

Influence of Fineness of Cement Produced from Industrial Wastes on Strength of Mortar

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ABSTRACT

The effect of the fineness of cement produced from waste-based clinker on mortar strength was studied. Combinations of wastes—namely, ark shell, waste limestone powder and water supply sludge—with the addition of hydrated lime were prepared with an appropriate mix proportion for the clinkerization process to produce cementitious material. Clinkers were ground in order to obtain a target fineness ranging from 2,000 to 3,500 cm²/g and then blended with 5% gypsum by weight to produce a waste-based cement similar to an Ordinary Portland Cement type I (OPC). The chemical and physical properties of the waste-based cement were investigated and compared with those of OPC. The results revealed that the mortar strengths of the waste-based cement increased with curing time but were relatively lower than those of OPC. Cracking and swelling could be observed in mortars produced from waste-based cement having relatively low fineness. The negative effects could be eliminated when cement fineness was increased, resulting in markedly increased strengths. Expansion behavior due to the reaction of free lime and the formation of ettringite in cement pastes was observed and its implications discussed.

Keywords: wastes utilization, cement, clinkerization, mortar, Blaine fineness

INTRODUCTION

Waste-based cement is a combination of certain types of industrial waste as raw material in the clinkerization process. Recently, reuse of industrial wastes has played an important role as a cost effective, alternative waste management approach (Thongdaeng *et al.*, 2010). Nontananandh *et al.* (1991) suggested that utilization of wastes would need to satisfy the NICE criteria (non-hazardous materials, improvability, compatibility and economic

feasibility). Many studies have also attempted to utilize industrial wastes as raw material in clinkerization (Ampadu and Torii, 2001; Alp *et al.*, 2008; Tsakiridis *et al.*, 2008). However, in Thailand, only a few researchers have focused on the production of waste-based cement. Among the pioneer studies, Pimraksa *et al.* (2009) synthesized a Belite cement using lignite fly ash with a relatively low burning temperature of 1,200 °C. However, their research seemed to concentrate mainly on phase compositions and some properties such as strength and setting time.

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As target raw materials for the study, industrial wastes such as ark shell, waste limestone powder and water supply sludge are produced in large quantities. According to the Bureau of Agricultural Economics Research of Thailand (2009), the amount of ark shell waste is approximately 80,000 tonne annually. The cement industry has estimated that approximately 8–10 million tonne of waste limestone powder is generated annually. (Noyes, 1994; The Office of Industrial Economics, 2010). According to the annual report of the Metropolitan Waterworks Authority (2009), the production of water supply sludge in Thailand was approximately 60,000 tonne per year. Converting industrial wastes into useful material not only has environmental benefits but also may conserve natural resources by creating new materials for engineering construction. A preliminary study therefore focused on determination of the appropriate proportions of these wastes in order to produce waste-based cement similar to Ordinary Portland Cement (OPC) (Yoobanpot *et al.*, 2010). However, the quality of waste-based cement in terms of the physical properties such as cement fineness needed further improvement.

Many researchers have indicated that the fineness of the cement influenced the performance of cement pastes and concretes. Cement having relatively high fineness could improve mortar strength (Shin *et al.*, 2003; Celik *et al.*, 2007). In addition, resistance to sulfate penetration could be improved in cement made with finer material (Binici *et al.*, 2007). As recommended by the ASTM C150 and AASHTO M85 standards, typical hydraulic cement should have a Blaine fineness value within the range 3,000–5,000 cm^2/g and a specific gravity of 3.15.

Initially, the current study concentrated on the utilization of industrial wastes to produce a cementitious material having hydraulic properties similar to OPC. In addition to reviewing the preparation approaches to produce waste-based

cement, the main objective was to investigate the effect of cement fineness on the strength of mortars using cement produced from industrial wastes. X-ray diffraction (XRD) analysis was also performed on the cement pastes in order to investigate the reaction products which affected subsequent swelling potential and those which contributed to a strength improvement in relation to the fineness of the cement.

MATERIALS AND METHODS

Preparation approaches for waste-based cements and chemical composition tests

In this study, the waste materials—namely, ark shell, waste limestone powder and water supply sludge—were sampled periodically to obtain the representative raw materials. Table 1 shows the results of tests for heavy metals, using an atomic absorption spectrophotometer (AAS; GBC equipment Model Avanta) with a flame ionizer. The analysis results revealed that the industrial wastes performed well in accordance with the proposed NICE criteria as the level of heavy metals contained were lower than the USEPA standard (1993).

The chemical composition, in terms of the major oxides in the industrial wastes, was tested using a standard titrimetry method, atomic absorption spectrometry and a gravity method at the Department of Science Service, Thailand. As indicated in Table 2, the results showed that the major oxide of ark shell (AS) and waste limestone powder (WLP) was calcium oxide (CaO), whilst that of the water supply sludge (WSS) was silicon dioxide (SiO_2).

Using general guidelines to control the clinker quality (Kamon and Nontananandh, 1991; Hewlett, 1998), raw materials for clinkerization were mainly formed by combined wastes such as ark shell (5%), waste limestone powder (50%) and water supply sludge (25%) with the addition of hydrated lime (20% by dry weight). Substantially,

the most appropriate proportion with a ratio of 5:50:25:20 could successfully produce a dark gray-colored clinker having self hardening properties. It was also found that a higher degree of clinkerization could be obtained when the wastes were ground initially, before being heated in an electric arc furnace using a heating pattern with a maximum temperature of 1,450 °C, as shown in Table 3.

After heating, the resultant burned clinker was cooled down to room temperature,

ground into powder and then blended with 5% gypsum by weight to prevent flash setting due to the hydration of C₃A. The blended products were ground to obtain the desired fineness values by passing the ground material through sieves No.100–No.230 (Table 4).

In order to obtain the target fineness within a range of 1,600–3,600 cm²/g, the fineness and specific gravity of the cement samples were measured using the Blaine air permeability test in accordance with ASTM C204-79 and ASTM

Table 1 Heavy metal amounts in the different wastes.

Material	Heavy metal (mg/kg)					
	Cu	Cd	Cr	Pb	Ni	Zn
USEPA (1993) standard	1,500	39	3,000	420	18	2,800
Ark shell (AS)	3.16	nd	0.80	nd	nd	5.03
Waste limestone powder (WLP)	3.34	0.05	1.85	nd	nd	5.34
Water supply sludge (WSS)	34.68	nd	32.76	24.22	38.88	102.01

Note : nd = Not detected

Table 2 Major chemical composition of wastes used in this study.

Material	Chemical composition (% by dry weight)								Total
	CaO	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Na ₂ O	MgO	K ₂ O	LOI**	
AS	53.91*	nd	0.07	0.02	0.50	0.03	0.002	44.70	99.22
WLP	51.70	nd	0.11	0.04	0.01	0.36	0.005	42.40	94.68
WSS	0.40	17.39	52.19	9.56	0.63	1.04	0.017	17.90	99.12

Note : * = Quantitative comparable, ** = Loss on ignition

Table 3 Heating pattern for clinkerization.

Heating stage	1	2	3	4	5
Rate of firing (°C/min.)	7	0	7	0	
Initial temperature (°C)	40	650	650	1,450	cool down
Target temperature (°C)	650	650	1,450	1,450	period
Heating duration (min.)	87	90	114	60	

Note: Total heating time was 351 min.

Table 4 Grinding details.

Sample	% Fineness (Sieve No.)	Grinding time (min)	Grinding apparatus
S1	No.100	15–30	Agate mortar and pestle sets
S2	No.170	20–25	Mechanical grinding apparatus
S3	No.200	25–30	Mechanical grinding apparatus
S4	No.230	30–40	Mechanical grinding apparatus

C188, respectively. The chemical composition of the compounds was investigated using x-ray fluorescence (XRF) and x-ray diffraction (XRD). Compressive strengths of $5 \times 5 \times 5 \text{ cm}^3$ mortar produced by waste-based cement, with different degrees of fineness, were tested in accordance with ASTM C109 after curing times of 3, 7, 28 and 90 d and then compared with OPC (control tests). Heavy metals tests were performed by atomic absorption spectrophotometry (AAS) with a flame ionizer to assure the quality of cement from an environmental viewpoint. The major reaction products of hydrate cement pastes were examined using XRD in order to correlate them with the compressive strengths of the mortars.

RESULTS AND DISCUSSION

Chemical composition of and compounds in waste-based cement

The chemical composition of the waste-based cement samples was analyzed and compared to those of OPC (Table 5). In addition, Table 6 shows the main cement compounds, as estimated using Bogue's equations (Bogue, 1955).

It was found that the waste-based cement had a chemical composition similar to that of OPC, consistent with the findings of Neville (2002). However, the free lime content in the waste-based cement was approximately 4 times higher than in

OPC. When compared to OPC, the waste-based cement was also formed mainly by C_3S , C_2S , C_3A and C_4AF compounds, indicating that the C_3S and C_2S compounds in waste-based cement were relatively lower than in OPC. However, the C_3A compound was about twice as pronounced as in OPC. Figure 1 shows the XRD patterns of OPC and waste-based cement. In addition, results presented in Table 7 indicate that the waste-based cement conformed well to the recommended NICE criteria since heavy metals were detected at levels lower than the USEPA (1993) standard.

Fineness and specific gravity of waste-based cements

The waste-based cements with different degrees of fineness and different specific gravities are shown in Table 8. The specific gravity of the cements increased with their Blaine fineness value. Figure 2 illustrates the relationship between Blaine fineness and specific gravity, which could be expressed as shown by a power function.

Compressive strength of mortars

After curing for 3 d, cracks could be observed due to expansion of the mortar produced from the S1 waste-based cement, while more swelling occurred over a 90-day period (Figure 3). The compressive strength of the mortar in this case could not be evaluated. It was assumed that

Table 5 Chemical composition of OPC and waste-based cement.

Type of cement	Chemical composition (%)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI	Free lime
OPC	20.26	6.05	3.11	65.63	1.07	2.67	1.49	1.21
Waste-based	18.42	9.25	2.63	64.31	1.23	0.09	1.06	4.98

Table 6 Bogue's compounds of Ordinary Portland Cement (OPC) and waste-based cement.

Type of cement	Main cement compounds (%)			
	C_3S	C_2S	C_3A	C_4AF
OPC	60.43	12.83	10.78	9.45
Waste-based	55.57	11.19	20.07	8.00

this swelling potential was affected by both the chemical and physical properties of the S1 waste-based cement. Further discussion is presented later to substantiate this assumption.

The experimental results revealed that the compressive strength of mortar for the S2, S3 and S4 waste-based cements increased with curing time (Table 9). It could also be observed that the

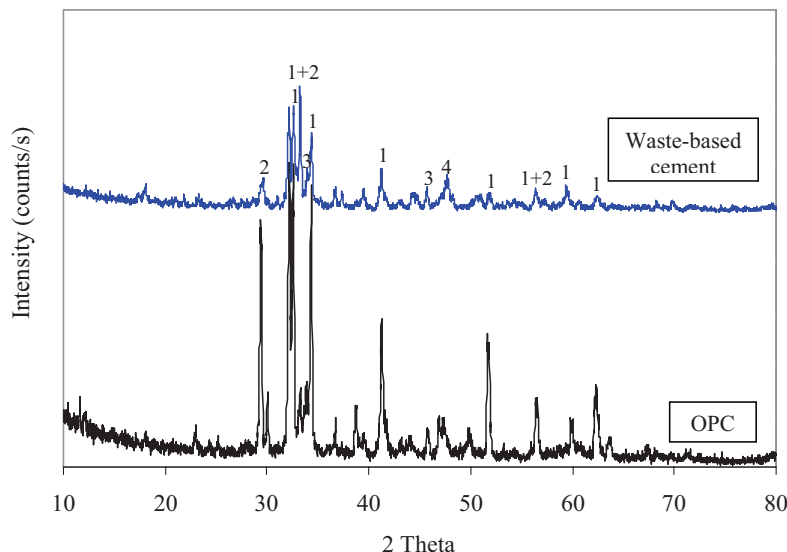


Figure 1 X-ray diffraction pattern of Ordinary Portland Cement (OPC) and waste based cement (tricalcium silicate, C_3S = 1; dicalcium silicate, C_2S = 2; tricalcium aluminate, C_3A = 3; tetracalcium ferroaluminate, C_4AF = 4).

Table 7 Heavy metal of waste-based cement compared to the (1993) standard.

Item	Heavy metal (mg/kg)					
	Cu	Cd	Cr	Pb	Ni	Zn
USEPA (1993) standard	1,500	39	3,000	420	18	2,800
Waste-based cement	28.53	nd	27.71	4.38	16.9	153.26

Table 8 Blaine fineness and specific gravity of waste-based cement samples.

Sample	Blaine fineness cm^2/g			Specific gravity		
	No.1	No.2	No.3	No.1	No.2	No.3
S1	2,314	1,944	1,693	2.72	2.59	2.57
		2,000 (mean)			2.63 (mean)	
S2	2,741	2,696	2,573	2.89	2.85	2.81
		2,670 (mean)			2.85 (mean)	
S3	3,006	2,951	2,811	2.94	2.91	2.90
		3,000 (mean)			2.92 (mean)	
S4	3,593	3,442	3,387	3.03	3.02	3.00
		3,500 (mean)			3.02 (mean)	

Note: S1–S4 components are provided in Table 4.

strength development characteristics of the mortars were substantially improved as the finenesses of cement increased (Figure 4). Therefore, the fineness of the cement affected strength

development. However, the strengths of the mortars were relatively lower than those of the control mortar (OPC) due to the fact that the waste-based cement in this study contained lower

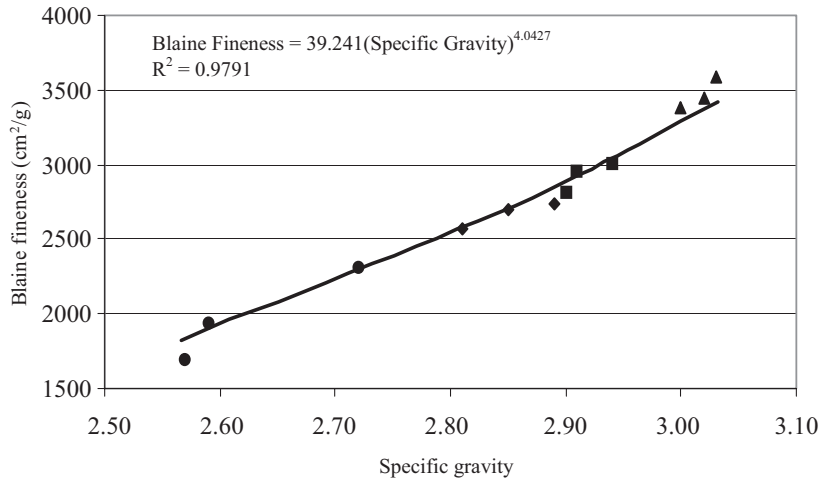


Figure 2 Relationship between Blaine fineness and specific gravity of waste-based cement samples. (S1= ●, S2= ◆, S3 = ■, S4 = ▲). S1–S4 components are detailed in Table 4.



Figure 3 Swelling and expansion on mortar produced from S1 sample after 90 d.

Table 9 Compressive strength of mortars after various curing times.

Sample	Compressive strength (kPa)			
	3 days	7 days	28 days	90 days
OPC	17,412	22,528	29,406	31,818
S2	1,804	2,663	2,953	3,116
S3	2,374	3,605	4,716	5,304
S4	6,062	8,438	9,850	16,917

Note: S2–S4 components are provided in Table 4.

amounts of the C_3S and C_2S compounds than OPC. However, the mortar strengths obtained were greater than those obtained by Pimraksa *et al.* (2009) whose reported average mortar strengths at 28 and 45 d of 1,615 and 1,890 kPa, respectively.

Correlation between compressive strength and Blaine fineness

The relationship between compressive strength and Blaine fineness is shown in Figure 5,

which indicates that the mortar strength increases exponentially with an increase in Blaine fineness for all curing times. Based on curve fitting by the least squares method, the relationships agreed well with exponential functions as summarized in Table 10. However, the fineness of hydraulic cement should not be greater than 5,000 cm^2/g since then the hydration of the cement is greatly accelerated, resulting in a short initial setting time and loss of cement flow (Aydin *et al.*, 2009). Furthermore, in

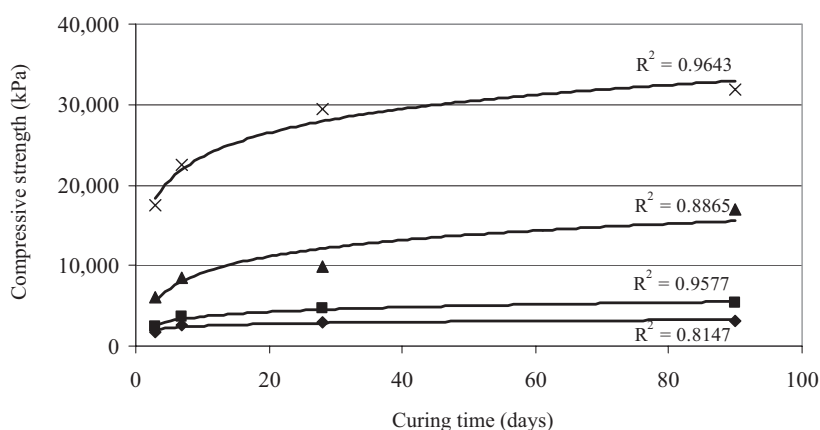


Figure 4 Development of compressive strength against curing time.

(S2 = ♦, S3 = ■, S4 = ▲, OPC = ×) S2–S4 components are detailed in Table 4.

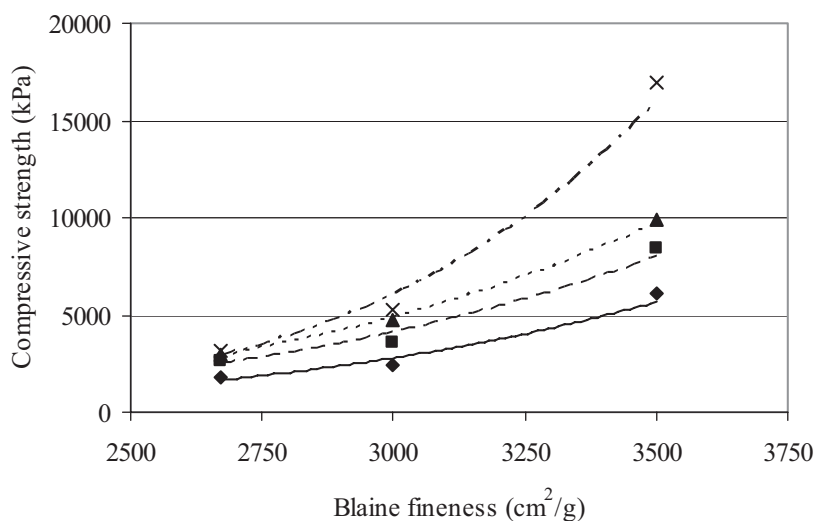


Figure 5 Compressive strength against Blaine fineness for different periods of curing (♦ = curing 3 days, ■ = curing 7 days, ▲ = curing 28 days and × = curing 90 days).

the cement industry, processing to achieve very fine cement consumes excessive grinding energy and grinding time that result in cost inefficiencies.

Expansion characteristics

As mentioned earlier, for mortars produced from S1 waste-based cement (2,000 cm²/g), swelling and expansion behaviors were

substantial, especially over the long term. Figures 6 (b)–(d) illustrate specimens of mortar produced from waste-based cements having different degrees of fineness (S2 < S3 < S4) after soaking for 90 d. Small cracks could be observed on the specimen that used S2 waste-based cement. When the cement fineness was greater than approximately 3,000 cm²/g, neither swelling nor

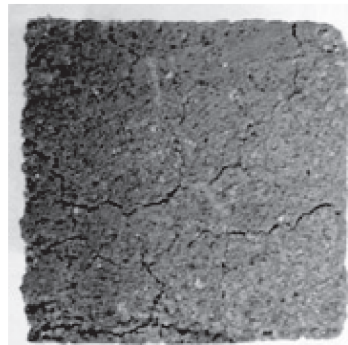
Table 10 Correlation between compressive strength and Blaine fineness.

Curing time (days)	Correlation	R ²
3	$CPS = 30.781 \times e^{(0.0015 \times BF)}$	0.9850
7	$CPS = 57.290 \times e^{(0.0014 \times BF)}$	0.9978
28	$CPS = 60.728 \times e^{(0.0015 \times BF)}$	0.9999
90	$CPS = 12.006 \times e^{(0.0021 \times BF)}$	0.9983

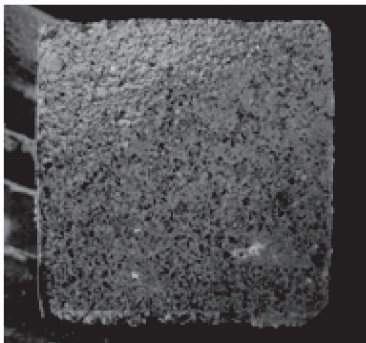
Note: CPS = compressive strength, BF = Blaine fineness



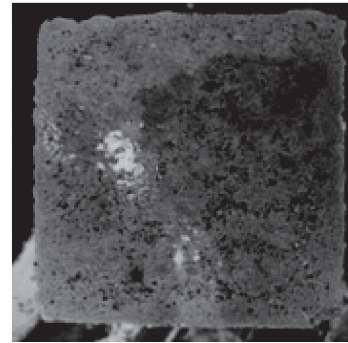
(a) Before testing



(b) S2 sample



(c) S3 sample



(d) S4 sample

Figure 6 Mortar samples (a) at day 0; (b)–(d) after soaking for 90 d. S2–S4 components are detailed in Table 4.

cracks could be observed. Therefore, as a result, cracks in the mortars tended to decrease with increasing cement fineness.

Expansion behavior causing substantial cracks could be attributed to the following reasons. For relatively low cement fineness with high free lime (S1 waste-based cement), crystallization of lime particles with Ca(OH)_2 from the early hydration could lead to a slight expansion. As the mortar hardens, excessive expansion becomes more difficult due to the confined pore spaces resulting in substantial cracks. This reason is consistent with results reported by Yamazaki *et al.* (1980) and Neville (2002).

Another assumption could be substantiated by the results obtained by XRD as shown in Figure 7. The main hydration products of calcium silicate hydrate (CSH), calcium hydroxide (CH) and ettringite (ET), as detected at angles of 2θ which were equal to 29.37, 18.03 and 26.67 degrees, respectively, were apparent in all specimens, the relative intensities of which are illustrated in Table 11.

When mortars were subjected to soaking, swelling and expansive potentials in cement pastes and substantial cracks could also be attributed to the formation of ettringite. No negative effects were observed for OPC and waste-based mortars

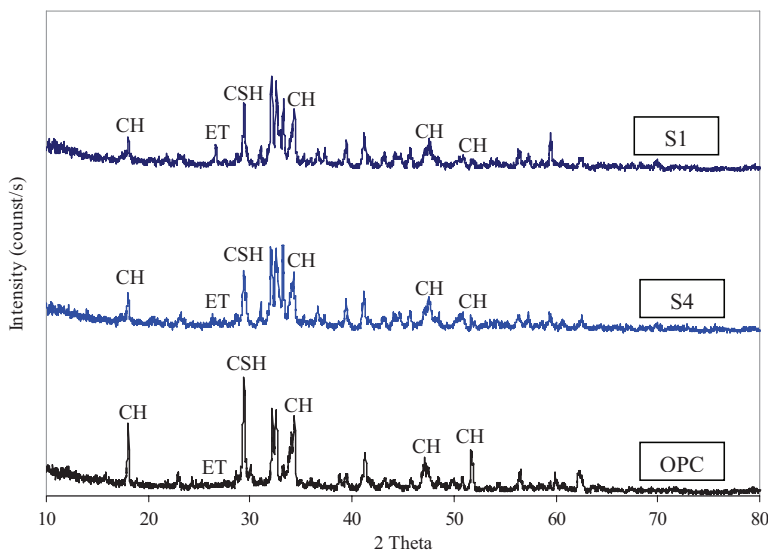


Figure 7 XRD patterns of S1 and S4 waste-based cements, and Ordinary Portland Cement (OPC) after curing for 3 days. (CSH = calcium silicate hydrate; CH = calcium hydroxide; ET = ettringite. S1 and S4 components are detailed in Table 4.)

Table 11 Hydration products at 3 days curing.

Sample	CSH (cps)	CH (cps)	ET (cps)	ET/CSH Ratio	ET/CH Ratio
OPC	420	263	43	0.102	0.163
S4	236	154	37	0.157	0.240
S1	216	115	93	0.431	0.809

Note: CSH = calcium silicate hydrate; CH = calcium hydroxide; ET = ettringite; OPC = Ordinary Portland Cement. S1 and S4 components are provided in Table 4. cps = counts per second and represents the intensity of the peak detected at a specific 2θ angle.

having relatively high strength. It could also be observed that CSH formation in OPC and the S4 waste-based cement was found to crystallize in higher intensity than in S1. As indicated by Mehta *et al.* (1979), the CSH phases detected at 2θ equal to 29.37 degrees (d-spacing = 3.1 – 3.02 Å) possessed cementitious characteristics which contributed to the strength development of the cement. The results therefore, indicated that higher strength mortars exhibit superior resistance to expansion. It was found that the higher the ratio of ettringite to CSH and CH (that is, ET/CSH and ET/CH), as shown in Table 11, the greater the expansion characteristics.

CONCLUSION

A combination of industrial wastes could potentially be used as raw materials in clinkerization to produce cementitious material. The main compounds, such as C_3S , C_2S , C_3A and C_4AF found in the waste-based cement, were similar to but present in lower amounts than those found in Ordinary Portland Cement. Deterioration associated with the expansion was found in mortars produced from low fineness cement. Expansion behavior was attributed to the reaction of free lime and calcium hydroxide associated with the formation of ettringite. Mortar strength was found to substantially increase with an increase in cement fineness. In addition, mortars having higher strength could exhibit superior resistance to expansion due to crystallization of CSH. Therefore, in order to obtain favorable strength and volume stability, a cement fineness of 3,000 cm^2/g or above was recommended as a result of this study.

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