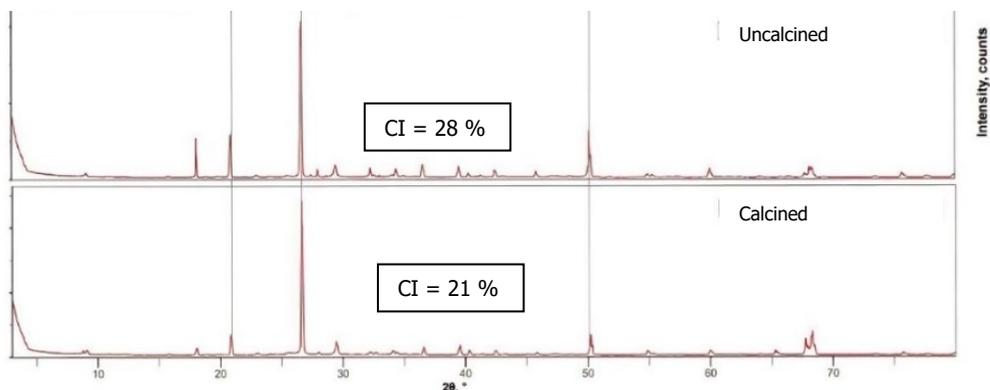
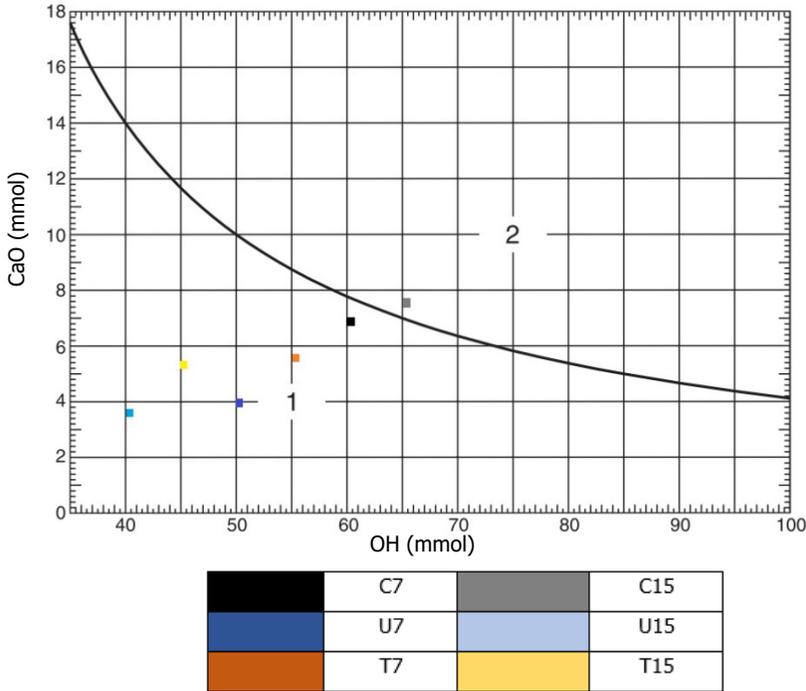


Fig. 4. X-ray diffractogram of specimens

In the Frattini test, the uncalcined SBEA sample, again, was the most reactive compared to both the calcined SBEA and control cement specimen. This was reflected in the highly diminished levels of OH<sup>-</sup> and CaO concentrations in calcined SBEA specimens (Fig. 5), proving that much more Ca(OH)<sub>2</sub> had reacted. This was observed for both testing ages of 8 and 15 days. The uncalcined SBEA had significant more residual Ca(OH)<sub>2</sub> remaining in the mix but not as much as the control, indicating some reaction had also taken place but not at the same pace as that of the calcined SBEA.

The Frattini results appear correspond well to the findings from the SAI tests and this is also corroborated by past studies using other materials such as dolomite waste [9].



**Fig. 5.** Frattini test result showing residual CaO and OH concentrations.

The result from SAI test is obviously affected by the percentage of water absorption and the presence of SiO<sub>2</sub>. As for the percentage of water absorption, the relatively high water absorption rate of calcined SBEA affects both the hydration process as well as the strength development of the mortar specimens as water is one of the main aspects for the hydration process to occur. The more water absorbed by the calcined SBEA meant less water will be available for reaction the cement. This also directly led to the reduced amount of CH being available to react with the silica oxides of the SBEA. Overall, this resulted in the reduction in the amount of C-S-H being produced.

## 4 Conclusions and recommendations

The main findings from this research are as follows:

1. SAI measurement of pozzolanic reactivity of SBEA correlates well with findings from the Frattini test. Both tests found that the uncalcined specimens had higher reactivity than calcined ones.
2. Despite this, it must be noted that SAI relies on results from mechanical testing of mortars and in order for these mortars have identical properties, they are required to

have the same flow as well. To achieve this for the calcined SBEA mortar mix required additional water and hence directly contributed to the reduced strength and lower SAI.

3. The reactivity measurement from XRD analysis contradicts with that of the SAI and the Frattini test results, showing that calcination in fact improved reactivity from the loss of crystallinity in the SBEA atomic structure.
4. Thus, the overall findings here indicate that there is indeed a difference in the pozzolanic reactivity assessment methods and that the choice in selecting the correct methods must be guided by an understanding of the way in which the measurement of reactivity is carried out.

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