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Utilization of municipal sewage sludge as additives for the production of eco-cement

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ABSTRACT

The effects of using dried sewage sludge as additive on cement property in the process of clinker burning were investigated in this paper. The eco-cement samples were prepared by adding 0.50–15.0% of dried sewage sludge to unit raw meal, and then the mixtures were burned at 1450 °C for 2 h. The results indicated that the major components in the eco-cement clinkers were similar to those in ordinary Portland cement. Although the C_2S phase formation increased with the increase of sewage sludge content, it was also found that the microstructure of the mixture containing 15.0% sewage sludge in raw meal was significantly different and that a larger amount of pores were distributed in the clinker. Moreover, all the eco-cement pastes had a longer initial setting time and final setting time than those of plain cement paste, which increased as the sewage sludge content in the raw meal increased. All the eco-cement pastes had lower early flexural strengths, which increased as the sewage sludge content increased, while the compressive strengths decreased slightly. However, this had no significant effect on all the strengths at later stages. Furthermore, the leaching concentrations of all the types of eco-cement clinkers met the standard of Chinese current regulatory thresholds.

1. Introduction

In China, a large quantity of municipal sewage sludge is produced annually in the main cities because of the rapid progress of urbanization and industrialization [1,2]. Among all the municipal sewage sludge disposal methods at present [3–9], the most common methods to dispose of sludge are sanitary landfills and disposal into the ocean [10–13], in addition to some being used in agriculture as organic fertilizer and for soil management [2,10,14–21]. However, because of the high cost of disposal, it is becoming increasingly difficult to find suitable landfill sites, which has prompted a search to find alternative methods to dispose of sludge [13,22].

An alternative for sludge disposal is the utilization of sludge in construction materials [23]. After incineration at high temperatures, the main components in sewage ash include SiO_2, CaO, Al_2O_3 and Fe_2O_3, and these compounds are also common in ordinary Portland cement (OPC) [24–28]. Therefore, sewage ash can be potentially used in concrete or mortar to partially replace Portland cement [29]. In recent years, studies have been carried out by many researchers on the use of sludge ash or sewage sludge as a part of the raw material in cement [30–44]. In general, sludge ash has been found to increase the setting time of cement [27,31–35], and the cement replacement ratio of sludge ash has been found to affect the compressive strength of mortar [33,35,36]. At present, more attention is being paid to an evaluation of its potential in developing a new type of cement [45–48]. However, little research has been conducted on how to combine cement plants with sewage sludge disposal even though toxic substances can be removed in the cement kiln during the high temperature of pyrolysis or in the combustion process, and heavy metals can be immobilized into a primary matrix material consisting of inert silicates [49]. In addition, the wasted kiln heat can be used to dry the sewage sludge, and emissions can be controlled by the flue gas treatment system that has already been equipped in the cement plant. Furthermore, by the use of cement plants to dispose of sewage sludge, energy consumption may be reduced by processing sewage sludge, and natural resources may be saved; finally, the load to disposal sites will be reduced [27].

The aim of this study is to compare the characteristics of eco-cement clinkers (made with sewage sludge substitution) with normal cement clinkers made in laboratory experiments. The

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flexural and compressive strength and setting time of eco-cement pastes, scanning electron microscope (SEM) micrographs, heavy metal leachability and changes of element content of eco-cement clinkers are also investigated.

2. Materials and methods

2.1. Materials

2.1.1. Sewage sludge

The sludge used in this study was obtained from a municipal wastewater treatment plant located in the suburbs of Guangzhou city (South China). The plant is capable of producing 550,000 m^3/d of wastewater. The sewage sludge was collected after being concentrated by centrifugation in the plant, and it was dried at 105 °C for 48 h. Finally, the dried sewage sludge was further pulverized in a ball mill (porcelain mill, XMCO-Φ 280 × 290) until the particles could pass through a #200 mesh (with 75 μm pore diameter) metallic sieve, and its chemical composition was then characterized.

2.1.2. Raw materials

The raw meal (including limestone, iron, shale, fly ash, sand powders) was collected from a cement plant in Guangzhou. The plant is capable of producing 9000 tons of cement clinker per day. All of these raw materials were over dried at 105 °C for 24 h, and the chemical composition was characterized. The raw materials were further pulverized in a ball mill until the particles could pass through a #200 mesh (with 75 μm pore diameter) metallic sieve, and then they were blended according to the cement clinker ratio, which was calculated with a consideration of the lime saturation coefficient:

$$KH = (CaO–1.65Al_2O_3–0.34Fe_2O_3/2.80SiO_2),$$

$$0.902 < KH < 0.915;$$

the Silica Modulus:

$$SM = SiO_2/(Al_2O_3 + Fe_2O_3),\ 2.25 < SM < 2.35;$$

the Iron Modulus:

$$IM = (Al_2O_3/Fe_2O_3),\ 1.30 < IM < 1.40;$$

and the Lime Saturation:

$$L.S.F = (CaO/2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3),$$

$$0.94 < L.S.F < 0.96;$$

[27,28,40].

The oxide composition of all the raw materials and the mixed raw meal are shown in Table 1, and the particle size distribution of the raw meal is shown in Fig. 1(a).

2.1.3. Eco-cement clinkers

The eco-cement raw meals were prepared by mixing various amounts of dried sewage sludge per 100 kg dried raw meal, and the resulting types of eco-cement raw meals contained sewage sludge at 0, 0.50, 1.0, 1.5, 2.0, 2.5, 3.0, 5.0, 8.0, 10.0, 12.0 and 15.0%, respectively (by weight of raw meal). All the grounded raw mixtures were burned in a programmable electrically heated furnace to form eco-cement clinkers. The high temperature furnace temperature was raised by 6 °C min^{-1} from room temperature and maintained at 1,450 °C for 2 h (the total process required 8 h). After burning, the resulting products were cooled rapidly in air. All the eco-cement clinkers were pulverized and thoroughly ground in a ball mill until most of them could pass through a #200 mesh (with 75 μm pore diameter) metallic sieve (retention on the mesh sieve

Table 1
Chemical composition of the raw materials and the raw meal.

Chemical composition	Limestone	Shale	Ferrate	Fly ash	Raw meal
LOI[a] (%)	38.12	3.51	8.31	3.16	34.9
SiO_2[b] (%)	7.25	75.21	34.56	46.82	12.10
Al_2O_3[b] (%)	1.71	12.08	12.71	33.7	3.08
Fe_2O_3[b] (%)	0.85	4.48	38.87	7.02	2.20
CaO[b] (%)	49.40	0.17	2.58	5.96	44.5
MgO[b] (%)	0.58	0.53	0.59	0.61	0.55
K_2O[b] (%)	0.14	2.26	0.61	0.66	0.38
Na_2O[b] (%)	0.09	0.32	0.12	0.32	0.12
SO_3[b] (%)	0.41	0.01	0.42	0.25	0.38
Cl[b] (%)	0.011	0.008	0.004	0.01	0.015
Cd[c] (mg/kg)	ND	0.74	7.50	ND	0.51
Co[c] (mg/kg)	ND	ND	20.77	ND	1.15
Cr[c] (mg/kg)	ND	45.64	25.13	43.83	4.60
Cu[c] (mg/kg)	ND	ND	ND	20.61	ND
Mn[c] (mg/kg)	123.62	1360.61	14764.25	328.71	1230.21
Ni[c] (mg/kg)	ND	5.77	26.32	10.87	2.02
Pb[c] (mg/kg)	3.23	2.33	61.08	6.53	6.80
Sr[c] (mg/kg)	349.66	25.52	6.51	652.09	307.43
Ti[c] (mg/kg)	239.45	1255.60	770.20	5423.84	325.89
V[c] (mg/kg)	ND	32.64	ND	74.84	1.32
Zn[c] (mg/kg)	28.80	62.21	324.12	85.57	45.63
Ba[c] (mg/kg)	16.91	317.79	459.09	494.76	61.25

ND: not detected.
[a] Analyzed by muffle furnace at temperature (950 ± 25) °C.
[b] Analyzed by XRF.
[c] Analyzed by ICP-AES.

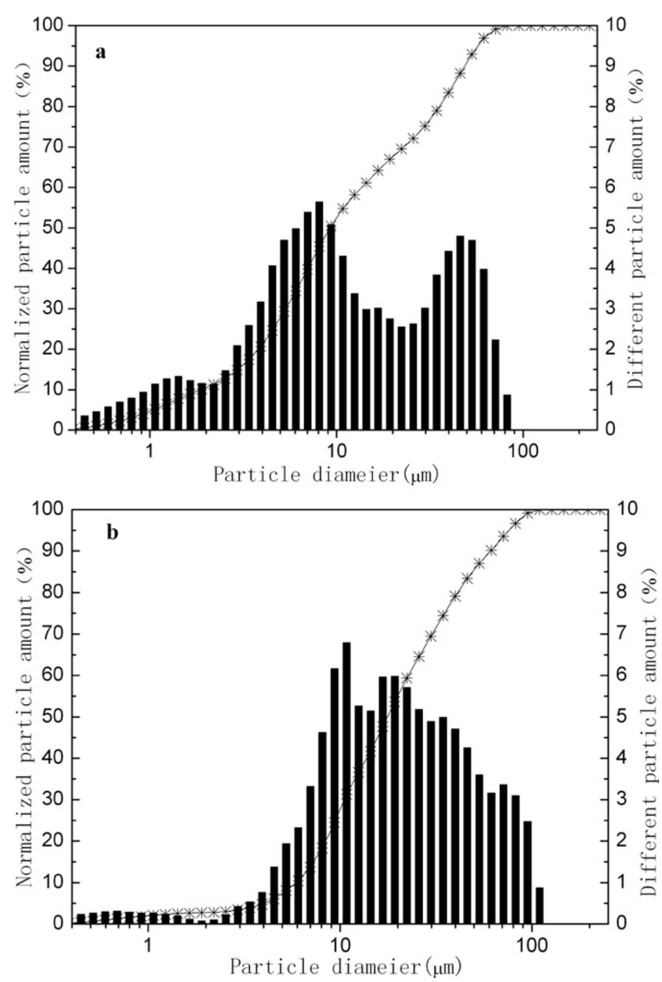

Fig. 1. Particle size distribution of the raw meal (a) and eco-cement clinker (b).

was less than 5% in weight. A particle size distribution of 5.0% is shown in Fig. 1(b)). Finally, a sample of each eco-cement clinker was co-ground with 5% and 15% per weight of gypsum and fly ash to produce the corresponding eco-cement.

2.2. Approach

2.2.1. Molding and curing of cement mortar specimens

The mortar mixtures of the above twelve eco-cement samples were prepared according to GB/T 17671-1999 (the standard test method for strength of hydraulic cement mortar in China). The ratio of sand/eco-cement (by weight) was 3:1, while the water to eco-cement ratio was fixed at 0.50. Mortars were put in $40 \times 40 \times 160$ mm molds for the purpose of obtaining specimens and were stored in a moisture room at 20 ± 1 °C for 24 h. Afterwards, all the specimens were demoulded and cured in a water bath with a steady temperature of 20 ± 1 °C for 3–28 days. Finally, the flexural strength and compressive strength development of the specimens were measured at the curing ages of 3, 7 and 28 days.

2.3. Analyses

Chemical and physical analyses of the eco-cement clinkers, ordinary Portland cement and eco-cement pastes were conducted as follows:

- Particle distribution test: A particle distribution test was carried out using a laser diffraction particle size analyzer (SALD-201, Japan), and its measure range of particle sizes was from 0.25 to 350 μm.
- Flexural strength and compressive strength test: GB/T 17671-1999.
- Setting time: The setting times of the eco-cement mixes were measured according to GB/T1346-2001 (test methods for water requirement of normal consistency, setting time and soundness of the Portland cements in China). This standard was similar to the ASTM C 191. The initial setting time was defined as when a Vicat needle (1.13 ± 0.05 mm) could penetrate the sample to a point 4 ± 1 mm from the bottom of the mold, and the final setting time was defined as when the Vicat needle could penetrate the sample to a point 0.5 mm from the bottom of the mold [27].
- Heavy metal leachability (TCLP): HJ/T300-2007. After the preliminary evaluation of the pH characteristic of the sample, extraction fluid 2# (pH 2.64 ± 0.05) was prepared for the experiment. This fluid was prepared by adding 17.25 ml of glacial acetic acid to 1 L of reagent water. A 25 g sample was placed in a 2 L polythene bottle (Nalegne), and 500 ml of extraction fluid was added to each polythene bottle (including the check sample). The samples were then agitated for 18 h with an electric porous rotator (3740-6-BRE, AMD of America). The slurry was filtered using a 0.7 μm Certified Glass Fiber Filter. The leachates were decomposed by acid (HNO_3:$HClO_4$ = 2:1) and preserved in a 5% nitric acid solution.
- Heavy metal concentration: The heavy metal concentration in the eco-cement clinkers and leachates were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Prodigy of America), and its minimum detection value was 0.000001 mg/L. All the samples (0.2500 g per sample) were digested with ultra-pure-grade acids using a three step procedure (HCl:HNO_3 = 6:2 ml; HF = 4 ml; $HClO_4$ = 4 ml). After evaporation, the samples were preserved in a 5% nitric acid solution with making exact 50 ml of each mixture solution. A reference material of soil which called laterite (Product ID: GBW07407) was used for the quality assurance and quality control for metals analysis. The results showed that the recoveries for the 12 elements (Al, Fe, Mg, Ti, Mn, Sr, Ba, Zn, Cr, Cu, Ni and Pb) were 93–105%, which met the criteria of 90–110%. This recovery demonstrates that negligible metals breakthrough occurred. The recoveries of metals internal standard solutions were all within their corresponding recovery criteria.
- Chemical composition: The chemical composition of the raw materials and raw meal was confirmed by using a wavelength dispersion X-ray fluorescence spectrometer (XRF PANalytical Axios of Netherlands).
- Mineralogy: The XRD analysis was conducted using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation and 2θ scanning ranging from 10° to 70°. The XRD scans were run in 0.02° steps, with a counting time of 17.7 s.
- SEM: Several eco-cement clinkers were investigated with an SEM (S-3700 N, Hitachi Ltd of Japan), and the microstructure changes of some parts of the clinkers were analyzed.

Table 2
Granulometric parameters of raw meal and eco-clinkers.

Materials	Granulometric parameters (μm)		
	D_{10}	D_{50}	D_{90}
Raw meal	1.87	10.07	48.76
Eco-clinker	4.89	17.70	61.37

3. Results and discussion

3.1. Particle size distribution of raw meals and eco-cement clinkers

The size distributions of raw meals and eco-cement clinkers are presented in Fig. 1 and their values of d_{10}, d_{50} and d_{90} are shown in Table 2. In Fig. 1(a) and Table 2, the diameter of particles of d_{10}, d_{50} and d_{90} are shown to be 1.87, 10.07 and 48.76 μm, respectively. The maximum size of sample was 82.19 μm, and the particle size of the raw meals was found to be mainly distributed in 0.39–71.11 μm, which attained the production requirements for burning cement clinker (retained on 80 mesh sieves at less than 10%). On the other hand, it can be seen from Fig. 1(b) and Table 2 that the median diameter (d_{50}) of eco-cement clinkers (sewage sludge content of 5%) was 17.70 μm. In addition, the diameters ranged from 0 to 10 μm, 10 to 30 μm, 30 to 60 μm, and those that were more than 90 μm were 27.50, 42.16, 19.20 and 1.84%, respectively. Therefore, the size distributions of both the raw meals and clinkers met the industrial quality criteria for cement.

3.2. Characterization of the eco-cement clinkers

Fig. 2 shows the X-ray diffraction (XRD) pattern results for the plain clinker and the eleven eco-cement clinkers. The results indicated that the major components of the eco-cement clinkers were C_3S [Ca_3SiO_5 and $Ca_3(SiO_4)O$], C_2S [Ca_2SiO_4 and $Ca_2(SiO_4)$)], C_3A [$Ca_3Al_2O_6$ and $Ca_3(Al, Fe)_2O_6$], C_4AF ($Ca_4Fe2Al_2O_{10}$) and all were similar to those of ordinary Portland cement. Moreover, the phase formation of $Ca_{54}MgAl_2Si_{16}O_{90}$ was identified in all the clinkers. However, the C_2S (α-C_2S or β-C_2S) phase formation increased with the increases in sewage sludge content. The XRD phase-identification study also demonstrated that the increase in C_2S was not obvious until the sewage sludge content exceeded 10% (per raw meal by weight), and it was easily seen to be higher at 12 and 15%. In addition, some phase formations containing heavy metals (Cr, Zn, Ni, Cu, et al.) could also be found when the sewage sludge content was greater than 5%. It is also shown in Fig. 2 that the number of peaks increased and become more complex with the increases in sewage sludge content. In general, the general trend was that

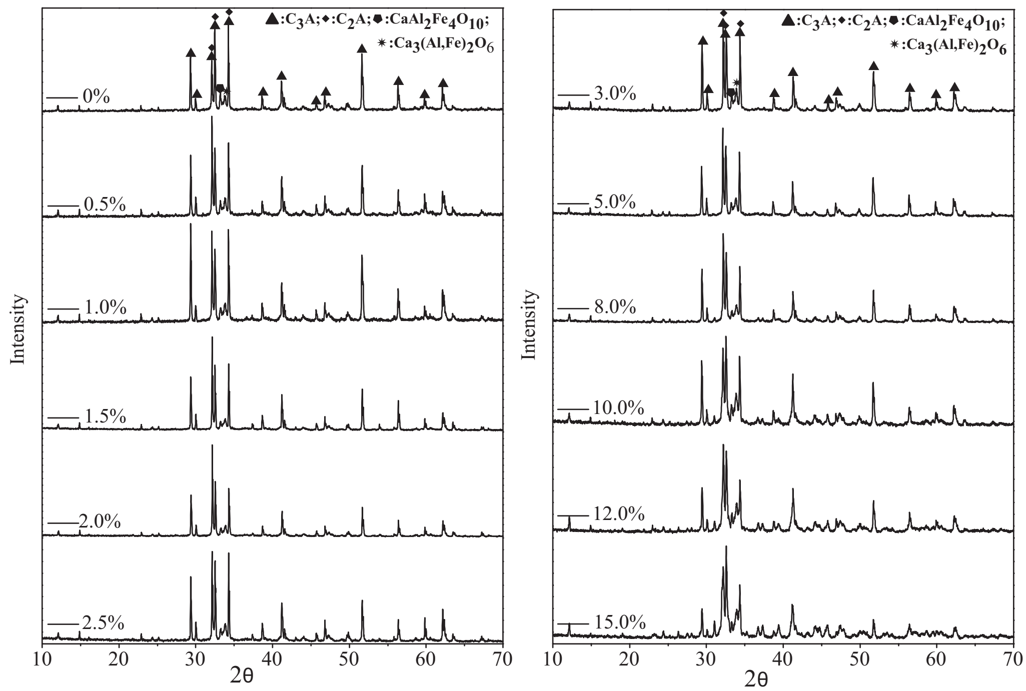

Fig. 2. XRD patterns of eco-clinkers.

C_2S and components with heavy metals increased with increases in sewage sludge content in the raw meal.

3.3. Microstructure of co-cement clinkers by SEM

To verify the XRD pattern results for the plain clinker and the eleven eco-cement clinkers, SEM examinations were performed. Fig. 3 shows the microstructure of clinkers with a sewage sludge content of 0% (a), 2.5% (b), 5.0% (c), 10.0% (d) and 15.0% (e). A discrepancy in the microstructure of the clinkers was found with different amounts of sewage sludge added into the raw meal. Moreover, as shown in Fig. 3(e), it can also be observed that the microstructure of the mixture containing 15.0% sewage sludge content in the raw meal showed significant differences in morphology compared with other samples, displayed as a larger amount of pores distributed in the clinker. Results from the XRD pattern indicated that C_2S was one of the major components in the sample, and one possible explanation for this was that the amount of components in the sludge led to increases in the pores. Furthermore, reports have shown that it is most likely that the doped heavy metals (especially Zn) change the viscosity of the liquid phase of clinkers during the burning process and therefore have influence on the total porosity and the distribution of pores [50].

3.4. Setting times for the eco-cement pastes

The setting times for the twelve eco-cement pastes and the plain paste are given in Table 3. The results indicated that the initial setting time and final setting time of the plain phases were 136 min and 185 min, respectively. All the eco-cement pastes had longer initial setting times and final setting times than the plain paste, and these times increased as the sewage sludge content in the raw meal increased. These results may be due to the formation phase from the raw meal with sewage sludge, which could have caused hydration to slow [38]. Moreover, another possible explanation is that these results might be attributed primarily to the increases in C_2S (α-C_2S or β-C_2S), which affect the rate of the pozzolanic reactions. Furthermore, the delays could also be due to some minor elements (Zn, Cr etc.) presenting in the sewage sludge, which might dissolve in the pore solution and then affect the hydration of the cement [34,50,51].

3.5. Strength development of plain paste and eco-cement pastes

Flexural and compressive strengths of the plain paste and eco-cement pastes after curing ages of 3, 7 and 28 days are also shown in Table 3. It can be seen that the flexural and compressive strengths of the plain paste and eco-cement pastes developed when the curing age was extended from 3 to 28 days. In comparison with the plain paste, the results demonstrate that the flexural and compressive strengths of eco-cement paste were similar under the same curing age conditions. However, the increases in sewage sludge content in the raw meals for curing ages of 3 and 7 days led to a greater decrease in flexural strengths, as well as to a small decrease in compressive strength. In contrast, from 7 to 28 days, the flexural and compressive strength increased and were similar to that of plain paste. Moreover, the strengths were decreased at all hydration times when the sewage sludge content in the raw meals was 15%.

The decreases in early strengths (before 3 days) might be partly due to changes in the content of pozzolanic active matter in the sewage sludge [29], which are believed to be more effective in a pozzolanic reaction and which may have in turn delayed early hydration. As discussed previously, the amounts of C_2S (α-C_2S or β-C_2S) and initial setting times increased with increasing sewage sludge content in the raw meal, so the lower early strength might be responsible for the delay in the hydration process.

3.6. Variations of the element content in eco-cement clinkers

The element concentrations of Al, Fe, Mg, Ti, Mn, Sr, Ba, Zn, Cr, Cu, Ni and Pb in the plain and eco-cement clinkers were analyzed by ICP-AES. The results of the element concentrations are shown in Fig. 4. It can be seen that Al and Fe, known to be the main compounds of cement, decreased slightly as the sewage sludge content in the raw meal increased. However, studies have shown

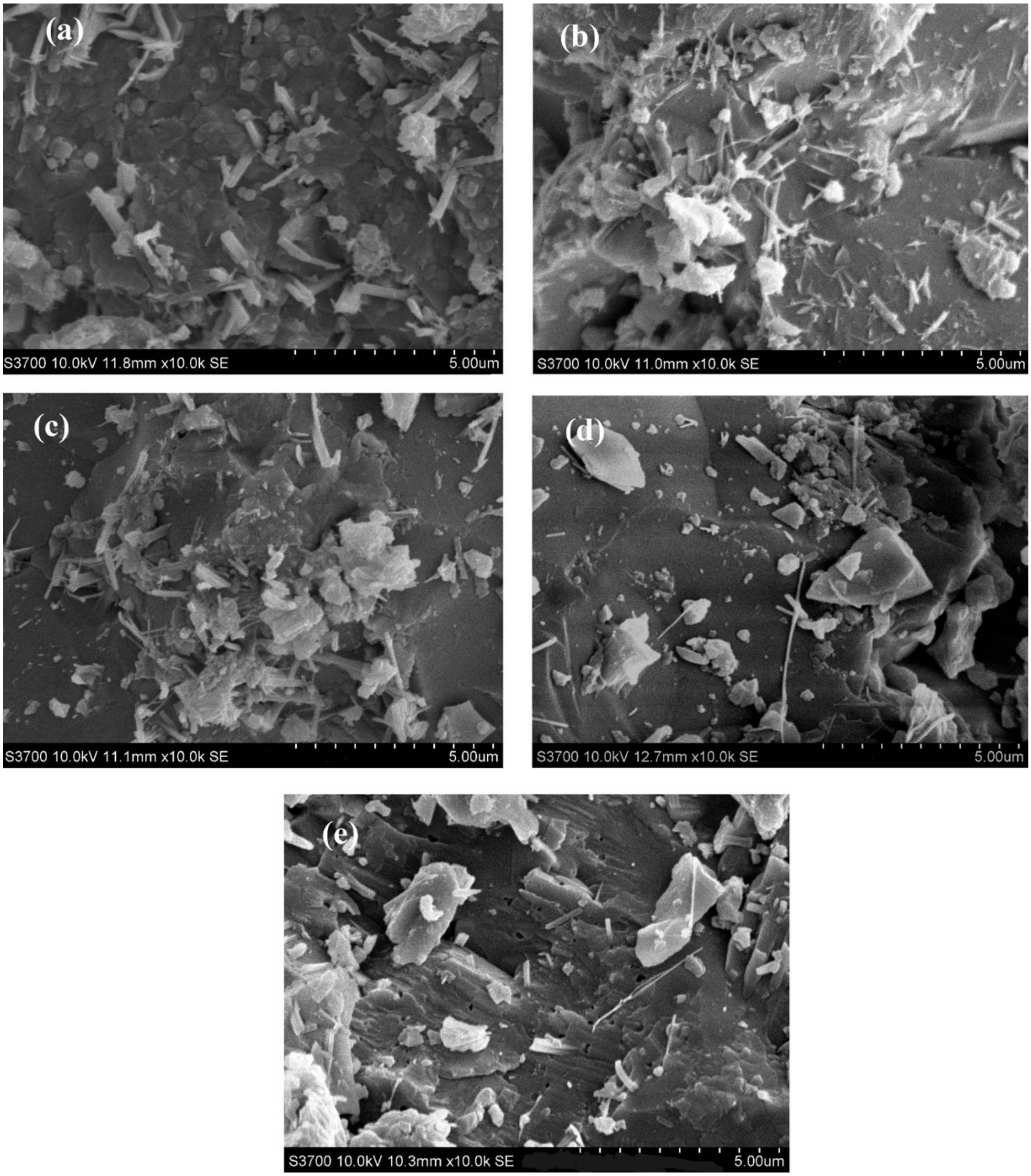

Fig. 3. SEM micrographs of the eco-cement clinkers with the addition of different percentages of sewage sludge in the raw meals: (a) 0%, (b) 2.5%, (c) 5.0%, (d) 10.0% and (e) 15.0%.

that properly increasing the amount of aluminum oxide in clinker can enhance early hydration and increase the early strength of the pastes [52]. The decreasing concentrations of Al and Fe might in part have led to the increases in the initial setting time and the lower early strengths of the eco-cement pastes. Although a small amount of Ti and Mn oxide could promote the strengths of the pastes, results from publications [53] have shown that increases in these elements slightly retard hydration during the first 2 days, and their effect on the hydration rate tends to become negligible at 28 days. As shown in Fig. 4, the Ti increased as the sewage sludge content in raw meals increased whereas the Mn did not exhibit obvious changes. Therefore, the two elements might have had a function contributing to later curing age (7–28 days) strengths. The temperature and viscosity of the formation in the liquid phase was shown to be reduced when a small concentration of Mg was added to the raw meal. However, it can be seen from Fig. 4 that the Mg decreased with the increasing sewage sludge content in the raw meal. Therefore, this might have had negative effects on the formation and development of the alite crystals [54] which then led to the increases in C_2S in the eco-cement clinkers. In addition, the Ba and the Sr could have an influence on the ability both to stabilize the β-phase and on the crystal sizes [55,56]. The Sr decreased obviously and had a higher concentration than Ba as the sewage sludge was increased, so the changes in Sr and Ba might have contributed to the delays in hydration times and to the lower early strengths.

The heavy metals Cr, Zn, Cu may have had an influence on the strength of the cement mortar and the initial setting or hydration of the cement when their concentrations were higher than normal

Table 3
Setting time, Flexural strength and Compressive strength of plain and eco-cement mortars.

Sewage sludge content (%)	Setting time (hour: minute)		Flexural strength (MPa)			Compressive strength (MPa)		
			Curing time (days)					
	Start	Final	3	7	28	3	7	28
0	2:16	3:05	6.02	7.56	9.65	31.42	45.27	63.15
0.5	2:19	3:12	5.98	7.55	9.62	30.28	44.79	62.56
1.0	2:20	3:13	5.75	7.62	9.67	32.59	43.66	64.01
1.5	2:28	3:25	5.74	7.69	9.59	32.63	42.55	61.72
2.0	2:35	3:35	5.65	7.59	9.62	31.78	43.51	65.44
2.5	2:40	3:45	5.43	7.53	9.62	28.07	43.33	63.52
3.0	2:42	3:46	5.41	7.51	9.65	30.02	42.58	63.48
5.0	2:46	3:49	5.22	7.52	9.56	31.25	43.21	62.58
8.0	2:55	3:55	5.21	7.56	9.61	30.02	41.85	61.95
10.0	3:10	4:08	5.16	7.35	9.49	29.95	42.68	60.64
12.0	3:12	4:17	5.08	7.16	9.45	29.86	40.28	60.98
15.0	3:20	4:23	4.98	7.02	9.55	28.64	39.33	60.48

levels in the clinker. Stephan [50,51,57–59] found Cr to accelerate the hydration and to reduce the initial setting of cement, lowering the strength and causing changes in the content of free lime and the modification of C_3S in clinkers. These results were similar to those of Sgirasaka et al. [60] and Murat and Sorrentino [61]. Moreover, other publications [50,53,58,61,62] have indicated that Zn retards heat liberation and delays the hydration of cement, leading to a retardation of the initial setting and also causing higher strength in cement pastes. In addition, Cu has been found to cause the greatest delay in the hydration rate of cement in all the elements in the clinker [53,60]. As shown in Fig. 4, the concentrations of Cr, Zn, Cu increased as the sewage sludge was added into the raw meal and the increasing degree of these three elements was in the order, Zn, Cr and Cu, respectively. The concentrations of Zn, Cr and Cu might have partly had an effect on the increases in the initial setting times and the lower early strengths of the pastes, as well as increases in C_2S in the eco-cement clinkers. On the other hand, most publications [50,51,53,58,59] have shown that the addition of Ni in raw meal does not affect the hydration of cement. Several heavy metals, such as lead and cadmium, which are known to be volatile, can immediately vaporize during the melting process.

3.7. Cement clinker paste hydrates

In order to demonstrate the hydration to slow of eco-clinkers after the addition of sewage sludge in raw meal as discussed above, tests of the hydration process for the clinker pastes were carried out. The hydration products of the four clinker pastes that had 0, 5.0, 10.0 and 15.0% sewage sludge added to the raw meal at the various curing times (3–28 days) can be seen through the XRD patterns shown in Fig. 5 (A-3 days, B-7 days and C-28 days), respectively. This revealed that higher peaks for $Ca(OH)_2$, calcium silicate hydrate (CSH) and calcium aluminum hydrates (CAH) could be identified for all the curing times, with the exception of the C_3S and C_2S peaks. It can be observed from these figures that the degrees of hydration for the three clinker pastes that had 0, 5.0 and 10.0% sewage sludge

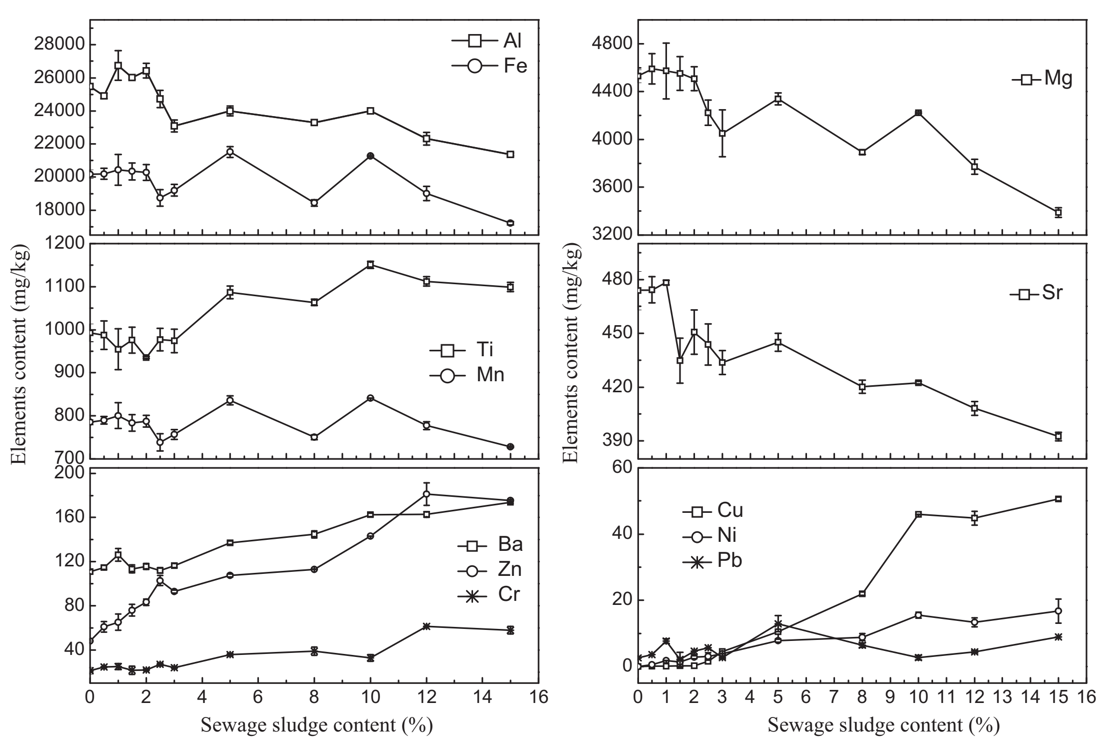

Fig. 4. Changes in the element content of plain and eco-cement clinkers with different sewage sludge content in raw meals.

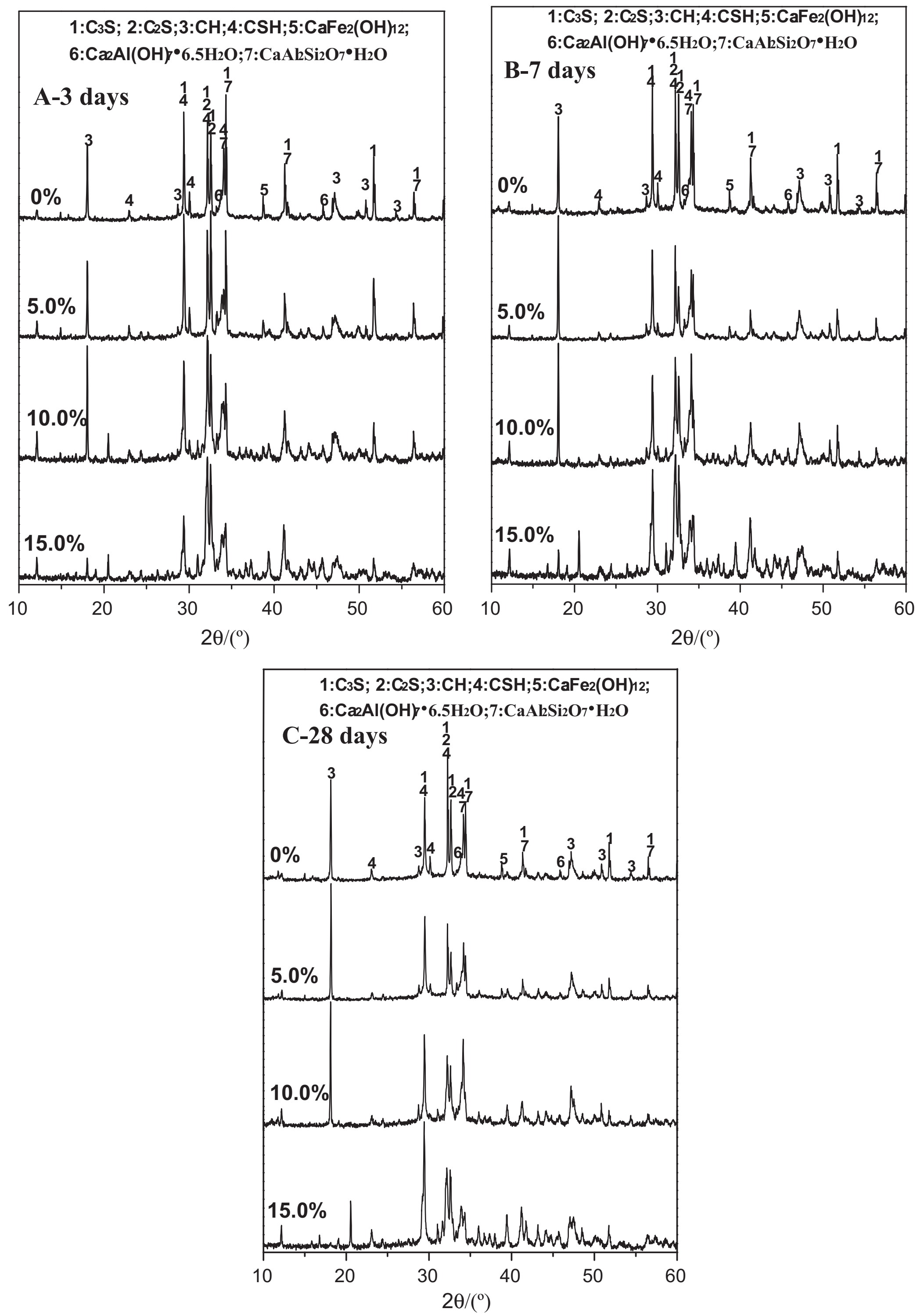

Fig. 5. XRD spectrum of cement clinkers after 3 (A), 7 (B) and 28(C) days hydration.

added to the raw meal were similar when curing age was extended from 1 to 28 days. However, the degrees of hydration for the clinker that had 15.0% sewage sludge added to the raw meal was obvious delayed, the result might be the sign of the increasing C_2S and most of the elements changed in the eco-cement clinkers. Therefore, we could draw the conclusion that the addition of sewage sludge into raw meal can potentially cause delayed hydration of the clinker pastes.

3.8. TCLP test of eco-cement clinkers

Table 4 shows the leaching concentrations of heavy metals and the limits of the extraction procedure toxicity standards in China. The regulatory threshold values in China are listed in accordance with GB 5085.3-2007 (Identification standards for hazardous wastes-Identification for extraction toxicity of China). It can be seen that only the Ba, Cr, Pb and Sr elements presented and that none

Table 4
TCLP leaching concentrations (mg/L) and the final pH of mixed liquids for the plain and eco-cement clinkers.

Sewage sludge content (w/w %)	pH	Elements(mg/L)											
		Ba	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sr	Ti	V	Zn
0	11.68	1.14	ND	ND	0.39	ND	ND	ND	ND	6.06	ND	ND	ND
1.0	11.55	1.41	ND	ND	0.09	ND	ND	ND	0.02	6.52	ND	ND	ND
3.0	11.66	1.70	ND	ND	0.02	ND	ND	ND	ND	6.68	ND	ND	ND
8.0	11.49	2.09	ND	ND	0.32	ND	ND	ND	0.01	7.03	ND	ND	ND
12.0	11.21	2.02	ND	ND	0.83	ND	ND	ND	0.01	6.64	ND	ND	ND
GB 5085.3–2007[a]	–	100	1	–	15	100	–	5	5	–	–	–	100

[a] Identification standards for hazardous wastes – Identification for extraction toxicity of China.

of them exceeded the regulatory thresholds. Moreover, in comparison with the leaching data for the eco-clinker, the increasing sewage sludge content in the raw meal resulted in higher amounts of leached heavy metals. This could be due to the higher heavy metal concentrations in the clinkers when adding sewage sludge, leading to an increased of the amount of heavy metals available for leaching. However, in fact, all of the heavy metals were barely detectable. This result could be related to either part of the heavy metals (primarily volatile metals) evaporating during the clinker burning process or to parts of them substituting for the major elements (Ca, Si, Al, Fe) so that they remained immobilized in the structure of the clinker minerals. In all cases, all the eco-cement clinkers produced in this study were leach-safe to the environment.

4. Conclusions

1. The X-ray diffraction patterns of all the clinkers showed that the major components present in the eco-cement clinkers were C_3S, C_2S, C_3A, C_4AF and that the phase formation of $Ca_{54}MgAl_2Si_{16}O_{90}$ was identified in all the clinkers. The C_2S (α-C_2S or β-C_2S) phase formation and peaks increased with increases in sewage sludge.

2. Investigations by SEM gave evidence of the C_2S (α-C_2S or β-C_2S) phase formation increasing with increases in sewage sludge content while the C_3S structures decreased. Particularly, the microstructure of the mixture in the clinker containing 15.0% sewage sludge was significantly different in that it displayed a larger amount of pore distribution.

3. All the eco-cement pastes had both delayed initial setting times and final setting times. The early flexural strengths of all the eco-cement pastes were lower than that of the plain paste, whereas their compressive strengths only were a little lower than the plain paste. The more sewage sludge that was added to the raw meals, the lower the flexural strengths of the eco-cement pastes. However, there was no significant effect on all the strengths at later curing ages. This might be primarily attributed to the increased amounts of C_2S in the eco-clinkers and the minor elements carried from the sewage sludge.

5. The concentrations of Ti, Ba, Zn, Cr, Cu, Ni and Pb in the clinkers increased with the sewage sludge addition into the raw meals, while Mg, Sr obviously decreased, and Al, Fe, Mn slightly decreased.

6. The leaching concentrations of all types of eco-cement clinkers met the standard of current Chinese regulatory thresholds.

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