



## The influence of heavy metals on the polymorphs of dicalcium silicate in the belite-rich clinkers produced from electroplating sludge

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### ARTICLE INFO

#### Article history:

Received 20 January 2009

Received in revised form 17 April 2009

Accepted 20 April 2009

Available online 24 April 2009

#### Keywords:

Belite-rich clinker

Heavy metal

X-ray diffraction

Transmission electron microscopy

Electroplating sludge

### ABSTRACT

The purpose of this study is to utilize an electroplating sludge for belite-rich clinker production and to observe the influence of heavy metals on the polymorphs of dicalcium silicate ( $C_2S$ ). Belite-rich clinkers prepared with 0.5–2% of NiO, ZnO, CuO, and  $Cr_2O_3$  were used to investigate the individual effects of the heavy metals in question. The Reference Intensity Ratio (RIR) method was employed to determine the weight fractions of  $\gamma$ - $C_2S$  and  $\beta$ - $C_2S$  in the clinkers, and their microstructures were examined by the transmission electron microscopy (TEM). The results showed that nickel, zinc, and chromium have positive effects on  $\beta$ - $C_2S$  stabilization ( $Cr^{3+} > Ni^{2+} > Zn^{2+}$ ), whereas copper has a negative effect. The addition of up to 10% electroplating sludge did not have any negative influence on the formation of  $C_2S$ . It was observed that  $\gamma$ - $C_2S$  decreased while  $\beta$ - $C_2S$  increased with a rise in the addition of the electroplating sludge. Moreover, nickel and chromium mainly contributed to stabilizing  $\beta$ - $C_2S$  in the belite-rich clinkers produced from the electroplating sludge.

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### 1. Introduction

Cement manufacturing is an industry that consumes a large amount of energy and emits high levels of  $CO_2$ ; producing one ton of cement typically requires approximately 3.2–6.3 GJ of energy and is accompanied by one ton of  $CO_2$  emissions [1]. These emissions principally arise from limestone calcination, fuel combustion, and electricity use. Some studies have estimated that the cement industry contributes as much as 5% of global anthropogenic  $CO_2$  emissions [2,3], and thus in recent years there have been a number of efforts aimed at reducing the  $CO_2$  emissions with the production of low-energy cements, e.g., alinite cements, sulfoaluminate cements, and belite-rich cements (also known as high belite cements) [4].

The large energy and raw-material requirements of cement manufacturing provide the industry with significant opportunities to consume enormous amounts of waste materials and fuels, and several researchers have studied the possibility of reusing these

waste materials for ordinary Portland cement production [5–7]. However, the amount of waste materials reused in these studies was usually limited, because excessive amounts of impurities interfered with the formation of alite ( $Ca_3SiO_5$ ,  $C_3S$ ) by hindering belite ( $Ca_2SiO_4$ ,  $C_2S$ ) from combining with lime (CaO). Therefore, it may be preferable to reuse non-conventional materials, e.g., metal-surface-treatment sludge [5], chemical-industry waste [6], and galvanic sludge [7], for the production of belite-rich cements. Compared to the vitrification process for thermal waste treatment [8,9], belite-rich cement production should also have the advantage of lower energy consumption.

Belite-rich cements, in which  $C_2S$  is the major constituent, have lower  $CO_2$  emissions than ordinary Portland cements because of their reduced sintering temperature and lower limestone requirement. In terms of engineering properties, belite-rich cements also have the advantages of low hydration heat, high flowability, good frost resistance, and excellent structural durability [10–12]. However, the hydraulic activity of belite-rich cements requires further consideration. It is known that  $C_2S$  exists in five polymorphs, namely  $\alpha$ ,  $\alpha'_H$ ,  $\alpha'_L$ ,  $\beta$ , and  $\gamma$ . The  $\gamma$  phase, which barely reacts with water, is stable at room temperature, while the other polymorphs in the pure state are stable only at elevated temperatures [13,14]. In the production of belite-rich cements, the  $\beta \rightarrow \gamma$  transformation of  $C_2S$  can be problematic, reducing the hydraulic activity. Some

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approaches, such as physical and chemical stabilizations, have been suggested to preserve  $\beta$ - $C_2S$  at room temperature. Physical stabilization is related to the cooling conditions and the particle size of  $C_2S$  [11,13,15], and the rapid cooling technique is often used with different cooling media, e.g., air, water, liquid nitrogen, and carbon tetrachloride [11]. Chan et al. [15] reported that the  $C_2S$  particles smaller than 10  $\mu\text{m}$  were completely retained as the  $\beta$  phase. The effects of foreign ions on chemical stabilization have also been investigated [16–19], and various judgment methods based on the Goldschmidt's ion radius ( $R_G$ ) [20], the ratio of charge to Pauling's ion radius ( $C/R_p$ ) [21], and the ion polarization ability ( $C^2/R_p$ ) [22] have been proposed to predict which ions can stabilize  $\beta$ - $C_2S$  at room temperature. Generally, the chemical approaches in the literature were effective in stabilizing  $\beta$ - $C_2S$ , without particularly controlling the cooling conditions or the particle size.

Reducing energy requirements and  $\text{CO}_2$  emissions and utilizing alternative materials are important tasks in modern cement manufacturing. Non-conventional materials containing some impurities are more appropriate for the production of belite-rich rather than ordinary Portland cement clinkers, and the foreign ions are beneficial to stabilizing  $C_2S$  in the  $\beta$  phase. The purpose of this study is thus to use electroplating sludge (EPS) for the production of belite-rich clinkers and to observe the influence of heavy-metal ions, including  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Cr}^{3+}$ , on the  $C_2S$  polymorphs. In order to assess the effectiveness, quantitative X-ray diffraction analysis was employed to determine the weight fractions of  $\beta$ - and  $\gamma$ - $C_2S$  in the clinkers by means of the Reference Intensity Ratio (RIR) method. In addition, the clinker microstructures were examined by the transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) techniques.

## 2. Experimental

### 2.1. Materials

The EPS used in this study was obtained from an electroplating factory manufacturing industrial and automobile components. The wastewaters from different electroplating processes were treated together, and thus EPS containing several heavy metals was generated in a chemical-precipitation process, where the wastewater was adjusted to a high pH level. The EPS lumps dried in an oven were collected and then crushed with a jaw crusher, and the fragments were then ground into powder with a particle size of less than 75  $\mu\text{m}$  (No. 200 mesh, USA standard testing sieve) by a centrifugal ball mill for further experiments. The chemical analyses of EPS were conducted with an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer Optima 2000 DV) following the microwave-assisted acid digestion procedure (USEPA, SW-846 Method 3051). The EPS powder was digested with nitric, hydrochloric, and hydrofluoric acids at  $\sim 175^\circ\text{C}$  for 24 min in a high-performance microwave digestion unit (Milestone, MLS 1200 MEGA). Table 1 shows the chemical compositions of the EPS and the raw mix for making belite-rich clinkers. The major constituents in EPS were CaO and  $\text{Fe}_2\text{O}_3$  (12.7 wt.% and 8.0 wt.%, respectively), meaning that it has potential for use as cement raw materials. In terms of heavy metals, copper, zinc, chromium, and nickel were detected at about 25,000–72,000 mg/kg in the EPS. The raw mix was primarily composed of CaO and  $\text{SiO}_2$  (with a molar ratio of CaO to  $\text{SiO}_2$  of 2.46), and there were no heavy metals present. This chemical composition of the raw mix was chosen on the basis of our previous study [23], in which it was found that a lime saturation factor (LSF) of 0.7 is appropriate to produce belite-rich clinkers at  $1,200^\circ\text{C}$ . In the produced clinkers, lime almost completely reacted and mainly combined with silica to form  $C_2S$ .

**Table 1**

The results of the chemical analyses of the raw mix and EPS.

Chemical composition (dry basis)	Raw mix	EPS	
	CaO	54.8	12.7
	$\text{SiO}_2$	23.9	2.8
	$\text{Al}_2\text{O}_3$	5.0	0.2
Metal content as oxides (wt.%)	$\text{Fe}_2\text{O}_3$	8.3	8.0
	MgO	0.3	0.8
	$\text{Na}_2\text{O}$	0.1	0.6
	$\text{K}_2\text{O}$	0.3	ND
	Ni	ND	72,353
Heavy metal (mg/kg)	Zn	ND	29,770
	Cu	ND	24,813
	Cr	ND	42,457
	Pb	ND	ND
	Cd	ND	ND

ND: not detected (<2 mg/kg).

### 2.2. Clinker preparation

The raw mix without EPS was used to prepare a reference clinker. In order to observe the influence of a single heavy metal, some clinkers were prepared from the raw mixes doped with 0.5–2% of  $\text{NiO}$ ,  $\text{ZnO}$ ,  $\text{CuO}$ , and  $\text{Cr}_2\text{O}_3$ . The raw mixes containing 2.5–10% of the EPS were synthesized and the proportions of CaO,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  were adjusted close to those in the original raw mix by using analytical-grade oxides. To produce clinkers, the raw mixes were shaped into cylindrical pellets (approximately 35 mm in diameter and 8 mm in height) under a uniaxial pressure of 9.8 MPa, and then sintered in an electrical furnace at  $1200^\circ\text{C}$  for 3 h. After the sintering procedure, the clinkers were cooled to room temperature in the furnace under an air atmosphere and then ground in an agate ball mill for 40 min by using cyclohexane as a grinding aid. The ground material was then placed in a gentle nitrogen stream to remove cyclohexane at room temperature.

### 2.3. Analyses

To acquire the mineralogical compositions of the clinkers, the X-ray powder diffractometry (XRPD) was conducted with an X-ray diffractometer (Bruker D8 Advance) with  $\text{Cu-K}\alpha$  radiation. The XRPD specimen was prepared by mixing a clinker with corundum ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) in the weight ratio of 10:1. This mixture was dispersed in a 0.5% (w/v) aqueous solution of polyvinyl alcohol to form a suspension in which the solid-to-liquid ratio was 1:2. The suspension was spray dried at  $150^\circ\text{C}$  and the collected particles were used for the XRPD analysis. This spray-drying procedure was used to minimize preferred orientation and to enhance the accuracy of the following quantitative phase analysis. This analysis was performed with the Reference Intensity Ratio method, which is an adaptation of the internal standard method [24–27]. The most general definition of RIR for the phase of interest  $\alpha$  and the reference phase  $s$  is given by:

$$\text{RIR}_{\alpha,s} = \left( \frac{I_{(hkl)\alpha}}{I_{(hkl)'s}} \right) \left( \frac{I_{(hkl)'s}^{\text{rel}}}{I_{(hkl)\alpha}^{\text{rel}}} \right) \left( \frac{X_s}{X_\alpha} \right) \quad (1)$$

where  $X$ ,  $I$ , and  $I^{\text{rel}}$  denote the weight fraction, intensity of a diffraction peak, and relative intensity, respectively. Rearranging Eq. (1) and using corundum as the reference phase, the equation for the RIR method can be given as Eq. (2).

$$X_\alpha = \left( \frac{I_{(hkl)\alpha}}{I_{(hkl)'\text{cor}}} \right) \left( \frac{I_{(hkl)'\text{cor}}^{\text{rel}}}{I_{(hkl)\alpha}^{\text{rel}}} \right) \left( \frac{X_{\text{cor}}}{\text{RIR}_{\alpha,\text{cor}}} \right) \quad (2)$$

$I_{(hkl)'\text{cor}}$  and  $I_{(hkl)\alpha}$  can be calculated from the experimental diffraction data, and the three required constants ( $I_{(hkl)'\text{cor}}^{\text{rel}}$ ,  $I_{(hkl)\alpha}^{\text{rel}}$ , and

**Table 2**RIR<sub>cor</sub> values and the corresponding peaks for the quantitative phase analysis.

Phase (ICDD-PDF no.)	Chemical formula	RIR <sub>cor</sub>	Peak		
			d-spacing (Å)	hkl	I <sup>rel</sup>
β-Dicalcium silicate (01-086-0398)	Ca <sub>2</sub> SiO <sub>4</sub>	0.76	2.88	120	27.8
γ-Dicalcium silicate (01-087-1257)	Ca <sub>2</sub> SiO <sub>4</sub>	1.30	4.32	021	33.9
Corundum <sup>a</sup> (00-010-0173)	Al <sub>2</sub> O <sub>3</sub>	1.00	3.48	012	75.0

<sup>a</sup> Reference phase (internal standard).

RIR<sub>α,cor</sub>) can be taken from the International Centre for Diffraction Data-Powder Diffraction File (ICDD-PDF) cards. Table 2 lists the RIR<sub>cor</sub> values and the corresponding peaks of the phases analyzed in this study. The weight fraction of phase α in the XRPD specimen (X<sub>α</sub>) can be obtained from the known X<sub>cor</sub>, and therefore that in the original sample (X'<sub>α</sub>) can be computed by Eq. (3). However, the results of the RIR method in this study should be considered as semi-quantitative, because this analysis was based on the tabulated constants from the ICDD-PDF cards.

$$X'_{\alpha} = \frac{X_{\alpha}}{1 - X_{cor}} \quad (3)$$

The level of heavy metals in the clinkers was determined with the ICP-OES following the microwave-assisted acid digestion procedure. To remove the interstitial phases and obtain a residue enriched in belite for microstructural examination, a selective extraction method that combines salicylic acid-methanol (SAM) extraction with KOH-sucrose (KOSH) extraction was used. This combined method was developed by Gutteridge [28], and is referred to as a modified SAM extraction. In the specimen preparation for microstructural examination, the clinker fragments were added into absolute alcohol as a suspension in advance of the procedure. A drop of the suspension was put on a copper grid with carbon film and then dried with a vacuum dryer. The microstructures of the fragments were examined with a field emission transmission electron microscope (FE-TEM, Hitachi HF-2000) with an energy dispersive spectrometer (EDS, Noran Voyager 1000).

### 3. Results and discussion

#### 3.1. Individual effects of heavy metals on clinker mineralogical compositions

The clinkers prepared from the raw mixes doped with 0.5–2% of a heavy-metal oxide were used to examine the influence of Ni<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, and Cr<sup>3+</sup> on the mineralogical compositions. Fig. 1 presents the XRPD patterns of the reference clinker and clinkers prepared with a single heavy-metal oxide. The identification of γ-C<sub>2</sub>S and β-C<sub>2</sub>S was made by using the resolvable diffraction peaks in spite of partial or complete peak overlaps especially on the high-angle side. It was observed that γ-C<sub>2</sub>S and β-C<sub>2</sub>S were both the predominant crystalline phases in the reference clinker. The interstitial phases including brownmillerite (Ca<sub>2</sub>FeAlO<sub>5</sub>) and gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>, C<sub>2</sub>AS) were also found. When the dosage of CuO or ZnO was raised to 2%, the diffraction peaks of γ-C<sub>2</sub>S were still clearly observable; in addition, the clinker prepared with 2% of CuO had a high diffraction intensity of gehlenite. The diffraction peaks of γ-C<sub>2</sub>S almost disappeared in the XRPD pattern of the clinker prepared with 1% of NiO or Cr<sub>2</sub>O<sub>3</sub>, which was accompanied by an increase in the β-C<sub>2</sub>S diffraction intensity.

Figs. 2 and 3 show the weight fraction of γ-C<sub>2</sub>S and β-C<sub>2</sub>S in the clinkers, respectively. The reference clinker, which was not doped with heavy-metal oxides, contained about 27 wt.% of γ-C<sub>2</sub>S and 34 wt.% of β-C<sub>2</sub>S. The stabilized β-C<sub>2</sub>S may be attributed to Al<sup>3+</sup> and Fe<sup>3+</sup>, which has been reported in several previous studies [16,18,19]. In those studies, Al<sup>3+</sup> and Fe<sup>3+</sup> were doped into a pure CaO–SiO<sub>2</sub> sys-

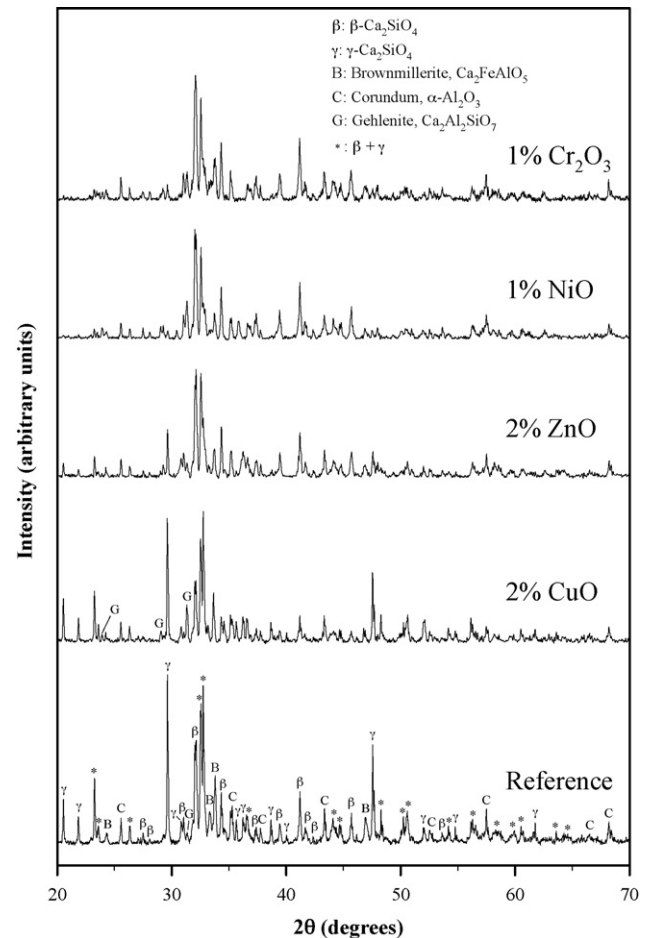
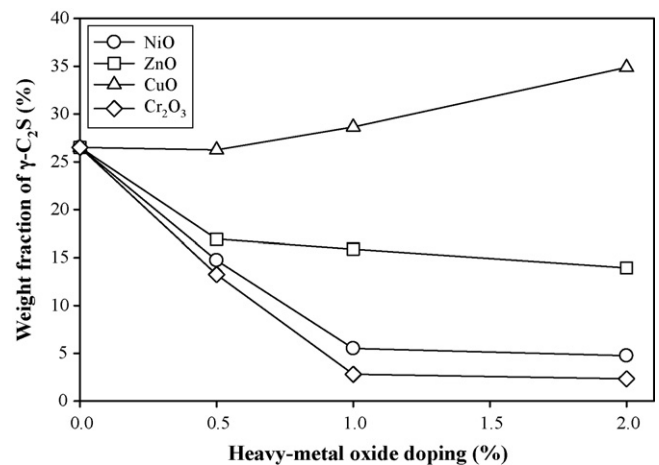


Fig. 1. The XRPD patterns of the clinkers prepared with a single heavy-metal oxide.

Fig. 2. The weight fraction of γ-C<sub>2</sub>S in the clinkers prepared with different amounts of heavy metal oxides.

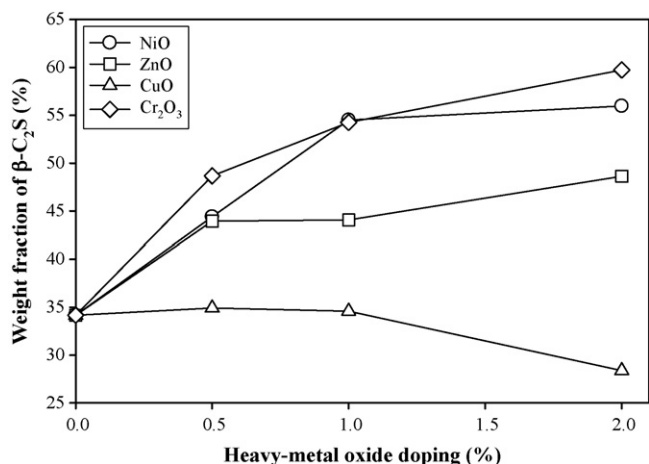


Fig. 3. The weight fraction of  $\beta$ -C<sub>2</sub>S in the clinkers prepared with different amounts of heavy metal oxides.

tem at 0.01–0.2 mol for 1 mol of C<sub>2</sub>S, and it was reported that Al<sup>3+</sup> and Fe<sup>3+</sup> could stabilize C<sub>2</sub>S in the  $\beta$  phase, which was contrary to the judgments for the determination of stabilizing ions [20–22]. In the heavy-metal oxide doped clinkers, the weight fraction of  $\gamma$ -C<sub>2</sub>S seemed to be negatively related to that of  $\beta$ -C<sub>2</sub>S, and the variations in the quantity of  $\gamma$ -C<sub>2</sub>S and  $\beta$ -C<sub>2</sub>S depended on the dosage and category of the doped heavy-metal oxides. It was found that Cu<sup>2+</sup> had a negative effect, while Ni<sup>2+</sup>, Zn<sup>2+</sup>, and Cr<sup>3+</sup> had positive effects on  $\beta$ -C<sub>2</sub>S stabilization. In addition,  $\gamma$ -C<sub>2</sub>S increased by ~8 wt.% when the CuO dosage increased to 2%. Cr<sup>3+</sup> was most effective in stabilizing  $\beta$ -C<sub>2</sub>S, and most of the C<sub>2</sub>S existed in the  $\beta$  phase when Cr<sub>2</sub>O<sub>3</sub> was 1% of the raw mix. These findings are in accordance with the study done by Saraswat et al. [29], which investigated the Cr<sub>2</sub>O<sub>3</sub> doped CaCO<sub>3</sub>–SiO<sub>2</sub> (2:1) system and found that the ratio of  $\gamma$ -C<sub>2</sub>S to  $\beta$ -C<sub>2</sub>S was close to the minimum when doped with 1% of Cr<sub>2</sub>O<sub>3</sub>. Ni<sup>2+</sup> was similar to Cr<sup>3+</sup>, whereas Zn<sup>2+</sup> was less effective than either of them. However, Ni<sup>2+</sup> and Zn<sup>2+</sup> were classified as failing to stabilize  $\beta$ -C<sub>2</sub>S by the judgment methods [20–22], and this discrepancy may result from differences in experimental conditions, such as the CaO to SiO<sub>2</sub> molar ratio, sintering and cooling processes, particle size, and the concentration of stabilizing ions [18]. As well as the discrepancies for Ni<sup>2+</sup> and Zn<sup>2+</sup> seen in this study, they have also been observed between the experimental results and judgments for Al<sup>3+</sup> and Fe<sup>3+</sup> by Suzuki et al. [16] and Kim and Hong [19].

### 3.2. Clinkers prepared with EPS

The XRPD patterns of the clinkers prepared with 2.5–10% of EPS are given in Fig. 4. When the EPS addition was 2.5%, the diffraction peaks of  $\gamma$ -C<sub>2</sub>S were still observable but the intensity was much lower than those in the reference clinker. In addition,  $\gamma$ -C<sub>2</sub>S almost vanished in the clinkers prepared with 5% or more EPS. The above results reveal that the  $\beta \rightarrow \gamma$  transformation of C<sub>2</sub>S can be interrupted completely by employing EPS as a raw material to provide sufficient stabilizing ions. The clinker produced with 10% EPS had the strongest diffraction intensity of  $\beta$ -C<sub>2</sub>S. It was also found that the interstitial phases, brownmillerite and gehlenite, were also affected by the addition of EPS, with the diffraction intensity of brownmillerite generally increasing as more EPS was added, while gehlenite disappeared after the amount of EPS reached 5%.

Fig. 5 presents the variations in the quantity of  $\gamma$ -C<sub>2</sub>S and  $\beta$ -C<sub>2</sub>S versus the amount of EPS added. The quantity of  $\gamma$ -C<sub>2</sub>S is reduced to the minimum value when the EPS addition is at 0–5%. In contrast,  $\beta$ -C<sub>2</sub>S gradually rises to the maximum value and the increasing variation appears to be slow when the amount of EPS added exceeds

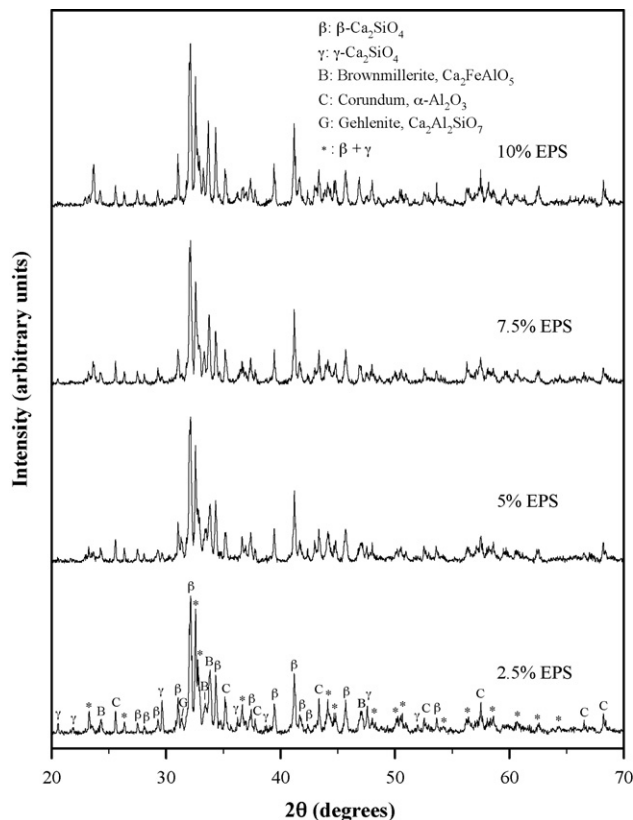


Fig. 4. The XRPD patterns of the clinkers produced with 2.5–10% EPS.

5%.  $\beta$ -C<sub>2</sub>S accounted for nearly 60 wt.% in the clinker produced with 10% EPS. The results indicate that the addition of EPS was beneficial with regard to  $\beta$ -C<sub>2</sub>S stabilization, and adding up to 10% did not have negative influence on the C<sub>2</sub>S formation. The clinkers produced from EPS contain approximately equivalent amounts of C<sub>2</sub>S, and the C<sub>2</sub>S exists in the  $\beta$  phase due to stabilizing ions from the EPS.

### 3.3. Residual heavy metals in clinkers

The level of heavy metals remaining in the clinkers is illustrated in Fig. 6, and, with the exception of zinc, this was linearly correlated with the EPS addition. Zinc was only detected in the clinkers

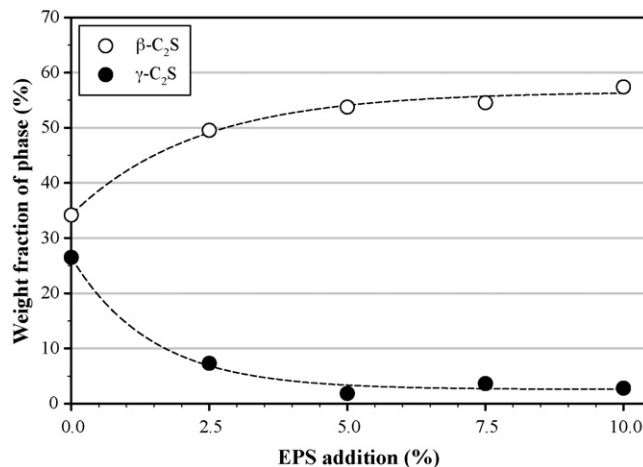


Fig. 5. The variations in quantity of  $\gamma$ -C<sub>2</sub>S and  $\beta$ -C<sub>2</sub>S versus the addition of EPS added.

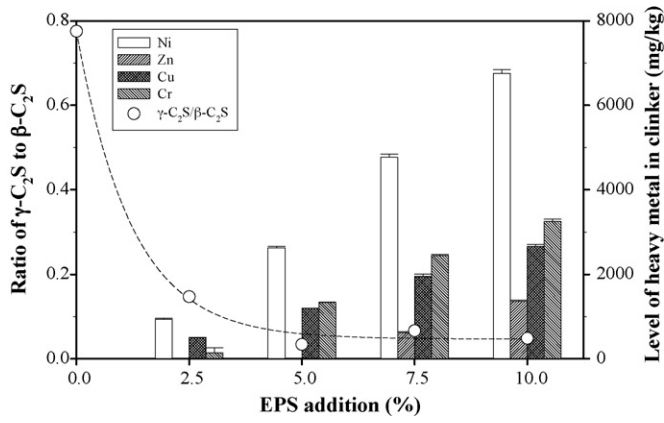


Fig. 6. The ratio of  $\gamma\text{-C}_2\text{S}$  to  $\beta\text{-C}_2\text{S}$  and the levels of residual heavy metals in the clinkers produced with EPS.

Table 3  
The EDS results of the clinker produced with 10% EPS.

Element	Weight (%)	Atom (%)
Ca	42.36	26.62
Si	16.75	14.91
O	40.26	58.17
Ni	0.38	0.19
Cr	0.25	0.11

produced with 7.5% and 10% EPS. It was found that the evaporation of zinc was much more significant than that of the other heavy metals, especially compared to copper, which accounted for even less than zinc in the EPS. Fig. 6 also shows the variation of  $\gamma\text{-C}_2\text{S}/\beta\text{-C}_2\text{S}$  versus the amount of EPS added. There is a large decrease in  $\gamma\text{-C}_2\text{S}/\beta\text{-C}_2\text{S}$  when EPS is added in the range of 0–5%, but the value stabilizes beyond this. The decrease in  $\gamma\text{-C}_2\text{S}/\beta\text{-C}_2\text{S}$  means that the

stabilization of  $\beta\text{-C}_2\text{S}$  is enhanced. Based on the above results, it is shown that nickel, zinc, and chromium are all capable of stabilizing  $\beta\text{-C}_2\text{S}$ . For the clinkers produced with 2.5% and 5% EPS, the values of  $\gamma\text{-C}_2\text{S}/\beta\text{-C}_2\text{S}$  are significantly smaller than that of the reference clinker, although in these two clinkers no zinc was detected. Consequently, the results show that  $\beta\text{-C}_2\text{S}$  stabilization in the clinkers produced with EPS can mainly be ascribed to nickel and chromium.

### 3.4. Microstructures of the clinkers

In order to reduce the interference from the interstitial phases, the clinker was treated with the modified SAM extraction before proceeding to the microstructural examination. Fig. 7 displays the XRPD patterns of the clinker produced with 10% EPS before and

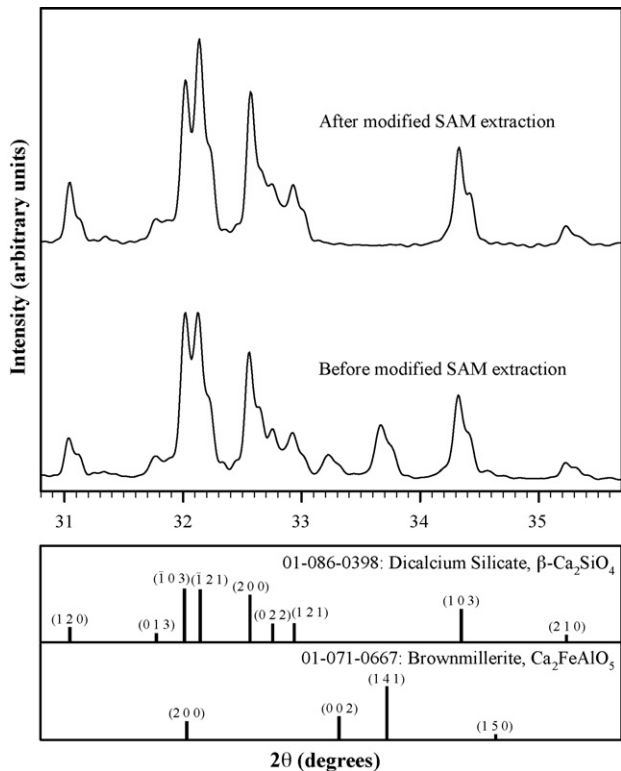


Fig. 7. The XRPD patterns of the clinkers produced with 10% EPS before and after the modified SAM extraction.

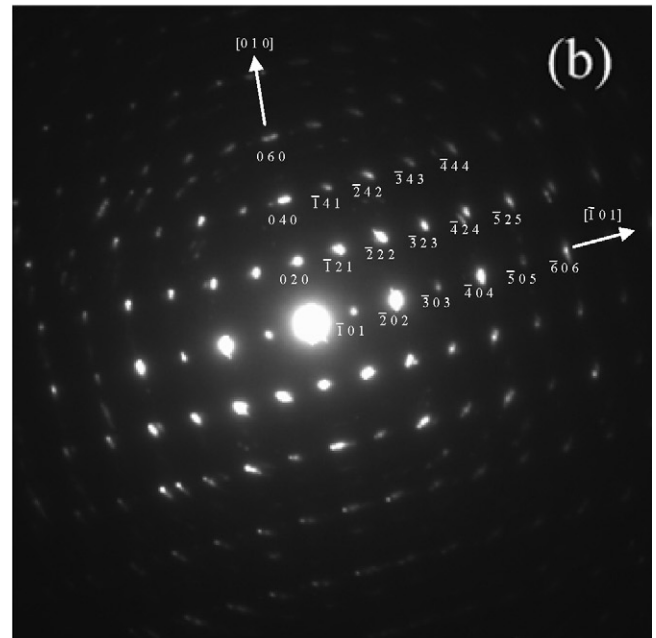
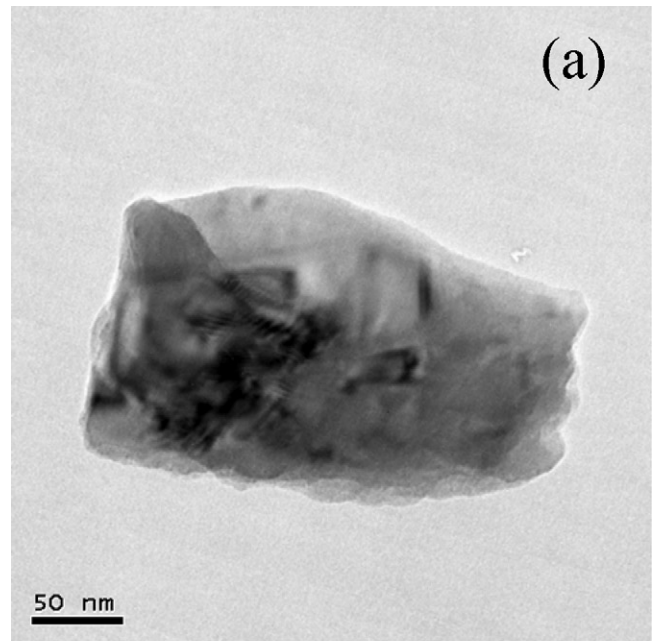


Fig. 8. (a) TEM image of the clinker produced with 10% EPS, and (b) the corresponding electron diffraction pattern.

after the modified SAM extraction. According to the ICDD card, the strongest diffraction line of brownmillerite is (1 4 1). This shows that brownmillerite was successfully removed, and the diffraction intensity of  $\beta$ - $C_2S$  was slightly enhanced after the modified SAM extraction.

Fig. 8a and b, respectively, present the TEM image and the electron diffraction pattern of the clinker produced with 10% EPS. In Fig. 8a, the characteristic twinned lamellar structure of  $\beta$ - $C_2S$  is clearly observed, as was seen in some previous studies [30–33]. By means of analyzing the electron diffraction pattern shown in Fig. 8b, the corresponding reflections and the transmission electron beam parallel to the [1 0 1] direction were found, and the crystal structure confirms that the fragment is indeed  $\beta$ - $C_2S$ . The elemental composition obtained from the EDS analysis is given in Table 3, which shows that calcium, silicon, and oxygen accounted for the great majority of this fragment. The atomic percentages of calcium and silicon were 26.62% and 14.91%, respectively, and thus the primary constituent is  $C_2S$ . Furthermore, it was found that nickel and chromium accounted for 0.38 wt.% and 0.25 wt.%, respectively. The above results support the idea that  $\beta$ - $C_2S$  is stabilized by nickel and chromium, and are consistent with the inference in Section 3.3.

#### 4. Conclusions

The following conclusions can be drawn from the present study on the  $C_2S$  polymorphs in the belite-rich clinker produced from EPS. In terms of the individual effects of the heavy metals, it was found that nickel, zinc, and chromium had a positive influence on  $\beta$ - $C_2S$  stabilization, while copper had a negative influence. The order of the heavy metals by their positive effectiveness can be expressed as follows:  $Cr^{3+} > Ni^{2+} > Zn^{2+}$ . In the clinkers produced from EPS,  $\gamma$ - $C_2S$  almost disappeared when 5% or more EPS was added, and EPS addition up to 10% showed no negative influence on  $C_2S$  formation. The evaporation of the heavy metals during the sintering procedure should be noticeable, especially for zinc. Based on the residual amounts of the heavy metals found in the clinkers, it is suggested that nickel and chromium mainly contributed to the stabilization of  $\beta$ - $C_2S$ . The characteristic twinned lamellar structure in the TEM image and the electron diffraction pattern both show that  $\beta$ - $C_2S$  existed in the clinker, while the results of the EDS analysis confirmed that nickel and chromium were incorporated into  $C_2S$  and stabilized it in the  $\beta$  phase.

#### Acknowledgement

The authors gratefully acknowledge the National Science Council, Taiwan for its financial support for this study (Contract No: NSC 96-2221-E-006-032-MY3).

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