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Cement and Concrete Research 35 (2005) 2110 – 2115

Cement and Concrete Research

Reuse of heavy metal-containing sludges in cement production

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Received 4 August 2005; accepted 23 August 2005

Abstract

The feasibility of the replacement of raw material for cement production by heavy metal-containing sludge from surface finishing and electroplating industries was investigated. The effect of heavy metal content in the cement raw mix on the crystalline formation in cement production was also examined by XRD analyses. It was found that both sludges were applicable for the replacement of raw mix for cement production by moderate conditioning of the sludge compositions with several compositional parameters. As the replacement of raw mix by sludge was within 15%, the formation of tricalcium silicate (C_3S) phase in cement would be enhanced by the introduced heavy metals. While owing to a high level of heavy metals concentration (>1.5%) in cement raw mix, C_3S crystalline in cement would be inhibited by a large sludge replacement (>15%). During the sintering process, over 90% of the high volatile elements such as Pb would evaporate in high temperature, yet 90% of the less volatile elements such as Cu, Cr and Ni would be trapped in clinkers. Most of all, the results of leaching test shows that the trapped elements in hydrated samples would not leach out under acidic conditions. The reuse of heavy metal-containing sludges as cement raw material would not cause leaching hazard from sintered clinkers. Heavy metal-containing sludges thus should have the potential to be utilized as alternative raw materials in cement production.

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Keywords: Waste management; Heavy metals; Ca_3SiO_5; X-Ray diffraction

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1. Introduction

Chemical precipitation is the most popular process in wastewater treatment among the available heavy metal removal processes including ion exchange, adsorption, reverse osmosis, membrane filtration and chemical precipitation [1–3]. Generally, the heavy metals are precipitated in alkaline solution to form metal hydroxide sludges. But metals in the sludges may be released under acidic conditions and cause environmental hazards. Consequently, further treatments for the hazardous sludges are needed. Although a number of technologies, including metal recovery and thermal processing, have been developed for treatment of the heavy metal-containing sludges [4–7], most of the treatment processes are either too expensive or not available in this stage. The traditional stabilization/solidification process is hence the Hobson's choice for the small business factories. Nevertheless, a landfill site is needed for the final disposal of the S/S derivatives. Limited by the availability of landfill space, the S/S process becomes more and more expensive. Also, the S/S process always causes a negative effect of waste volume expansion, which is opposite to the reduction strategy in the integrated solid waste management. Therefore, the reuse of metal-containing sludge is a better alternative than the S/S process for the management of heavy metal-containing sludges.

On the other hand, the suitable natural materials for cement production are exhausting in some areas. From the viewpoint of resource recovery and recycling, the use of industrial and other wastes as raw materials for the production of cement is of interest and has been intensely investigated [8–13]. Industrial inorganic wastes such as municipal solid waste incinerator ash, waste gypsum, non-ferrous iron slag, red mud from alumina production plants, low-calcium fly ash and even municipal solid waste have been widely tested as the alternatives to clay, shale, fuel etc. for cement production.

Judging by the inorganic content, heavy metal-containing sludges should also be used as an alternative for cement raw material. Researchers conducted on this topic [14–16] have

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0008-8846/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.cemconres.2005.08.006

mostly focused either on the emission of heavy metals or on the qualitative description of crystalline phases during clinker formation. Nonetheless, from an engineering viewpoint, further quantitative studies on the major crystalline forms (calcium silicates, aluminum silicates) in clinkers are required.

In this study, the use of heavy metal-containing sludges as an alternative raw material for cement production is proposed. Sludges from various industries are sampled and conditioned for cement clinker sintering. The crystalline phases of the resultant cement clinkers are identified by X-ray powder diffraction. Furthermore, the effects of the heavy metal intake on crystalline formation were investigated by semi-quantification of the crystalline phases. To assess the impact of clinker products on the environment, the heavy metals trapped in the clinkers during the sintering process and the leaching toxicity of hydrated clinkers were also tested in the present work.

2. Experimental

2.1. Materials

Two types of heavy metal-containing sludges were collected in this study. The sludges were produced by chemical precipitation of wastewater treatment from a metal surface finishing (SFS) and an electroplating (EPS) industry. Sludge, after dewatering by a filter press, was sampled for the experiments. Water content in the sampled sludge was estimated by drying to constant weight at 105 °C. The surface finishing and electroplating sludge contain 39.8% and 62.9% of moisture, respectively. Then the dried sludge was crushed by a jaw crusher and ground to 74 μm (ASTM 200 mesh) size with a centrifugal ball mill. Chemical compositions of the sludges were analyzed by microwave-assisted digestion followed by inductively coupled plasma spectrometry (ICP-OES, Perkin Elmer Optima 2000). The results of physical and chemical analyses are given in Table 1. Literature [17] suggests that the reactivity of cement raw mix could be increased in the presence of metal oxide. With the abundance of metal contents, the sludges might have potential to be used as the alternative raw material in cement production.

Table 1
Chemical analysis of the sludges

	Chemical composition	Surface finishing sludge	Electroplating sludge
Approximate analysis (%)	Water content	39.8	62.9
	L.O.I.	7.3	12.1
	Ash	52.9	25.0
Metal contents as oxides (%) (dry basis)	CaO	4.1	17.5
	SiO_2	3.9	1.1
	Al_2O_3	0.2	0.2
	Fe_2O_3	65.4	1.1
	MgO	0.7	4.3
Heavy metals (mg/kg) (dry basis)	Zn	237	360
	Ni	714	104,616
	Cu	50,190	22,541
	Pb	51,748	22,811
	Cd	14	ND
	Cr	109	41,585

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

2.2. Cement raw mix preparation

When inorganic waste is to be used as a cement raw mix replacement, our experiences in previous study [8] pointed out that the chemical composition of raw mix is important. A set of compositional parameters in cement chemistry, listed as follows (Eqs. (1)–(4)), should be fulfilled in advance. Typically, the composition parameters of modern cement clinkers are controlled at SR values around 2.0–3.0, AR values around 1.0–4.0, LSF values around 0.92–0.98, and HM values around 2.1–2.4 [18].

$$\text{Lime saturation factor (LSF)} = \frac{\mathrm{CaO}}{2.8\mathrm{SiO_2} + 1.2\mathrm{Al_2O_3} + 0.65\mathrm{Fe_2O_3}} \tag{1}$$

$$\text{Silica ratio (SR)} = \frac{\mathrm{SiO_2}}{(\mathrm{Al_2O_3} + \mathrm{Fe_2O_3})} \tag{2}$$

$$\text{Alumina ratio (AR)} = \frac{\mathrm{Al_2O_3}}{\mathrm{Fe_2O_3}} \tag{3}$$

$$\text{Hydration modulus (HM)} = \frac{\mathrm{CaO}}{\mathrm{SiO_2} + \mathrm{Al_2O_3} + \mathrm{Fe_2O_3}}. \tag{4}$$

Nevertheless, the chemical analysis of the sludges listed in Table 1 shows a significant insufficiency of calcium oxide content in sludges. To formulate the cement raw mixes, analytical grade pure oxides including silicon dioxide (Katayama Chemical, Japan), calcium oxide (Merck, Germany), aluminum oxide (Merck, Germany), and iron oxide (Merck, Germany) were added to the sludges in the fashion that LSF, SR, AR and HM were within the range of modern cement clinkers. With further calculations, the amounts of pure oxides' addition were determined. Compositions of sludges and oxides, and chemical analysis of the raw mixes in this study are shown in Table 2.

Sludges were homogenized with appropriate amounts of pure oxides to form raw mixes. Then raw mixes were pelletized into 20 mm diameter cylindrical pellets at 49 MPa uniaxial compression pressure before sintering. To simulate the calcining process in cement production, the pellets were heated to 900 °C for 1 h with the ramp rate of 30 °C/min in an electric furnace (Nabertherm HT08, Germany), then slowly heated to 1400 °C for 3 h then cooled in the furnace to room temperature. Clinkers were ground to ASTM 200 mesh for future analysis.

2.3. Analysis

Toxicity characteristic leaching procedure (TCLP) was performed according to USEPA Method 1311 [19]. Leachates from TCLP were also analyzed by ICP-OES. The crystalline phases of the materials were analyzed with an X-ray diffractometer (Philip, PE Model 1729) using Cu Kα radiation. Crystalline phases were identified from the International Center

Table 2
Compositions, chemical analysis and modules of the raw mixes from sludges

	OPC	SFSC	EPSC	EPSC70	EPSC35	EPSC15	EPSC10
Compositions (%)							
Dry sludge	–	6.3	93.8	65.6	32.8	14.1	9.4
CaO	–	67.8	0.9	21.4	45.3	59	62.4
SiO_2	–	21	4.4	9.5	15.6	19	19.9
Al_2O_3	–	4.9	1	2.2	3.6	4.4	4.6
Fe_2O_3	–	0	0	1.3	2.7	3.6	3.8
Chemical analysis — oxides (%)							
CaO	63.8	68.1	17.3	32.9	51.0	61.5	64.0
SiO_2	19.8	21.2	5.4	10.2	16.0	19.2	20.0
Al_2O_3	5.0	4.9	1.2	2.3	3.7	4.4	4.6
Fe_2O_3	3.5	4.1	1.0	2.0	3.1	3.8	3.9
MgO	2.1	0.0	4.0	2.8	1.4	0.6	0.4
Chemical analysis — heavy metal (mg/kg)							
Zn	–	13	338	236	118	51	34
Ni	–	45	98,130	68,628	34,314	14,751	9834
Cu	–	3162	21,143	14,787	7393	3178	2119
Pb	–	3260	21,397	14,964	7482	3216	2144
Cd	–	ND	ND	ND	ND	ND	ND
Cr	–	7	39,007	27,280	13,640	5863	3909
Modules							
LSF	1.00	1.00	1.00	1.00	1.00	1.00	1.00
AR	2.33	2.35	2.45	2.35	2.37	2.34	2.35
SR	1.43	1.19	1.15	1.15	1.20	1.18	1.18
HM	2.25	2.25	2.26	2.26	2.25	2.25	2.25

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

for Diffraction Data database (JCPDS-ICDD). The clinkers were mixed with lithium fluoride (15% by weight), homogenized in alcohol by supersonic vibration, and then dried in 60 °C for the XRD analysis of crystalline phases. Peak intensities for the specific crystalline species were then compared with that of lithium fluoride to get relative phase compositions.

3. Results and discussions

3.1. XRD patterns of sintered clinkers

The XRD patterns of the sintered clinkers are shown in Fig. 1 together with the pattern for a commercial ordinary portland cement (OPC). Alite (Ca_3SiO_5), belite (Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_6$) and calcium oxide, the major crystalline phases in OPC (JCPDS-ICDD file numbers 86-0402, 86-0399, 33-0251 and 04-0777), are all presented in the SFS made clinker (SFSC). The major crystalline phase intensities in the SFSC are almost the same as for OPC. The EPS made clinker (EPSC) shows a very different outcome. Most of the major crystalline phases of OPC are absent; and strong peaks due to nickel oxide (NiO, JCPDS-ICDD file number 02-1216), calcium aluminum silicate ($Ca_2Al_2SiO_7$, JCPDS-ICDD file number 35-0755) and calcium magnesium silicate ($Ca_2MgSi_2O_7$, JCPDS-ICDD file number 74-0990) are observed. These results indicate that the controlling of compositional parameters could produce the target crystalline phases in certain circumstance, notably for SFSC. Nevertheless, it is not the case in EPSC; correct compositional parameters did not guarantee a success. Factors other than compositional parameters should be taken into consideration.

Table 2 shows the compositions of sludges and oxides of SFSC and EPSC, respectively. Because iron oxide is the primary component in SFS (Table 1) and considering the compositional effect, a large amount (approximate 67.8%) of calcium oxide was added to this raw mix. The sludge content in the SFSC raw mix is only about 6.3%, and hence the heavy metal concentration in raw mix is relatively low. At low heavy metal concentrations, no influence on the clinker phases is observed. In contrast, the ratios of oxides in EPS are very close to those found in ordinary cement raw mix; and only mild addition of other oxides is required. The sludge content in EPSC raw mix could be up to 93.8%, and the heavy metal concentrations in EPSC raw mix are high. In EPSC raw mix, the concentrations of Ni and Cr are 9.8% and 3.9% (w/w), respectively. Stephan et al. [20] pointed out that heavy metals such as Ni, Cr and Zn have no influence on the formation of clinker phases, even at concentrations that are 10 to 20 times higher than the concentrations observed in normal clinkers. But very high intakes (approximate 2.5%) of heavy metals could cause changes in clinker phases. The concentrations of Ni and Cr in EPSC raw mix are much higher than 2.5% and might be expected to cause adverse effects on the clinker phase formation. Thus, the formation of crystalline phases of C_3S, C_2S, C_3A and C_4AF are hindered, while NiO, $Ca_2Al_2SiO_7$ and $Ca_2MgSi_2O_7$ become the dominant crystalline phases in the EPSC clinker.

3.2. Effect of heavy metals on the clinker structures

Even though the qualitative description of the impact of heavy metal on cement crystalline formation has been widely discussed, little work has been conducted on the tolerable heavy metal concentrations in cement raw mix. To investigate the tolerable heavy metal concentration in raw mix, different percentages of EPS were used for the preparation of raw mixes containing different heavy metal concentrations. EPS were homogenized with calculated amounts of oxides in keeping the

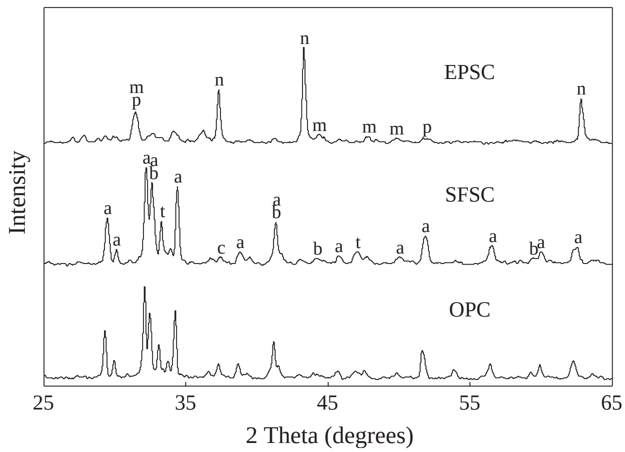

Fig. 1. X-ray powder diffraction patterns of sintered clinkers (EPSC and SFSC) and ordinary portland cement (OPC). a=alite, b=belite, c=calcium oxide, m=calcium magnesium silicate, n=nickel oxide, p=calcium aluminium silicate, t=tricalcium aluminate.

compositional parameters unchanged as listed in Table 2. XRD patterns of the sintered clinkers are shown in Fig. 2. With small replacement percentage of sludge (EPSC10 and EPSC15), the XRD patterns are almost the same as commercial OPC. The major crystalline phases seem to be unaffected by the heavy metals present in the raw mix. When the sludge replacement percentages of raw mix increase beyond 35% (EPSC35 and EPSC70), the XRD pattern is significantly different. Nickel oxide, calcium aluminum silicate, and calcium magnesium silicate gradually dominate the crystalline phases in clinkers.

Though XRD patterns provide a qualitative description of the crystalline phases, in the effort to investigate the threshold of heavy metal addition for cement production, a quantitative description of phases from XRD pattern is needed. The quantification method conducted in this study could be described as following equations. In theory, if there are N crystalline phases present in a mixture, the XRD peak intensity of a specific crystalline phase m in a mixture could be written as (Eq. (5)).

$$I_\mathrm{m} = \frac{K_\mathrm{m} v_\mathrm{m}}{\bar{\mu}} \tag{5}$$

I_m is the peak intensity of the crystalline phase m, K_m is a coefficient that depends on the nature of the crystalline phase m (structure parameters of crystalline phase) and on working condition (geometry and operation of apparatus), v_m is the volume fraction of crystalline phase m in mixture. $\bar{\mu}$ is the average linear absorption coefficient that could be obtained from the volume fraction and the X-ray absorption coefficient of crystalline phases present in the mixture as (Eq. (6)).

$$\bar{\mu} = \frac{\sum_{j=1}^{N} \mu_j v_j}{\sum_{j=1}^{N} v_j} = \frac{\sum_{j=1}^{N} \mu_j \left(x_j/\rho_j\right)}{\sum_{j=1}^{N} \left(x_j/\rho_j\right)} = \frac{\sum_{j=1}^{N} x_j \mu_j^*}{\sum_{j=1}^{N} \left(x_j/\rho_j\right)} \tag{6}$$

μ_m^* is the mass adsorption coefficient of individual mineral m. The relationship between volume fraction v_m and mass fraction x_m could be calculated with the density (ρ_m) of crystalline phase m, as presented in (Eq. (7)).

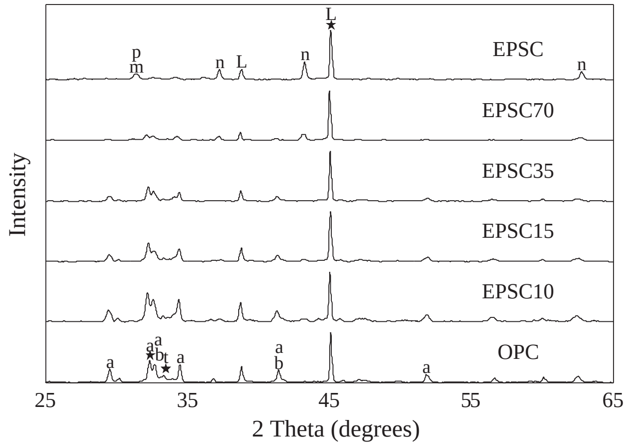

Fig. 2. X-ray powder diffraction patterns of sintered clinkers with different sludge replacement. a=alite, b=belite, L=lithium fluoride, m=calcium magnesium silicate, n=nickel oxide, p= calcium aluminium silicate, t=tricalcium aluminate. ★Peaks selected for semiquantification analysis.

$$v_\mathrm{m} = \frac{x_\mathrm{m}/\rho_\mathrm{m}}{\sum_{j=1}^{N} \left(x_j/\rho_j\right)} \tag{7}$$

Therefore, the peak intensity of crystalline phase m, by substituting (Eqs. (6)) and (Eqs. (7)) into (Eq. (5)) gives (Eq. (8)).

$$I_\mathrm{m} = K_\mathrm{m} \frac{x_\mathrm{m}/\rho_\mathrm{m}}{\sum_{j=1}^{N} x_j \mu_j^*} = \frac{K_\mathrm{m} x_\mathrm{m}}{\rho_\mathrm{m} \overline{\mu^*}} \tag{8}$$

$\overline{\mu^*}$ represents the average mass absorption coefficient that depends on the mixture, and could be calculated by multiplying the mass fraction by the X-ray mass absorption coefficient of each crystalline content present in the mixture.

To acquire quantification result from the intensity data, all crystalline phases present in the mixture should be identified for the calculation of $\overline{\mu^*}$, in which case, it is almost impossible for environmental samples with multiple crystalline phases. Therefore, internal standard method was used in this study. Since aluminum oxide is added to the raw mix for the composition adjustment, to avoid the possible interference by the unreacted aluminum oxide on the XRD pattern analysis, lithium fluoride is selected instead of corundum as internal standard. In this method a diffraction line from the phase being determined is compared with a line from a standard analytical grade lithium fluoride (Merck, Germany) mixed with the sample in 15% (w/w). In a mixture, the peak intensity of lithium fluoride (I_l) and phase being identified (I_m) could be presented based on (Eq. (8)),

$$I_\mathrm{l} = \frac{K_\mathrm{l} x_\mathrm{l}}{\rho_\mathrm{l} \overline{\mu^*}}$$

$$I_\mathrm{m} = \frac{K_\mathrm{m} x_\mathrm{m}}{\rho_\mathrm{m} \overline{\mu^*}} \tag{9}$$

Mass fraction x_m of crystalline phase m could be calculated by dividing these two equations in (Eq. (9)),

$$x_\mathrm{m} = x_\mathrm{l} \times \frac{I_\mathrm{m}}{I_\mathrm{l}} \times \frac{K_\mathrm{l} \rho_\mathrm{m}}{K_\mathrm{m} \rho_\mathrm{l}} = x_\mathrm{l} K^* (I_\mathrm{m}/I_\mathrm{l}) \tag{10}$$

K^* depends on the density, the crystalline parameters of these two phases and the working condition of the apparatus. Assuming that same proportion of lithium fluoride were added into the sintered clinker, and that the mixtures were analyzed under the same equipment and working condition, the K^* between mixtures could be canceled out. The change on the amount of crystalline could be simply calculated by the measured intensities.

$$\frac{x_\mathrm{m2}}{x_\mathrm{m1}} = \frac{x_\mathrm{l} K^* (I_\mathrm{m2}/I_\mathrm{l2})}{x_\mathrm{l} K^* (I_\mathrm{m1}/I_\mathrm{l1})} = \frac{(I_\mathrm{m2}/I_\mathrm{l2})}{(I_\mathrm{m1}/I_\mathrm{l1})}. \tag{11}$$

In this study, the d-spaces selected for lithium fluoride, C_3S and C_3A were 2.01, 2.78 and 2.69 Å, respectively. Dividing the relative intensity to reference (I_{m2}/I_{l2}) in clinker by the relative intensity to reference (I_{m1}/I_{l1}) in the commercial OPC individually, a description of crystalline amount is then obtained by (Eq. (11)). Fig. 3 shows both the relative crystalline amount of C_3S and C_3A in the cement clinkers with different sludge replacement levels. Small percentage of sludge in raw mix might improve the crystalline formation of C_3S. For instance, a positive contribution to C_3S formation was observed in EPSC10 by the increasing relative amounts of C_3S to 139%. But the C_3S formation is inhibited as the replacement percentage increases beyond 15%, and the relative amounts of C_3S show a decline trend. In the range of 70~100% replacement, no C_3S could be observed. The relative amounts of C_3A show a similar result. As replacement percentage increases, the formation of C_3A reduces. To summarize, 10~15% of sludge replacement and heavy metal concentration under 1.5% seem to be an adequate replacement percentage.

These results are consistent with the study conducted by Kolovos et al. [17], who concluded that 1% (w/w) of foreign cations like Cu, Pb and Ni could have positive or marginal effect on the reactivity of $CaO-SiO_2-Al_2O_3-Fe_2O_3$ mixtures. In this study, the heavy metal concentrations are 0.98%, 0.21%, 0.21% and 0.39% for Ni, Cu, Pb and Cr in the EPSC10 raw mix. The enhancement of C_3S formation by the trace amounts of heavy metals was observed at the low heavy metal content.

Nevertheless, as the replacement percentage increases to 15% or above, the concentrations of Ni and Cr in the raw mix is higher than 1%. Researchers [21,22] pointed that low addition of Ni and Cr might only cause a transformation of C_3S from the T_1 to T_2 polymorph in C_3S system. When the addition of Ni is more than 2.5%, no further change in the XRD patterns is detectable. But when the addition of Cr is more than 2.5%, some of the C_3S is decomposed into C_2S and C. In C_3A system, new compounds such as $Ca_4Al_6O_{12}CrO_4$ and $Ca_6Al_4Cr_2O_{15}$ could be identified. NiO could be found due to high intakes in raw material. The results of this study are consistent with the observation mentioned above. The high Ni and Cr contents could be incorporated into the clinkers, and the incorporated heavy metals might cause the transformation of C_3S polymorph, the decomposition of C_3S or the formation of new compounds. Large addition of heavy metal concentration is identified to have adverse effect on the quantity of crystalline phases. However, due to the complication of heavy metal species, the form of interference on the crystalline phases is still unknown.

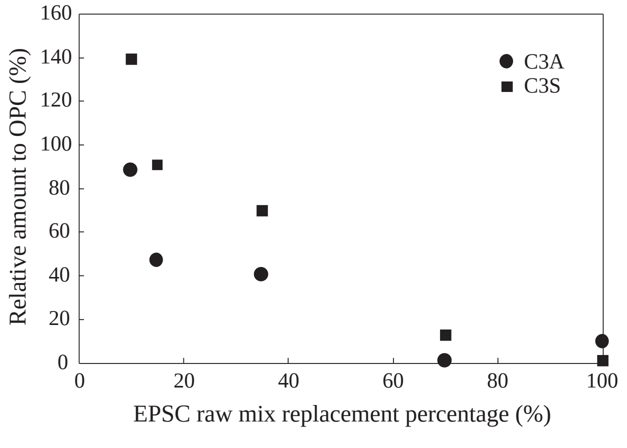

Fig. 3. Relative amounts of crystalline phases in clinkers compared with different EPSC raw mix replacement percentage.

Table 3
Determined heavy metal concentrations in clinkers (mg/kg)

	SFSC	EPSC	EPSC70	EPSC35	EPSC15	EPSC10
Zn	ND	ND	ND	ND	ND	ND
Ni	45	135,442	80,198	35,292	14,644	10,321
Cu	2799	31,317	16,321	7093	2858	1889
Pb	104	142	225	123	114	118
Cd	ND	ND	ND	ND	ND	ND
Cr	ND	41,460	29,807	14,613	5757	3883

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

3.3. Evaporations during sintering and toxicity leaching characteristics of heavy metals

The determined heavy metal concentrations in clinkers were measured after each burning as listed in Table 3. On account of the weight loss on ignitions of raw mixes, heavy metals are concentrated in clinkers. Hence the heavy metal concentrations in clinkers are higher than those in raw materials. With mass balance by weight losses, 90% of the highly volatile elements (Pb) evaporated at high temperature during the burning process. Meanwhile, 90% of the Ni, Cr and Cu were trapped in the clinkers. These results are in agreement with the study concerning the volatility of minor elements during the burning process of cement raw material [17]. The foreign cations could be divided in to three groups, high volatile (<20% remained in clinker, like Pb), moderate volatile (like Ni and Cr), and low volatile (almost 100% remained in clinkers, like Cu). Nevertheless, as the authors specifically pointed out in the paper, the high retention of the moderately volatile elements might be due to the batch thermal operation in the study. In practical rotary

Table 4
Concentrations of heavy metals in TCLP leachates from hydrated samples

Curing age	Species	SSC	10ESC	15ESC
3 day	Zn	ND	ND	ND
	Ni	ND	ND	ND
	Cu	ND	ND	ND
	Pb	ND	ND	ND
	Cd	ND	ND	ND
	Cr	ND	0.17	0.7
7 day	Zn	ND	ND	ND
	Ni	ND	ND	ND
	Cu	ND	ND	ND
	Pb	ND	ND	ND
	Cd	ND	ND	ND
	Cr	ND	0.40	0.64
28 day	Zn	ND	ND	ND
	Ni	ND	ND	ND
	Cu	ND	ND	ND
	Pb	ND	ND	ND
	Cd	ND	ND	ND
	Cr	ND	0.55	0.60

ND: Not detected (<0.01 ppm).

kiln operations, heavy metals might be affected by composition of raw meal, burning conditions and atmosphere during the burning process that are not considered in this study.

The heavy metals incorporated into the clinkers might be leached in an acidic environment. To investigate this possibility, toxicity characteristic leaching procedure (TCLP) was performed on hydrated samples at different curing ages. The samples selected were SFSC, EPSC10 and EPSC15, which match the criteria that the relative amount of C_3S is higher than 75% w/w. The results of TCLP in Table 4 show that, among all the investigated elements, only Cr can be detected in the leachates of TCLP at all curing ages. Importantly, the concentration of Cr is still far below the regulatory standard (5 ppm). It can be concluded that the hydrated samples present no immediate threat to environment.

To be noticed, the retained heavy metals, Ni, Cr and Cu are in relative high level (e.g. 10 321, 3883 and 1889 mg/kg in EPSC10 clinker) compared with the ordinary cement clinkers. Researchers [23] reported the hydration behaviors of clinkers produced from raw mixes doped with 200 to 25 000 mg/kg of heavy metals. Low heavy metal concentrations have no influence on the hydration behavior of the cement. Nevertheless, very high intakes of heavy metals could cause changes in hydration properties. For instance, Cr would accelerate the hydration and hence the shorter initial setting time. Ni would have only little influence on the hydration properties, the developed strength and setting time is almost the same with control. In our research, the heavy metal concentrations in EPSC10 and SFSC are far below the reported concentrations. Little influence should be observed. For the feasibility study, however, further tests on the physical properties of the produced clinkers should be taken. Limited by the scope of this study, the influence of heavy metals on the produced crystalline structure is discussed instead of the physical properties of produced clinkers.

4. Conclusion

In this study, it was found to be feasible to use heavy metal-containing sludges as alternative cement raw materials. By controlling the compositional parameters (lime saturation factor, silica ratio, alumina ratio, and hydration modulus) in the range of modern cement, the replacement could be taken up to 15% of sludge in the cement raw mix in this study. The effect of heavy metals on the formation of the crystalline phases in the cement clinker was also examined. At low levels of sludge replacement, the heavy metals carried by the sludge would have the positive contribution to the phase formation in cement clinker. However, if too high of heavy metal concentration (>1.5%) was present in the raw mix, an adverse effect on cement production was observed. Low volatile heavy metals such as Ni, Cr, and Cu in the sludge were almost totally trapped in the clinker, and once trapped these did not present a leaching hazard to environment. Reuse of heavy metal-containing sludge as alternative cement raw material could be a promising alternative for the management of waste sludges.

Acknowledgement

The authors express their gratitude to the National Science Council, Taiwan (Contract No: NSC 91-2211-E-006-062) for its financial supports.

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