



Influence of phosphate of the waste sludge on the hydration characteristics of eco-cement

Kae-Long Lin^{a,*}, D.F. Lin^b, H.L. Luo^b

^a Department of Environmental Engineering, National I-Lan University, I-Lan 26047, Taiwan, ROC

^b Department of Civil and Ecological Engineering, I-Shou University, 1, section 1, Hsueh-Cheng Rd., Ta-Hsu Hsiang, Kaohsiung County 84008, Taiwan, ROC

ARTICLE INFO

Article history:

Received 19 June 2008

Received in revised form 10 January 2009

Accepted 26 February 2009

Available online 13 March 2009

Keywords:

Phosphate

Eco-cement

Clinker

Degree of hydration

Setting time

ABSTRACT

This study investigated the effects of phosphate on the hydration characteristics of three eco-cement clinkers made utilizing water purification sludge ash, sewage sludge ash and industry sludge ash. Analytical results demonstrate that the eco-cement A (ECO-A) pastes had a similar setting times, final setting times, compressive strengths and degree of hydration as ordinary Portland cement (OPC) pastes. Analytical results also show no damage to the hydration existed during the clinkerization process when adding up to 20% sludge. Increasing the P_2O_5 content in the investigated clinker resulted in the formation of α - C_2S . Compressive strength, degree of hydration and delay in setting time observed in the ECO-B and ECO-C pastes may be attributed to large amounts of α - C_2S . When the amount of phosphate in ECO-C exceeded 0.46%, the amount of C_3S in the clinker decreased, setting time increased and the strength of the eco-cement decreased.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

A large amount of waste sludge is produced annually in Taiwan. Waste sludge largely consists of silicon, calcium, aluminum and iron oxides, all of which are similar to other raw materials in cement. Utilizing waste sludge to replace some raw materials in cement is one strategy for disposing of such waste. However, waste sludge typically contains trace amounts of interference substances such as phosphates and heavy metals. When some raw materials in cement are replaced by waste sludge, such interference can generate adverse effects on cement burning or hydration.

Murat and Sorrentino investigated the effects on cement properties when adding 10% $CrCl_3$ and other metal chlorides to raw cement meal. They determined experimentally that roughly 84% of Cr was trapped in Portland cement [1]. Espinosa and Tenório analyzed galvanic sludge containing Cr as the predominant heavy metal. They demonstrated that adding galvanic sludge up to 2.0 wt.% did not influence the clinkerization process [2]. Heavy metals Cr, Ni, and Zn at concentrations typical a clinker had no impact on cement mortar strength or initial setting time or hydration of cements; even at concentrations 10–20 times higher than normal, no changes were detected [3–6].

The P_2O_5 content in Portland cement is typically as high as 0.2%. However, cements produced from clinkers with 2.5% P_2O_5 are good

quality but low strength due to the decomposition of C_3S to obtain C_2S rich in P_2O_5 . Increasing the P_2O_5 content increases the free-CaO content and reduces the $C_3S:C_2S$ ratio [7]. Caponero and Tenório investigated the effects on the clinkerization process by adding different amounts of phosphates in sludge. The X-ray diffraction analysis showed no significant modification in the yielded clinker proportional to the amount of sludge added; additionally, no atypical phases formed when adding up to 5.0% phosphate in sludge [8]. Li et al. confirmed that the effects of phosphorous slag prolonged cement setting time. Furthermore, early strength clearly decreased setting time [9]. Very few studies have determined the effects of phosphate in waste sludge on eco-cement hydration characteristics [10]. This study investigates the influence of phosphate on the hydration properties of eco-cement made with waste sludge.

2. Materials and methods

2.1. Clinker preparation

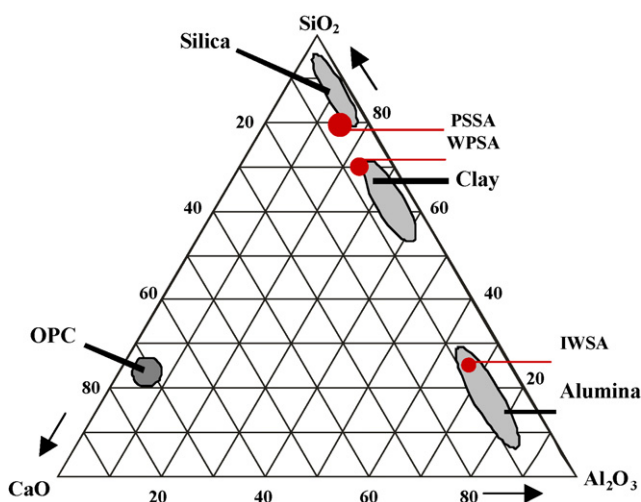
Water purification sludge ash (WPSA), primary sewage sludge ash (PSSA), industrial wastewater sludge ash (IWSA), limestone, and ferrate were used as raw materials in tests. Table 1 shows the oxide composition in these raw materials on a loss-free basis. As depicted by the ternary diagram in Fig. 1, it is possible to recycle SSA, WSA, and ASA as substitutes for silica, clay, and alumina, respectively, in raw materials of cement. A computational model [11] was utilized to formulate the composition of raw clinkers.

* Corresponding author. Tel.: +886 39357400x749; fax: +886 39364277.
E-mail address: klilin@niu.edu.tw (K.-L. Lin).

Table 1
Chemical composition of the raw materials.

Chemical composition	IWSA	WPSA	PSSA	Ferrate	Limestone
SiO ₂ ^a (%)	12.19	54.47	63.31	3.17	7.30
Al ₂ O ₃ ^a (%)	43.54	29.12	15.38	1.63	1.10
Fe ₂ O ₃ ^a (%)	7.44	7.25	6.81	40.50	0.66
CaO ^a (%)	2.65	0.93	1.80	5.73	62.10
MgO ^a (%)	0.59	1.12	1.03	0.23	1.23
SO ₃ ^a (%)	3.20	0.08	1.01	0.82	0.18
Na ₂ O ^a (%)	1.24	0.67	0.70	0.08	0.22
K ₂ O ^a (%)	0.55	3.55	1.51	0.07	0.01
P ₂ O ₅ ^a (%)	1.51	ND	7.20	ND	ND
Cu ^b (mg/kg)	19,826	76	1321	ND	ND
Cr ^b (mg/kg)	1210	1	16	ND	ND
Cd ^b (mg/kg)	54	1	15	ND	ND
Pb ^b (mg/kg)	4254	4	284	ND	ND
Zn ^b (mg/kg)	6258	96	1084	ND	ND

ND: not detected.

^a Analyzed by XRF.^b Analyzed by ICP-AES after HF/HClO₄/HNO₃ digestion.**Fig. 1.** Ternary diagram of the raw materials.

Raw materials were blended using three different ratios: [eco-cement A (ECO-A), eco-cement B (ECO-B), and eco-cement C (ECO-C)]. Each eco-cement clinker ratio was computed after considering the hydration modulus ((HM) = CaO/(SiO₂ + Al₂O₃ + Fe₂O₃), 1.7 < HM < 2.3), lime saturation factor ((LSF) = CaO/(SiO₂ + 1.18Al₂O₃ + 0.65Fe₂O₃), 0.8 < LSF < 0.95), silica modulus ((SM) = SiO₂/(Al₂O₃ + Fe₂O₃), 1.9 < SM < 3.2), and iron modulus ((IM) = Al₂O₃/Fe₂O₃, 1.7 < IM < 2.5). The four unknown modulus were solved using simultaneous first-order equations. Clinker composition was estimated using ASTM C150, and by checking the moduli. Table 2 presents the blend ratios.

The burning process can be summarized as follows. Incinerated sewage sludge, industrial wastewater sludge and water purification sludge ashes were separated, then dried and pulverized in a pretreatment process. The pretreated incinerated ash was mixed with other raw materials (e.g., ferrate) and supple-

Table 2
Blend ratios of the clinkers.

Type of blend	ECO-A (%)	ECO-B (%)	ECO-C (%)
Limestone	80.58	79.20	79.43
WPSA	12.38	7.15	6.18
PSSA	4.86	11.39	9.29
IWSA	–	–	3.00
Ferrate	2.18	2.26	2.10

Table 3
Chemical composition of the OPC and eco-cement clinkers.

Composition	OPC	ECO-A	ECO-B	ECO-C
SiO ₂ (%)	21.65	21.24	23.15	22.53
Al ₂ O ₃ (%)	6.50	7.11	6.39	8.32
Fe ₂ O ₃ (%)	3.20	3.55	3.67	4.64
CaO (%)	63.70	64.83	63.12	61.18
MgO (%)	1.90	1.28	1.11	1.11
SO ₃ (%)	2.20	1.92	1.95	2.03
TiO ₂ (%)	0.14	0.33	0.31	0.31
P ₂ O ₅ (%)	ND	0.46	0.75	0.85
f-CaO (%)	0.31	0.30	0.20	0.20
Constituents				
C ₃ S (%)	46.71	48.65	35.60	13.98
C ₂ S (%)	27.33	24.20	38.37	54.05
C ₃ A (%)	11.81	12.83	10.72	14.20
C ₄ AF (%)	9.70	10.80	11.17	14.12
Moduli				
LSF	0.90	0.92	0.85	0.80
HM	2.03	2.03	1.93	1.72
SM	2.23	1.99	2.26	1.74
IM	2.03	2.00	1.74	1.79

ments (e.g., limestone). The ground mixtures were burned in a programmable electrical furnace. The compound material was then burned for 6 h at 1400 °C to form eco-cement clinkers. Sintering was maintained at the maximum temperature for 240 min. After burning process, the resultant clinkers cooled rapidly to room temperature. The clinkers generated were ground in a laboratory ball mill with 3.5% per weight of gypsum to produce the eco-cements (i.e., ECO-A, ECO-B and ECO-C (Table 3)). After burning, the eco-cement clinkers were mixed with 3.5% gypsum ground at 320 m²/kg Blaine's fineness. The eco-cement was mixed with water at w/b = 0.38. The ASTM-type □ ordinary Portland cement, obtained from Taiwan Cement Works, Inc., was used as the reference material.

2.2. Preparation approach

Three types of eco-cement clinkers prepared as above were used. The pastes using the aforementioned blends were prepared with a water to binder ratio of 0.38. 25.4 mm × 25.4 mm × 25.4 mm (1 in. × 1 in. × 1 in.) test cubes were prepared according to ASTM-305, followed by a moulding process (ASTM C31-69). The specimens were then demoulded and cured in a container at 95% humidity and at 25 °C for 3–90 days. The compressive strength development of three samples of each type of eco-cement paste was measured at different ages, according to ASTM C39-72. The leachability of the specimens was analyzed by the toxicity characteristic leaching procedure (TCLP) tests. Changes in the composition and hydrates were analyzed using X-ray diffraction (XRD) techniques. The hydration of the pulverized and sieved (#300) samples was terminated at the desired testing age by immersion in acetone in a vacuum for 24 h before further characterization.

2.3. Analyses

The following chemical and physical analyses of the OPC and the three types of eco-cement pastes were conducted at different ages:

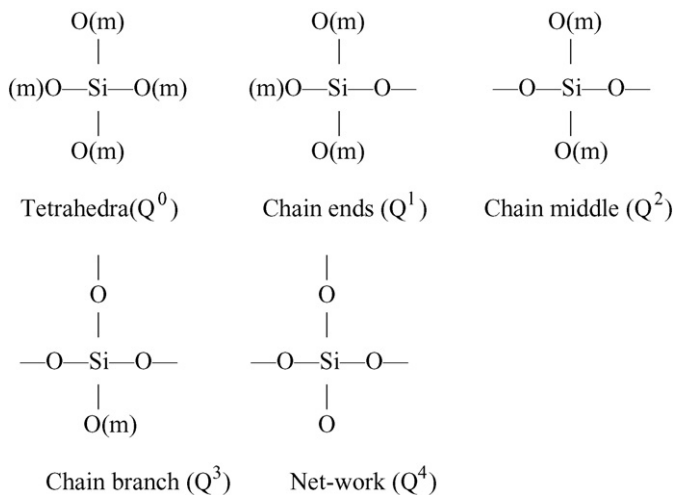
- Unconfined compressive strength (UCS): ASTM C39-72.
- Setting time: The setting times of the cement mixes were determined according to ASTM C191 using a Vicat apparatus operated at room temperature. The initial setting time was defined as when a Vicat needle 1 mm in diameter would penetrate the sample to a point 5 ± 1 mm from the bottom of the mould. The final setting

time was defined as when a 5-mm cap ring would leave no visible mark when placed on the surface of the sample.

- Heavy metal leachability (TCLP): SW-846-1311.
- Heavy metal concentration: The heavy metal concentrations in the samples were confirmed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The samples were crushed, and the heavy metals were extracted by acid (HF:HClO₄:HNO₃ = 2:1:1).
- Mineralogy: The XRD analysis was carried out by a Siemens D-5000 X-ray diffractometer with Cu K α radiation and 2 θ scanning, ranging between 5° and 70°.
- Chemical composition: The X-ray fluorescence (XRF) was performed with an automated RIX 2000 spectrometer. The specimens were prepared for XRF analysis by mixing 0.4 g of the sample and 4 g of 100 Spectroflux, at a dilution ratio of 1:10. Homogenized mixtures were placed in Pt–Au crucibles, then treated for 1 h at 1000 °C in an electrical furnace. The homogeneous melted sample was recast into glass beads 2 mm thick and 32 mm in diameter.
- Chemical shift of linear polysilicate anions in C–S–H: ²⁹Si nuclear magnetic resonance (²⁹Si MAS/NMR).

The degree of hydration of the OPC and eco-cement pastes, and the average length of linear polysilicate anions in the calcium silicate hydrate (CSH) gels, which are primarily responsible for the strength, were analyzed by using high-resolution solid-state ²⁹Si MAS/NMR techniques.

The calcium silicate hydrates, the hydration products in the cement, could be semi-quantified using chemical shifts in the ²⁹Si nuclei in the Si–O–X groups, for which the structures are shown below.



High-resolution ²⁹Si MAS/NMR spectra were recorded at 39.72 MHz on an MSL Bruker MAS/NMR-200 solid-state high-resolution spectrometer, using rapid (about 3 kHz) sample spinning at the magic angle to the external magnetic field. The ²⁹Si chemical shifts are given relative to the primary standard liquid tetramethylsilane (TMS) in the delta-scale (the negative signs correspond to up-field shifts). The degree of hydration (designated as α) of the cement clinkers, C₂S and C₃S, can be evaluated by the integral

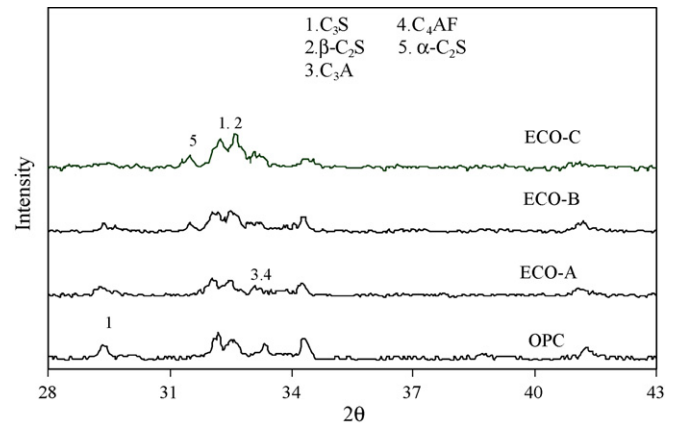


Fig. 2. XRD patterns of eco-cement clinkers.

intensity of the signals at -70 ppm (Q^0), for both the hydrated cement paste and cement powders, i.e., $I^0(Q^0)$ and $I(Q^0)$, respectively [12,13]:

$$\alpha = \left[\frac{1 - I(Q^0)}{I^0(Q^0)} \right] \times 100 \quad (1)$$

3. Results and discussion

3.1. Characteristics of eco-cement clinkers

The clinkers generated were subjected to X-ray fluorescence analysis to determine the main constituents (Table 3). Theoretical phase compositions were predicted using a modified Bogue calculation. The principal constituents of C₃S, C₂S, C₃A and C₄AF were also present in the clinkers. The amounts of C₃S, C₂S, C₃A and C₄AF in the ECO-A clinker were similar to those in the ordinary Portland cement (OPC). The C₃S content in the ECO-B and ECO-C clinkers was less than that in the OPC. The Na₂O and K₂O, which as so-called alkalis, are typically present in all components of raw cement. Alkali content is typically 0.18–0.32% in Portland cement and eco-cement. The P₂O₅ content in Portland cement can be as high as 0.2%; however, the eco-cements produced from the clinkers had 0.75% P₂O₅, lead to the decomposition of C₃S to obtain C₂S rich in P₂O₅. Increasing the P₂O₅ content decreased the C₃S/C₂S ratio.

All tested eco-cement clinkers met the toxicity characteristic leaching procedure (TCLP) requirements. All clinker leaching concentrations also met regulatory thresholds (Table 4).

Fig. 2 shows the XRD patterns of eco-cement clinkers. In the ECO-A clinker the major phases formed were C₃S ($2\theta = 32.3^\circ$), β -C₂S ($2\theta = 32.8^\circ$), C₃A ($2\theta = 33.3^\circ$), and C₄AF ($2\theta = 33.6^\circ$) and were similar to those in ordinary Portland cement. The ECO-B and ECO-C clinkers had significant α -C₂S ($2\theta = 31.6^\circ$) peaks. The α -C₂S phase formation was greater in the ECO-C clinker than in the ECO-B clinker; however, none existed in the ECO-A clinker. The XRD phase-identification study demonstrated the absence of any α -C₂S peak until PSSA content was at least 9.3%, which increased the formation of α -C₂S. The general trend is that α -C₂S increases as phosphate content in clinkers increases.

Table 4

Leaching concentrations of the OPC and eco-cement clinkers.

	Cu (mg/L)	Cr (mg/L)	Cd (mg/L)	Pb (mg/L)	Ni (mg/L)	Zn (mg/L)
OPC	ND	ND	ND	0.72 ± 0.02	ND	0.33 ± 0.01
ECO-A clinker	ND	ND	ND	0.62 ± 0.01	ND	0.22 ± 0.01
ECO-B clinker	ND	ND	ND	0.73 ± 0.02	ND	0.34 ± 0.01
ECO-C clinker	ND	ND	ND	0.68 ± 0.02	ND	0.46 ± 0.02

Table 5
Setting time of the eco-cement pastes.

Sample	Initial set (h)	Final set (h)
OPC paste	3.02	5.28
ECO-A paste	4.27	5.92
ECO-B paste	7.80	10.85
ECO-C paste	8.80	11.43

3.2. Setting characteristics of eco-cement pastes

Table 5 lists the setting times for Portland cement paste and the three eco-cement pastes. Analytical results indicate that as the amount of phosphate increased, initial and final setting times increased. The final set retardations times for ECO-A, ECO-B and ECO-C pastes were 0.64, 5.57 and 6.15 h, respectively. When the amounts of phosphate in clinkers increased further to 0.85%, increased significantly, particularly in final setting time, compared with the control mixture. The observed delay in setting time is

likely attributable to the rate of hydration reactions. Increasing the amounts of phosphate in eco-cement clinkers increased α -C₂S content, which delayed setting time.

3.3. Compressive strength of eco-cement pastes

Compressive strengths of eco-cement pastes were measured after being cured for 3, 7, 14, 28, 60 and 90 days (Fig. 3). These compressive strengths were compared with the compressive strength of type I ordinary Portland cement paste. Comparison results demonstrate that the compressive strength of ECO-A cement paste was similar to that of ordinary Portland cement paste. However, the compressive strengths of ECO-B and ECO-C cement pastes were lower than that of ordinary Portland cement at all hydration stages. The formation of α -C₂S may have contributed to strength development in samples containing phosphate during all hydration stages. Typically, the P₂O₅ content in Portland cement can be as high as 0.46%; however, eco-cements generated from clinkers with more than 0.75% P₂O₅ had a lower strength than OPC paste, due to the decomposition of C₃S to obtain C₂S rich in P₂O₅. The high phosphate content in clinkers, presented as calcium phosphate and α -C₂S, likely retards hydration of calcium silicates, thus adversely affecting the strength characteristics of pastes [14,15]. In ECO-B and ECO-C clinkers, the reduction in strength was due to increased formation of the α -C₂S phase.

3.4. NMR analysis of OPC and eco-cement pastes

Figs. 4–7 present the ²⁹Si MAS/NMR spectra of hydrated samples of OPC pastes and eco-cement pastes at various stages. Fig. 4 presents absorption peaks of hydrated OPC paste, which appeared at -71.5, -81.5 and -89.5 ppm. The amount of Q⁰ species decreased with curing time. It is indicated that the Q⁰ species were transformed into Q¹ and Q².

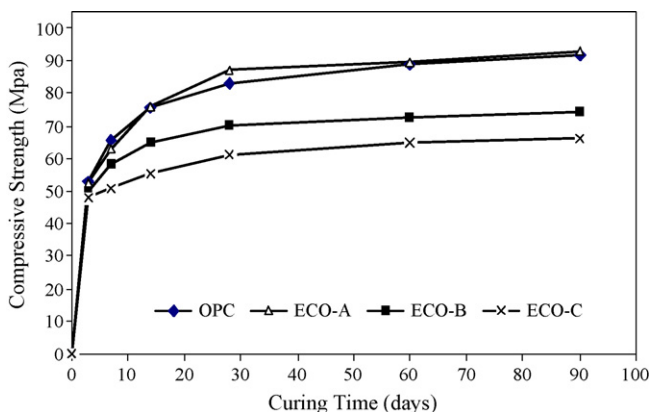


Fig. 3. Compressive strength of eco-cement pastes.

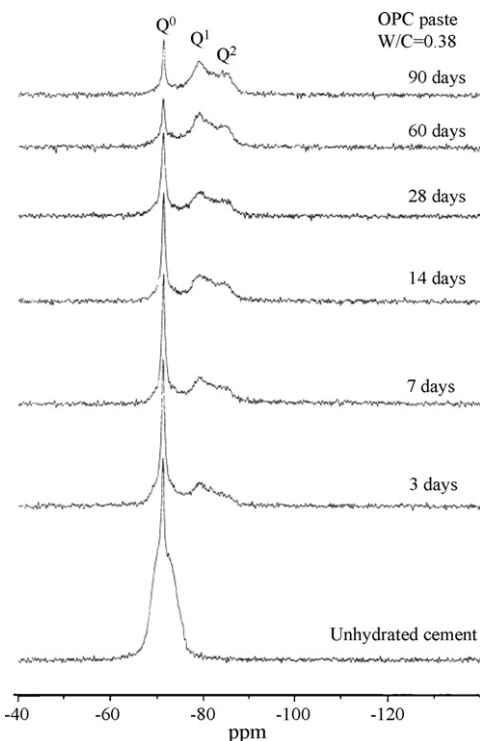


Fig. 4. ²⁹Si MAS/NMR spectra of hydrated OPC paste samples.

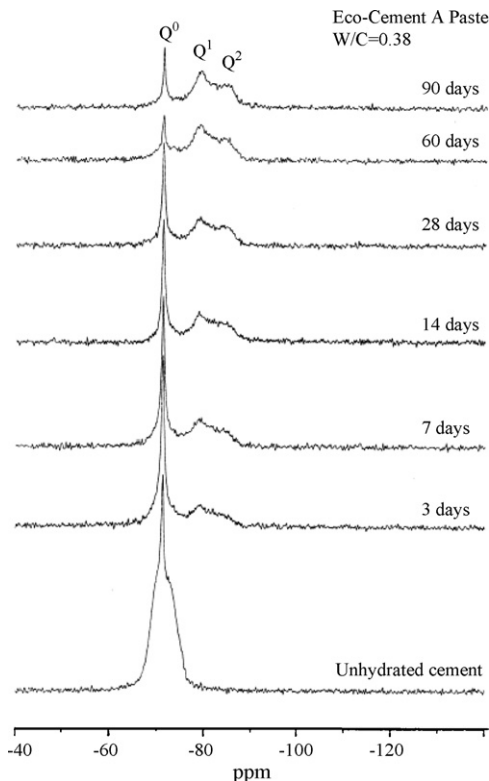


Fig. 5. ²⁹Si MAS/NMR spectra of hydrated ECO-A paste samples.

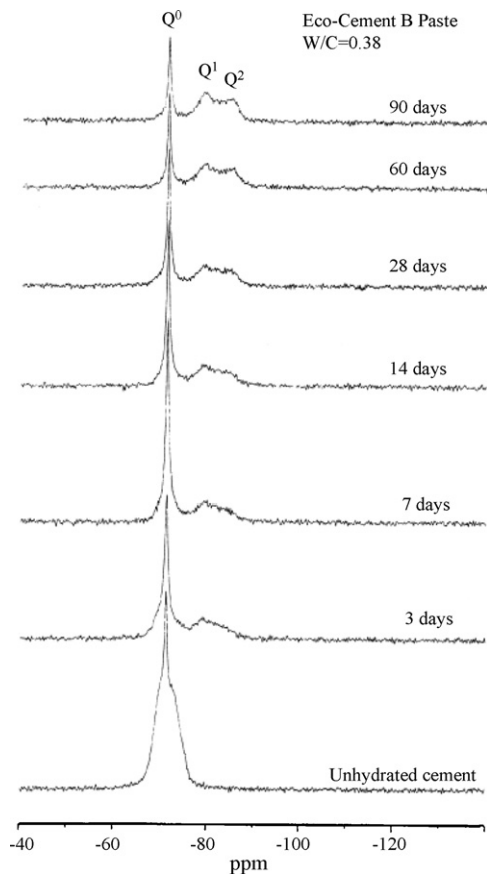


Fig. 6. ^{29}Si MAS/NMR spectra of hydrated ECO-B paste samples.

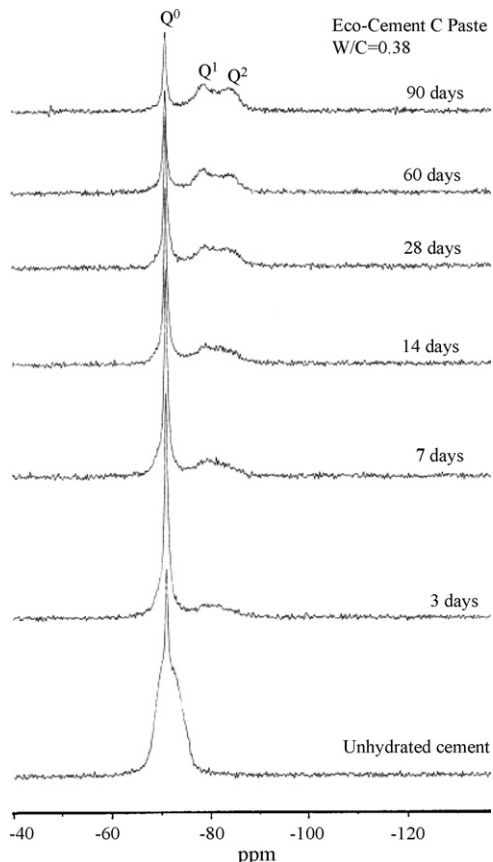


Fig. 7. ^{29}Si MAS/NMR spectra of hydrated ECO-C paste samples.

Table 6
 ^{29}Si MAS/NMR in hydrated OPC and eco-cement paste samples.

Sample	Curing time (day)	^{29}Si NMR integral intensities of Q^n (mm^2)			Degree of hydration (%)
		Q^0	Q^1	Q^2	
OPC					
	3	385	149	89	43.1
	7	305	163	114	51.2
	14	266	172	120	56.4
	28	241	182	127	61.7
	60	183	215	167	66.8
	90	187	217	179	68.8
ECO-A					
	3	410	145	87	40.8
	7	328	150	91	50.7
	14	292	177	122	55.3
	28	261	180	134	60.9
	60	201	211	159	66.2
	90	172	214	163	71.3
ECO-B					
	3	413	136	69	38.1
	7	411	138	75	42.1
	14	374	152	92	45.3
	28	311	155	101	49.6
	60	254	169	115	59.7
	90	221	183	125	61.7
ECO-C					
	3	489	119	54	29.5
	7	452	124	63	35.9
	14	382	136	87	42.5
	28	303	142	92	50.7
	60	213	159	106	55.9
	90	199	173	117	56.9

The amount of Q^1 and Q^2 increased as hydration time increased (Figs. 5–7 and Table 6). The CSH formed by the hydration of calcium silicates is generally dominated by Q^1 sites or has abundant Q^1 and Q^2 sites. The ratio of silicone sites in hydrated products, Q^2/Q^1 , also increases after mechanical activation of eco-cement. However, no apparent increase existed in the amount of Q^1 and Q^2 in ECO-C paste with hydration time.

Table 6 shows the degree of hydration of OPC pastes and eco-cement pastes up to 90 days. The degree of hydration in the OPC increased with time up to 90 days. The degree of hydration of the ECO-A paste was similar to that of the OPC. All ECO-C pastes had low hydration values at all hydration ages. The main reason for these low hydration values is that the amount of $\alpha\text{-C}_2\text{S}$ caused the degree of hydration in the ECO-C paste to decrease to a value lower than that of Portland cement.

4. Conclusions

The following conclusions are based on investigation results for three eco-cements prepared using waste sludge as components in raw mixes.

1. The main constituents of C_3S , C_2S , C_3A and C_4AF were present in clinkers.
2. Increasing P_2O_5 content reduced the $\text{C}_3\text{S}:\text{C}_2\text{S}$ rate. Increasing P_2O_5 content in the clinkers investigated resulted in the formation of $\alpha\text{-C}_2\text{S}$.
3. When the amounts of phosphate in clinkers were increased to 0.85%, setting time increased significantly, particularly final setting time compared with that of the control mixture.
4. Compressive strength of the ECO-A cement paste was similar to that of ordinary Portland cement paste. Producing eco-cements that have an acceptable 90-day strength using waste sludge as a component in the raw mix is possible.

5. The XRD-phase identification results demonstrate the absence of a peak for α -C₂S until PSSA reached 9.3%.
6. The results indicate that it is feasible to use 20% or more of sludge ash and ferrate waste to replace the mineral components of the raw materials in cement mixtures. This investigation is considered in two aspects: (1) it suggests a new solution-route for a solid waste elimination problem; and it generates a new construction material for engineering application.

References

- [1] M. Murat, F. Sorrentino, Effect of large additions of Cd, Pb, Cr, Zn to cement raw meal on the composition and the properties of the clinker and the cement, *Cem. Concrete Res.* 26 (1996) 377–385.
- [2] D.C.R. Espinosa, J.A.S. Tenório, Laboratory study of galvanic sludge's influence on the clinkerization process, *Resour. Conserv. Recycl.* 31 (2000) 71–82.
- [3] G. Kakali, G. Parissakis, Investigation of the effect of Mo, Nb, W and Zr oxides on the formation of Portland cement clinker, *Cem. Concrete Res.* 20 (1990) 131–138.
- [4] D. Stephan, R. Mallmann, D. Knöfel, R. Härdtl, High intakes of Cr, Ni, and Zn in clinker. Part I. Influence on the hydration properties, *Cem. Concrete Res.* 29 (1999) 1949–1957.
- [5] D. Stephan, R. Mallmann, D. Knöfel, R. Härdtl, High intakes of Cr, Ni, and Zn in clinker. Part II: influence on burning process and formation of phases, *Cem. Concrete Res.* 29 (1999) 1959–1967.
- [6] D. Stephan, H. Maleki, D. Knöfel, B. Eber, R. Härdtl, Influence of Cr, Ni, and Zn on the properties of pure clinker phases. Part II: C₃A and C₄AF, *Cem. Concrete Res.* 29 (1999) 651–657.
- [7] F.M. Lea, *The Chemistry of Cement and Concrete*, 3rd ed., Chemical Publ. Co., New York, 1970.
- [8] J. Caponero, J.A.S. Tenório, Laboratory testing of the use of phosphate-coating sludge in cement clinker, *Resour. Conserv. Recycl.* 29 (3) (2000) 169–179.
- [9] D. Li, J. Shen, L. Mao, X. Wu, The influence of admixtures on the properties of phosphorous slag cement, *Cem. Concrete Res.* 35 (7) (2000) 1169–1173.
- [10] K.L. Lin, C.Y. Lin, Hydration characteristics of waste sludge ash utilized as raw cement material, *Cem. Concrete Res.* 35 (2005) 1999–2007.
- [11] H.F.W. Taylor, *Cement Chemistry*, Academic Press, New York, 1997.
- [12] C.K. Lin, J.N. Chen, An NMR, XRD and EDS study of solidification/stabilization of chromium with Portland cement and C₃S, *J. Hazard. Mater.* 56 (1997) 21–34.
- [13] K.L. Lin, D.F. Lin, Hydration characteristics of municipal solid waste incinerator bottom ash slag as a pozzolanic material for use in cement, *Cem. Concrete Comp.* 28 (2006) 817–823.
- [14] P.K. Mehta, *Concrete: Structure, Properties and Materials*, Prentice-Hall Inc., Englewood Cliffs, 1986, pp. 65–85.
- [15] I.B. Javed, J.R. Kenneth, Compressive strength of municipal sludge ash mortars, *ACI Mater. J.* 86 (4) (1989) 394–400.