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ACCELERATION OF EARLY STRENGTH DEVELOPMENT IN MORTARS CONTAINING SOLUBLE SILICA EXTRACTED FROM PALM OIL CLINKER

Soluble silica from palm oil clinker was extracted using Laine's method. It involved two major steps, namely water reflux and distillation. The use of 480 g of POCP and 12 hours of distillation in the extraction experiment resulted in 53.50% of dissolved silica, which was the highest gain among the trial experiments and was chosen as an optimum parameter for the subsequent characterisation analysis. In addition, its effect on cement hydration was studied by including it as a filler in mortar mixtures. Mortar with 7.50% of extracted silica gained high strength in the early days of curing and performed well throughout the maturing age. The rapid hardening properties of soluble silica-based mortar would promote the potential of soluble silica as an additive for rapid hardening.

Keywords: Palm oil clinker powder; soluble silica; extraction; rapid hardening; mortar

1. Introduction

The increasing awareness of sustainability in the construction industry has driven researchers to discover more alternative materials to replace conventional cement. This effort is critical since cement has become one of the most demanded construction materials. Moreover, introducing a new alternative material will help provide alternative binder options that are more environmentally friendly. It will support the initiative to reduce the high carbon footprint from cement production.

Cement industries have been accountable for the 8.00% of global emissions [1]. A study from Yehia et al. [2] mentions how industrial wastes such as fly ash (FA), silica fume (SF) and ground granulated blast furnace slag (GGBS) are renowned as cement replacement materials from a significant proportion of amorphous silica in their particle [3-7]. The amorphous silica in these wastes has pozzolanic characteristics and reacts with Portlandite ($Ca(OH)_2$) from cement's hydration to form additional calcium silicate hydrate (C-S-H) products. The additional C-S-H helps produce denser microstructures for concrete and improves the late strength [8].

Agro-based wastes are widely reused and recycled as filler or cement replacement material. Even though the proportion of silica is relatively as high as other industrial wastes, palm oil clinker (POC) is not a superior choice due to its low reactivity and porous structure [9]. Karim et al. [10] and Abutaha et al. [11] conducted mechanical and thermal treatments to enhance the pozzolanic reactivity of POC and increase its specific surface area. However, the chemical treatment to increase POC reactivity has yet to be extensively studied. Therefore, this study aims to determine the effect of acid leaching on POC and the feasibility of soluble silica extraction. The soluble silica is expected to take part more effectively in the pozzolanic reaction. The silica would be easily dispersed during the mixing process, producing a more homogeneous mortar mixture in a soluble form. The common method that has been extensively utilised to extract silica from silica-containing materials is the alkaline extraction method [12-14]. Alkali is applied as a solvent for silica dissolution because silica is highly soluble at a high pH value. In another study, Richard Laine and his team introduced a newly found silica extraction method, which was claimed as Laine's method [15].

In Laine's method, a catalytic quantity of base is added to catalyse the reaction between silica in the rice husk ash and liquid polyol to extract soluble silica in the form of alkoxysilane solution [15]. This study adopted Laine's extraction method by considering the quantity of base required. Furthermore, it included the amount of source material and distillation

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duration as the parameters. Thus, the appropriate combination suitable for palm oil clinker can be generated based on the amount of soluble silica. This study also aimed to evaluate the contribution of soluble silica to mortar in terms of its strength development.

2. Experimental Method

POC was used as the raw material in this study. This solid waste was collected as the by-product of mesocarp fibres and oil palm shell burning at high-temperature incineration from a palm oil mill at Lepar Hilir, Malaysia. Clinker appeared in blackish-grey colour, as shown in Fig. 1. In its raw state, POC was low in reactivity and porous in nature. Therefore, additional treatments were needed to enhance its pozzolanic reactivity.

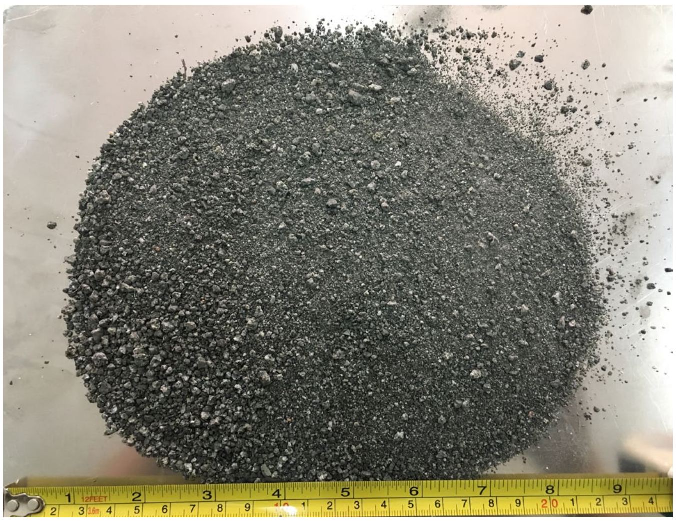

Fig. 1. The appearance of palm oil clinker powder

This study used two treatment phases prior to the soluble silica extraction process. In the first phase, POC was ground to smaller particle sizes using the steel ball mill of the LA Abrasion Machine. The steel drum was rotated for 3000 cycles to ensure a thorough grinding process. The finer particles resulting from this phase were referred to as palm oil clinker powder (POCP). This powder was then sieved through a 300 µm screen to filter the coarser particles. If any coarser particles were retained on the sieve, they would be returned to the LA machine for the second milling round. Next, the finer particles were tested for their chemical oxide composition before being transferred to the subsequent phase. TABLE 1 shows the proportion of primary chemical oxides in POCP used in this study.

ASTM C618 has required Class F pozzolanic material to have a summation of three oxides proportion, $SiO_2 + Al_2O_3 + Fe_2O_3$, at least 70.00% (wt%). Meanwhile, the summation of those oxides in non-treated POCP is only 66.82% (wt%). Therefore, the second treatment phase was carried out to elevate the pozzolanic reactivity of this material, mainly from the perspective of its reactive silica proportion. The second phase would involve a chemical treatment process using an acid solution.

2.1. Chemical treatment process

The chemical treatment process was carried out to remove residual organics or excessive impurities from the raw POCP and break down the ash structure to extricate the silica compound. The process comprised two essential steps: heating the pre-treatment solution at the designated temperature and filtration to obtain treated POCP. First, 100 g of POCP was stirred in 1000 ml of 0.1 M HCl solution with a temperature of 80 ± 5°C. The stirring process was performed magnetically on the electrical hotplate to obtain a stable temperature for 1 hour. The treated POCP was then tested for its chemical oxide composition as source material in the succeeding soluble silica extraction experiment.

2.2. Soluble Silica Extraction by Laine's Method

After promoting the silica proportion in palm oil clinker powder (POCP) through acid leaching treatment, soluble silica was then extracted from POCP using Laine's Method [15]. In this study, ethylene glycol (EGH_2) and potassium hydroxide (KOH) were used as a solvent and catalyst for the dissolution of silica from POCP, respectively. The extraction was conducted by first boiling the mixture of treated POCP (120 g and 480 g) and 1 litre of water in a round-bottomed flask at 100°C for 24 hours under the reflux condition (Fig. 2a). During water reflux, the basic components in the source material would dissolve in water to achieve an aqueous pH value >9, the desired condition for silica extraction. After 24 hours, while keeping the reaction hot, the reflux condenser was switched to distillation mode to distil water (Fig. 2b). For every 200 ml of distilled water collected during distillation, 200 ml of ethylene glycol (EGH_2) was added to the reaction solution. At the first addition of EGH_2, 10 g of KOH solution dissolved in 25 ml of water was also added as a catalyst, and the temperature was increased to 200°C. After 6 and 12 hours of reaction between EGH_2 and POCP, the solution left in the round-bottomed flask (dissolved silica) was collected and filtered to remove the undissolved solid material.

TABLE 1

Chemical oxide composition of palm oil clinker powder

Specimens	Chemical composition of POCP by weight percentage (wt%)							
	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	MgO	P_2O_5	LOI
POCP	52.85	3.26	10.71	17.07	8.61	2.22	4.25	0.02

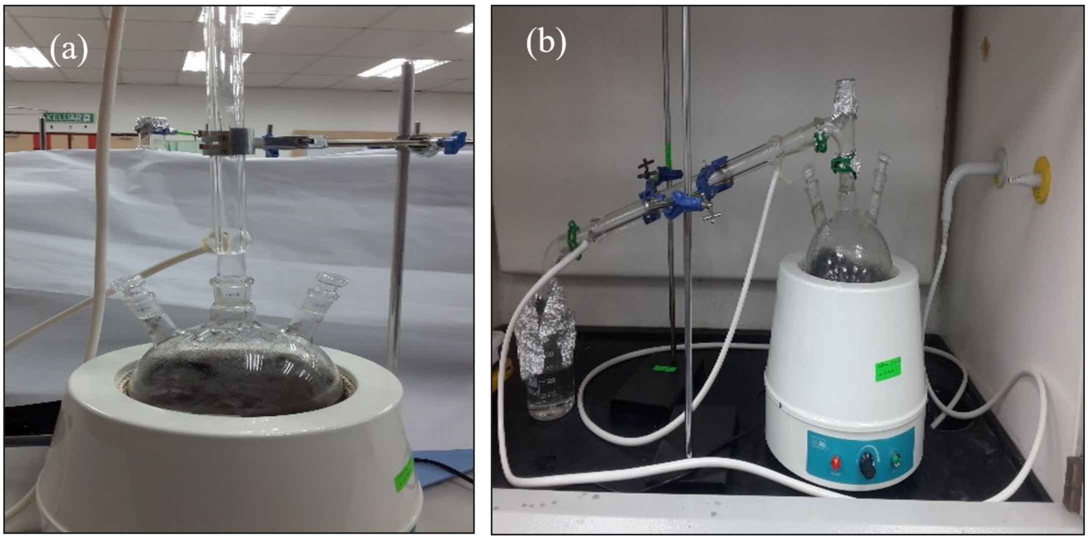

Fig. 2. Extraction process (a) under reflux condition; (b) distillation mode

2.3. Mortar Mixtures

The extraction of soluble silica was assessed as cement replacement material by introducing it into mortar mixtures. Silica from POCP was expected to react with Portlandite from the hydration of cement to enhance the cementitious matrix and produce denser and stronger mortar. Different percentages of soluble silica from 2.5, 5.0 and 7.5% (by weight of cement) were used in this study. The control mixture was designed to achieve the characteristic strength of 20 MPa on the 28th day. TABLE 2 shows the detail of the mixture proportions used in this study.

A conventional mortar mixing method was adopted in this study. Fine aggregate and cement were stirred for 1 minute until homogeneously mixed. Water and soluble silica were then gradually introduced into the mixture, and the mixing was continued for 2 minutes. At the end of the mixing process, the fresh mortar was manually mixed to ensure its homogeneity. These fresh mixtures were then cast into 50 mm × 50 mm × 50 mm cube moulds and kept at room temperature for 24 hours. The hardened specimens were then demoulded and transferred to the water curing until the testing day at 3, 7 and 28 days

3. Result and discussion

3.1. Chemical oxide composition

Analysis of chemical oxides composition was conducted to study the effect of HCl concentration and soaking period in removing impurities and relatively increasing the proportion of silica. During the chemical pre-treatment process, the impregnation of POCP with hydrochloric acid solutions played an important role in degrading the rigid structure of lignocellulosic from the POCP. TABLE 3 shows the oxide compositions of chemically pretreated POCP where SiO_2, K_2O, Fe_2O_3, CaO, P_2O_5 and Al_2O_3 are dominantly present.

Based on TABLE 3, the proportion of silica increased up to 8.00% after being chemically pretreated with HCl solutions. The pre-treatment process was also able to reduce the proportion of alkali and alkaline earth metals, i.e. potassium oxide (K_2O), magnesium oxide (MgO) and calcium oxide (CaO). The low acid concentration in the treatment process has effectively assisted in solubilising hemicellulosic components from the source material and abetted the enzymatic digestibility [16]. Acid leaching

TABLE 2

Proportion of mortar

Sample	Cement (kg/m^3)	Soluble Silica (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)
Control	720.0	—	504.0	2660.0
Soluble Silica 2.5 (SS2.5)	702.0	18.0	504.0	2660.0
Soluble Silica 5.0 (SS5.0)	684.0	36.0	504.0	2660.0
Soluble Silica 7.5 (SS7.5)	666.0	54.0	504.0	2660.0

TABLE 3

Chemical oxide composition after impregnation with HCl

Specimen	Chemical composition of POCP by weight percentage (wt %)							
	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	MgO	P_2O_5	$SiO_2 + Al_2O_3 + Fe_2O_3$
POCP	60.23	2.14	9.13	14.84	4.59	1.58	2.64	71.5

helps shatter the cellulose and lignin layers of POCP to allow the digestion process, thus helping remove impurities, as mentioned above. In addition, the summation of three principal oxides, SiO_2 + Fe_2O_3 + Al_2O_3, was more than 70.00% and has passed the defined specification of ASTM C618 Class F pozzolan.

3.2. Extraction process

The manipulated variables for soluble silica extraction process were the weight of POCP used and the distillation period. Using 480 g of POCP for silica extraction resulted in a higher percentage of dissolved silica in the solution than 120 g of POCP. As the weight of the POCP increases, the source of soluble silica directly increases. This higher amount of source material would promote the higher reaction of silica with the solvent through the dissolution process. Thus, it brings a positive contribution to the silica dissolution rate.

Meanwhile, conducting distillation for 12 hours resulted in a higher percentage of dissolved silica in the solution than 6 hours of distillation. The silica dissolution increases with time and only stops when an unknown saturation point is reached. The extended period helps the dissolution of silica due to its unpredictable reaction with the solvent. TABLE 4 illustrates major inorganic oxides incorporated in extracted soluble silica.

Based on TABLE 4, the dominant inorganic oxides found in the soluble silica solution were silica, SiO_2 and potassium oxide, K_2O. A high percentage of K_2O was present in the extracted solution because potassium hydroxide, KOH, was added as the catalyst for the silica extraction process. All experiments showed consistent results. The extracted solutions were primarily dominated by K_2O, except for the solution extracted from 480 g of POCP and 12 hours of distillation. Therefore, the soluble silica used at the next stage of study was produced by conducting 24-hours-water reflux and 12-hours-distillation with 480 g of POCP. Furthermore, the parameter was also used for the subsequent test on the effect of this powder in cementitious mortars.

3.3. Compressive strength

As observed in Fig. 3, it is evident that sample SS5.0 had the highest compressive strength among all the mortar batches, which were 13.01 MPa and 16.90 MPa on day-3 and day-7, consecutively on early days. The compressive strength of sample SS5.0 on day-3 and day-7 was 5.24% and 6.20% higher than that of reference mortar (control). The early age strength of soluble silica-based mortar was against the conventional pozzolanic trend. All the soluble silica-based mortar specimens possessed compressive strength higher than the reference mortar (control) on day-3 and 7. The result of high compressive strength for soluble silica-based mortar during early age is consistent with the previous study by Mahmud, Megat-Yusoff, Ahmad and Farezzuan [17]. They discussed that the use of extracted nano-sized particles in the cement-based mortar would affect the microstructure of the mortar, particularly in filling the voids between cement grains and bringing enhancement in the hydration during early age. The aqueous medium enabled silica to be well dispersed in the fresh mortar and reacted actively in the cementitious framework. It caused the pozzolanic reaction to occur earlier in the fresh cementitious framework and contributes notably to the early strength development of the cementitious system.

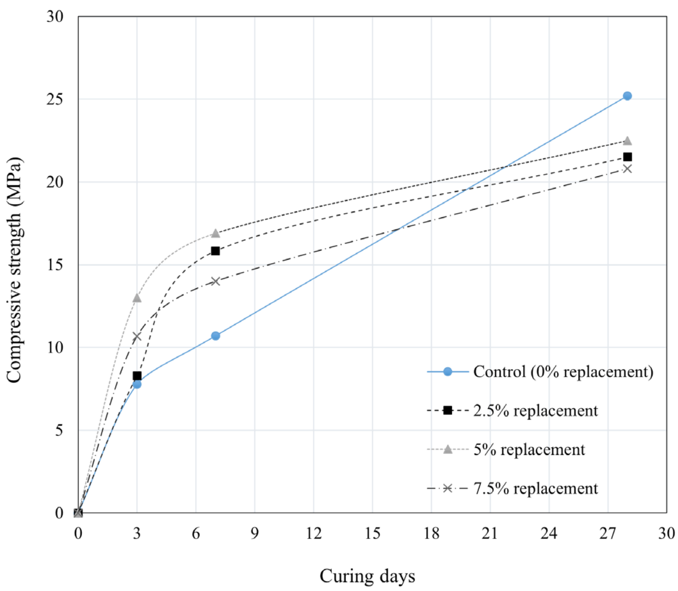

Fig. 3. Compressive strength development of mortar mixtures

Based on Fig. 3 above, the strength performance of all mortars increased throughout the curing period. However, the compressive strength of soluble silica-based mortars at later age was lower than that of control mortar. Compared with control mortar, the slower strength development of soluble silica-based mortars during later age was noticed. The slow strength development of soluble silica-based mortar during later age indicates that the active silica used to replace cement might have been finished consumed during early age and brought no contribution

TABLE 4

Inorganic oxides content of soluble silica extracted from POCP

POCP amount	Distillation period	Inorganic Oxides content of soluble silica (%)				
		SiO_2	Al_2O_3	Fe_2O_3	K_2O	P_2O_5
120g	6 hours	13.93	3.64	5.07	75.71	1.65
	12 hours	40.56	4.47	1.44	52.49	1.03
480g	6 hours	46.87	1.34	1.89	48.37	1.53
	12 hours	53.50	0.86	1.99	43.11	0.55

to the strength development during later age. Nevertheless, all of the soluble silica-based mortar achieved the targeted strength of 20 MPa on the 28th day.

4. Conclusion

The application of Laine's Method to extract soluble silica from POCP is practicable. Using 480 g of POCP and 12 hours of distillation in Laine's Method could produce soluble silica with 53.50% purity. The effect of partially replacing cement or mortar with soluble silica on compressive strength was analysed. A new trend of strength development for soluble silica-based mortar was determined based on the result and analysis of the compressive strength test. The compressive strength development of soluble silica-based mortar was rapid at an early age but slow at a later age. The rapid strength development of soluble silica-based mortar during early age was caused by the earlier taken place pozzolanic reaction induced by the active silica added. The ability of soluble silica-based mortar to achieve the targeted strength indicates that the extracted soluble silica is qualified as a partial cement replacement material in terms of strength. Future research on the other properties of the soluble silica-based mortar is recommended.

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