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Original Research

Role of Municipal Sewage Sludge in Incorporating Cr, Ni, Cu, and Zn into Cement Clinker

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Abstract

While simultaneous processing of heavy metal-rich waste and municipal sewage sludge (MSS) in cement kilns may be a useful measure for protecting the environment, simultaneous co-disposal of these two types of wastes has seldom been reported in detail. In this study, we examined how MSS influenced the fixation of heavy metals during clinkerization and determined the main controlling mechanisms through analyzing the polymorphism of tricalcium silicate (C_3S), mineral composition of MSS, and element distribution in the clinker. The results showed that MSS had negative effects on the fixation of heavy metals, with reductions of 12.9%, 8.7%, 3.2%, and 1.2% in the amounts of Cu, Ni, Cr, and Zn fixed, respectively. These changes were mainly attributed to the presence of trace elements – in particular phosphorus from the MSS, which caused the polymorphism of C_3S to change in the order: rhombohed ral→monoclinic→triclinic. As well as occurring as C_2S-C_3P, phosphorus also occurred in new phases of $K_2NiP_2O_7$, $K_2Cu(PO_3)_4$, and $Cu_4O(PO_4)_2$ in cement clinker. In general, trace elements from the MSS, especially phosphorus, decreased the solubility of heavy metals in cement clinker through changing the polymorphism of C3S, and resulting in a decrease in the fixation ratios of heavy metals.

Keywords: heavy metals-rich waste, municipal sewage sludge, co-processing, cement kiln, polymorphism

Introduction

Processes carried out in cement kilns have various fundamental characteristics, namely high temperatures and long residence times, good turbulence and mixing conditions, and no generation of such by-products as slag, ashes, or liquid residues [1-2]. These characteristics mean that cement kilns are suitable for the co-disposal of industrial wastes, including heavy metal-rich wastes that frequently contain Cr, Ni, Cu, and Zn [3-5]. The co-disposal approach for industrial wastes in cement kilns has been widely and successfully used in the United States, Europe, Japan, and other developed countries for several decades and, in recent years, has also been widely used in China [6]. Furthermore, the characteristics of the cement kiln process also mean that co-processing is a sustainable disposal option for municipal sewage sludge (MSS) [7-8]. At present, MSS is produced at a rate of about 600

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million tons of dry sludge (DS) per year in China [9], and production is predicted to reach 1,200 Mt DS/y by 2020. In an attempt to solve this huge and environmentally sensitive problem, MSS has been co-processed in cement kilns in China since 2008.

Various policies and national standards have been introduced to encourage and support co-processing of wastes containing heavy metals and MSS in China, such as the code of design for industrial waste co-composition in cement kilns (GB 50634-2010) [10] and the code of design for sludge co-processing in cement kilns (GB 50757-2012) [11]. Numerous studies have examined the effects of heavy metals or MSS on cement clinkerization. The main components of common Portland cement clinker are C_3S ($3CaO·SiO_2$, 60 wt.%), C_2S ($2CaO·SiO_2$, 20 wt.%), and interstitial material that includes C_3A($3CaO·Al_2O_3$), C_4AF ($4CaO·Al_2O_3·Fe_2O_3$), free CaO, and metal-rich compounds [12-13]. It has been reported that Portland cement clinker can trap and incorporate about 84% of chromium in interstitial materials [14]. Chromium compounds such as $Ca_6Al_4Cr_2O_{15}$, $Ca_5Cr_3O_{12}$, $Ca_5Cr_2SiO_{12}$, and $CaCr_2O_7$, with chromium oxidation states of +3, +4.6, +5, and +6, respectively, are commonly found in modern clinker [15-16]. Ni mainly combines with Mg in the form of $MgNiO_2$ at a distribution ratio of 61.2%, and is also present in C_3S and C_4AF at distribution ratios of 24.9% and 10.3%, respectively [17]. Other studies have shown that CuO can promote the consumption of CaO, accelerate the formation and growth of C_3S, and transform C_3S from rhombohedral to monoclinic [18]. These effects of CuO were mainly attributed to the quantity and properties of the liquid phase, namely formation temperature, quantity, and viscosity [18-19]. It was reported that ZnO caused the formation of C_3A to decrease sharply and formed new compounds of $Ca_6Zn_3Al_4O_{15}$ and $Ca_3ZnAl_4O_{10}$ [20-21]. In addition, many studies have reported the effects of MSS on cement clinkerization [22-24]. For example, the contents of the major components of clinker that contained MSS were reported to be similar to those in ordinary Portland cement, but the C_2S content was slightly higher because of phosphorus from MSS [24].

However, while policies, national standards, and previous research may have considered the effects of heavy metals or MSS on cement clinkerization, they have not considered the simultaneous co-disposal of wastes containing heavy metals and MSS. Actually, many cement works, including cement plants in Beijing and Guangzhou, have production lines that co-process the two kinds of waste at the same time [25]. Therefore, the effects of MSS on the disposal of heavy metal-containing waste during cement clinkerization need to be clarified. To enable optimization of the simultaneous co-disposal process, further studies of the mechanisms are also needed.

In this study, we determined the effects of MSS on heavy metal fixation ratios and on the cement clinker crystalline phases by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and x-ray diffraction (XRD). We also considered the mechanisms that influenced the fixation ratios of heavy metals through an examination of the polymorphism of C_3S, the mineral composition of MSS, and the distribution of elements in interstitial material.

Materials and Methods

Materials

We obtained raw meal (RM) cement from a cement plant in Beijing. We collected MSS samples from a municipal wastewater treatment plant in Beijing that used the anaerobic-anoxic-oxic process to remove nitrogen and phosphorus from the wastewater. The chemical compositions of the RM and MSS are shown in Table 1.

Preparation of Clinkers

The composition of Chinese cement clinkers are typically controlled at silica ratios (SM, $SiO_2/(Al_2O_3+Fe_2O_3)$) of around 1.70-2.70, alumina ratios (IM, Al_2O_3/Fe_2O_3) of approximately 0.90-1.90, and lime saturation (KH, $(CaO-1.65Al_2O_3-0.35Fe_2O_3)/2.80SiO_2$) values of approximately 0.85-0.96 [26-27]. In this study, the ratios of the three compositional parameters, SM, IM, and KH, were maintained at 1.82, 1.23, and 0.87, respectively. In the reference samples, different amounts of heavy metals (Cr_2O_3 2%, NiO 1.5%, CuO 2 wt%, and ZnO 1.5%) were homogenized with RM to simulate co-processing of waste containing heavy metals in a cement kiln. In the experimental samples, 9 wt% of both MSS and heavy metals were mixed with RM to simulate the combined co-processing of MSS and heavy metal-containing wastes. To ensure that the three compositional parameters would not be changed by MSS, 2.6 wt% of SiO_2 (AR), 2.35 wt% of Al_2O_3 (AR), 2.4 wt% of CaO (AR), and 1.05 wt% Fe_2O_3 (AR) were added to the raw mixtures of the experimental samples. The raw mixtures of the above two groups were prepared with deionized water, put into cylindrical molds, and pressed into 40×5 mm slices by applying a pressure of 30 MPa. To form clinkers, the slices were then heated in a furnace to 1,450ºC at a rate of 10ºC/min, after which they were held for 1 h in the furnace, and then cooled to room temperature.

Table 1. Major chemical properties and heavy metal concentrations of RM and MSS.

Sample names	Chemical compositions (%)				
	LOI[a]	SiO_2	Al_2O_3	Fe_2O_3	CaO
RM	28.78	14.30	2.68	2.48	47.60
MSS	38.93	6.80	3.10	8.60	30.50
Sample names	MgO	P_2O_5	SO_3	Na_2O	K_2O
RM	2.72	N.D.	0.30	N.D.	0.54
MSS	1.20	3.3	4.3	0.17	0.49

[a]. LOI: Loss on ignition at 1,000ºC.

Sample Analysis

Chemical Composition of MSS, RM, and Clinkers

The chemical composition of pre-treated vacuum freeze-dried MSS, RM, and clinker samples were confirmed with a wavelength dispersion x-ray fluorescence spectrometer (XRF; PW2404, Philips, Amsterdam, NL).

Heavy Metal Concentrations in Raw Mixtures and Clinkers

Approximately 0.2000 g of the mortar sample was accurately weighed into a 100 ml Teflon beaker, to which 1.5 ml of concentrated hydrogen peroxide (30% H_2O_2) and 20 ml of aqua regia (HNO_3: HCl = 1:3) were then added. Samples were microwave-digested (Milestone ETHOS1) at 200ºC for 30 min. The solution was then cooled to room temperature, filtered, diluted with deionized water, and acidified to pH 4 with HNO_3 in a 100 ml flask. The element concentrations in the solutions were determined by ICP-AES (Agilent 720ES, National Instruments, USA).

Major Phases in Clinkers

Clinker crystalline phases were identified with a diffractometer (D8-Advance, Bruker Optics, Germany), with a two-theta range from 25° to 65° in 0.02° steps, and a step-length of 4 s. The radiation source was Cu Ka at a wavelength of 0.1541 nm (40 kV).

Element Distributions in Clinkers

A field emission scanning electron microscope coupled with an energy-dispersive x-ray spectrometer (JSM-7800 FPRIME, JEOL, Japan) was used to obtain detailed observations of the morphology and element distribution of the clinkers [28].

Results

Effects of MSS on Heavy Metal Fixing Ratios

We used the heavy metal concentrations in the raw mixtures and clinkers to calculate the fixation ratios, as shown in Eq. (1):

$$Fixation\ ration_i = \frac{K_i}{S_i}(1 - LOI) \quad (1)$$

…where i refers to the heavy metal species; and K and S are the heavy metal concentrations in the clinkers and raw mixtures, respectively.

Table 2. Fixation ratios of different heavy metals (with and without MSS).

Items	Cr	Ni	Cu	Zn
Samples without MSS	93.5	98.9	87.1	77.4
Samples incorporated MSS	90.3	90.2	74.2	76.2
Amounts of reduction (%)	3.2	8.7	12.9	1.2

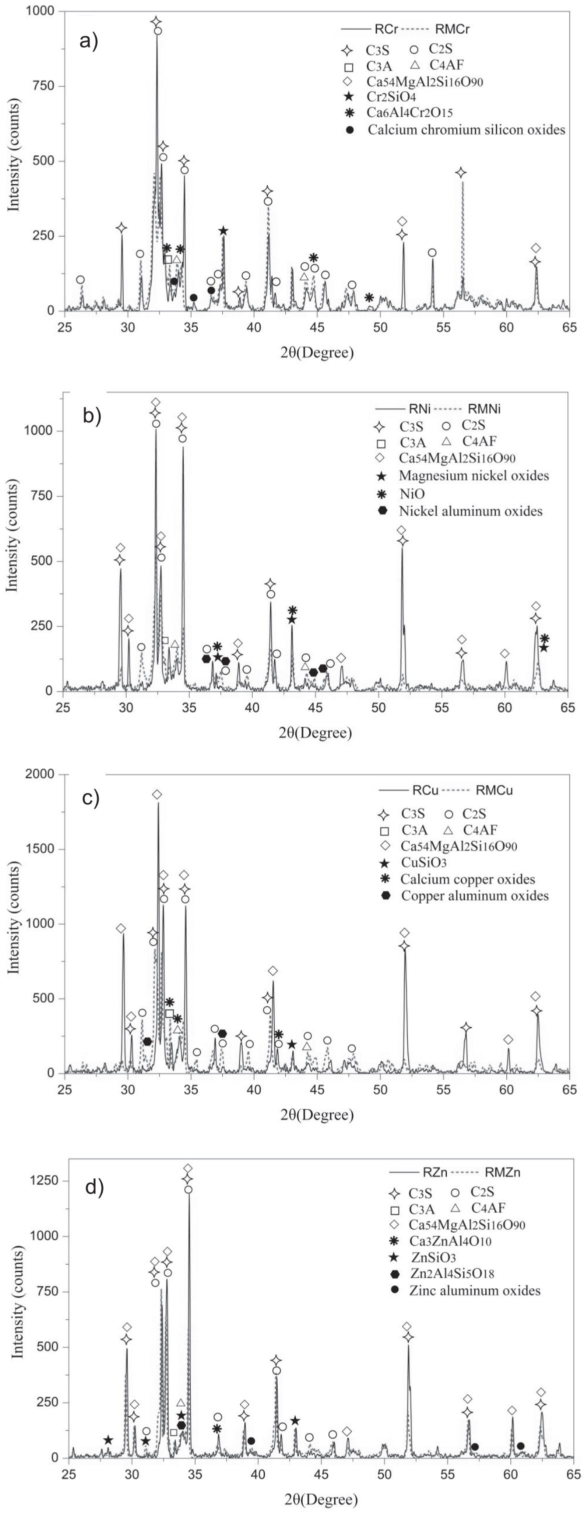


Fig. 1. XRD patterns of clinkers sintered with different types of heavy metals with and without MSS.

Table 3. Major metal-containing phases and substitution patterns of different clinkers.

Samples names	Metal-containing minor phases	Substitution pattern
RCr	Cr_2SiO_4	Cr→Ca
RMCr	$Ca_6Al_4Cr_2O_{15}$, $Ca_3Cr_2Si_3O_{12}$ $Ca_5Cr_2SiO_{12}$	Cr→Ca/Si
RNi	$MgNiO_2$, $Mg_{0.4}Ni_{0.6}O$	Ni-Mg compound
RMNi	$MgNiO_2$, $NiAlO_4$, $Ni_2Al_{18}O_{29}$, $NiAl_{32}O_{49}$	Ni-Mg and Ni-Al compounds
RCu	$CuSiO_3$, $CaCuO_2$, $CaCu_2O_3$, $CaCu_7O$	Cu→Ca
RMCu	$CaCuO_2$, $CaCu_2O_3$, $CaCu_7O$, CuA_1O2	Cu→Ca, Cu-Al compounds
RZn	$Ca_3ZnAl_4O_{10}$, $ZnSiO_3$	Zn→Ca
RMZn	$Zn_2Al_4Si_5O_{18}$, $Zn_4Al_{22}O_{37}$, $Zn_3Al_{94}O_{144}$	Zn→Ca, Zn-Al compounds

The calculated results are shown in Table 2**.** Without MSS, clinkerization effectively immobilized Cr, Ni, Cu, and Zn. After adding MSS, however, the fixing ratios of Cr, Ni, Cu, and Zn decreased by different degrees; for example, the fixation ratio of Cu decreased from 87.1% to 74.2% after MSS was introduced.

Effects of MSS on Crystalline Phases of Cement Clinkers

Changes in the crystalline phases of cement clinkers were detected by XRD. Major phases, such as C_3S and C_2S, and interstitial phases, such as metal silicate and aluminum oxides, are shown in the XRD patterns in Fig. 1.

As shown in Fig. 1, additions of MSS had a remarkable influence on the major crystalline phases of clinker that contained Cu and Ni. The comparative intensities of C_3S at 29.2°, 51.7°, 56.5°, 60.09°, and 62.46° almost disappeared when MSS was added. Correspondingly, the comparative intensities of Cr and Zn that contained clinkers also decreased after adding MSS, but by relatively small amplitudes. The changes in the amplitudes in the XRD pattern are consistent with the changes in the fixation ratios shown in Table 2, which indicates that the fixation of heavy metals during clinkerization was closely related to the polymorphs of the major clinker crystalline phases [18, 29-30].

Introductions of MSS also impacted the species of interstitial material in clinker, and, in particular, on metal-containing phases. The metal-containing phases in each clinker sample and the substitution patterns for each metal from the XRD pattern shown in Fig. 1 are summarized in Table 3. The heavy metal-containing phase in the reference clinkers (without MSS) was similar to those reported in existing studies [17, 20]; for example, Ni mainly combined with Mg to form $MgNiO_2$ and Cu mainly formed $CaCuO_2$. In the experimental samples that contained MSS, metal-containing phases not only existed in the above forms but also as new metal-Al compounds, such as nickel aluminum oxides, copper aluminum oxides, and zinc aluminum oxides, which was consistent with the results reported by Yuanyuan Tang et al. [31].

Discussion

Mechanisms that Determined Heavy Metal Fixation in Cement Clinker

During cement clinker calcination, it is impossible to avoid impacts on the structure of the crystals in the crystalline phases. This characteristic of crystal chemical means that clinker lattices can accept impure ions. Therefore, heavy metals can become fixed in the clinker by substitution with either Ca or Si to form a solid (isomorphous replacement) or by interring the space of the lattice (interstitial solid solution).

As one of the principal components of Portland cement clinker, C_3S has seven polymorphs, including three triclinic (T_1, T_2, and T_3), three monoclinic (M_1, M_2, and M_3), and a rhombohedral R. These modifications appear in this order, via successive phase transformations, when heated:

$$T_1 \xleftrightarrow{620^oC} T_2 \xleftrightarrow{920^oC} T_3 \xleftrightarrow{980^oC} M_1 \xleftrightarrow{990^oC} M_2 \xleftrightarrow{1060^oC} M_3 \xleftrightarrow{1070^oC} \mathrm{R}$$

At room temperature, pure C_3S only exists in the T_1 form. The other six modifications are stable only at higher temperatures or as solid solutions with stabilizing foreign oxides. Common foreign oxides are Cr_2O_3, NiO, CuO,

Table 4. Relationships between C_3S polymorphs and metal oxide contents.

Metal oxides	Polymorphism of C_3S	Percentage of oxides	Specimen	Author
Cr_2O_3	M_1	4-5.0%	Pure C_3S	N.K. Katyal et al. [29]
	T_2	1-2.0%		
	T_1	0-0.5%		
NiO	T_2	2.5%	Pure C_3S	D. Stephan et al. [33]
	T_1+T_2	0.02-0.05%		
CuO	M_2	3%	$CaCO_3$ and SiO_2	Wang Peiming et al. [32]
	T_2	1-2%		
ZnO	R	1.5-1.6%	Clinker	Ivan Odler et al. [34]
	M_1+M_2	1.2%		
	T_2	0.4-1.0%		
	T_1	0-0.3%		

and ZnO. The percentages of these oxides are directly related to the metastability and polymorphism of C_3S [18, 32]. Conversely, the C_3S polymorph of the heavy metal-containing clinker can reflect the solid solubility of the metal. The relationships between the C_3S polymorph and metal oxide contents reported in previous studies are shown in Table 4 [29, 32-34]; these studies report decreases in the solubility of C_3S in the order: rhombohedral C3S > monoclinic C3S > triclinic C3S. Therefore, by analyzing C_3S polymorphism in clinker samples, we can obtain information on the amounts of heavy metals that are incorporated in C_3S.

Effects of Municipal Sewage Sludge on Polymorphism of Tricalcium Silicate (C3S)

As discussed in section 4.1, polymorphism of C_3S in clinker can reflect the amount of heavy metals that are incorporated in C_3S. Furthermore, the peaks that appear between 32° and 33° and also between 51° and 52° in the XRD patterns of the C_3S polymorphs are good indicators of the polymorph symmetries [35-36]. Because the reflections in each group are equivalent in R, a non-splitting peak appears in each range. When the R cell is distorted to form a monoclinic subcell, the peak in these ranges split into doublets. The triclinic modifications have a triclinic subcell, which gives triplet peaks in those ranges [32]. We carried out a detailed examination of the XRD peaks from 32-33° and 51-52° in Fig. 2.

As shown in Fig. 2a), non-smooth doublet peaks observed at 32-33° and 51-52° appear almost as one smooth peak. This shows that C_3S polymorphs in RCr are mainly composed of M_2. After introducing MSS (Fig. 2b), both the peaks of 32-33° and 51-52° become triplets. Moreover, the intensity of 51-52° diffraction peaks becomes weak. These indicate that the C_3S polymorph of RMCr is mainly T_2. For the Ni-contained clinkers, the XRD pattern of RNi (Fig. 2c) shows doublet peak at 32-33°, and 2θ of

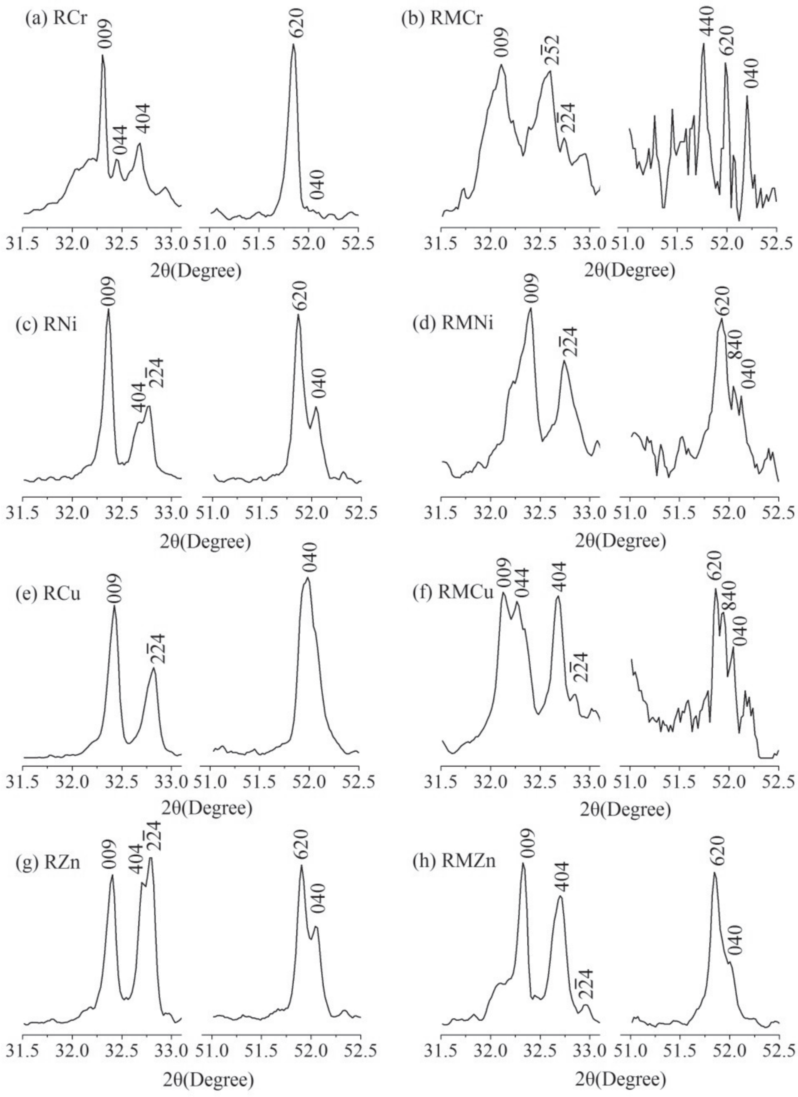


Fig. 2. Details of the XRD peaks that appeared from 32-33° and from 51-52° of different samples; (a-b) Cr: $M_2 \rightarrow T_2$; (c-d) Ni:$M_3 \rightarrow T_3$; (e-f) Cu:R$\rightarrow T_2$; and (g-h) Zn: $M_3 \rightarrow M_2$.

Table 5. Trace element oxide concentrations in different clinker samples (wt.%).

Sample names		Polymorphism of C_3S	Trace element oxides						
			P_2O_5	SO_3	Na_2O	K_2O	MgO	TiO_2	MnO
Clinker samples without MSS	RCr	M2	0.10	0.16	0.22	0.13	4.25	0.38	0.09
	RNi	M3	0.12	0.12	0.14	0.14	2.46	0.34	0.10
	RCu	R	0.13	0.15	0.13	0.08	3.27	0.37	0.11
	RZn	M3	0.12	0.11	0.11	0.11	3.03	0.32	0.10
Clinker samples with MSS	RMCr	T2	0.46	0.39	0.25	0.17	4.62	0.46	0.11
	RMNi	T3	0.46	0.31	0.25	0.19	2.46	0.37	0.16
	RMCu	T2	0.46	0.35	0.18	0.10	3.39	0.38	0.12
	RMZn	M2	0.48	0.18	0.15	0.14	3.12	0.44	0.11

51-52° also appears as a smooth doublet peak. However, after adding sludge, a small diffraction peak is added at 33° (Fig. 2d), the peaks at 32-33° changed into triplets. These indicate that the RNi sample is mainly composed of M_3, whereas the C_3S polymorph of RMNi is close to T_3. For the sample RCu (Fig. 2e), smooth doublet peaks are observed at 32-33° and 51-52°, which also appear as one smooth peak, which shows typical characteristic of R. After introducing MSS, the splitting of peaks at 32-33° is triplets and peaks around 57.1°, and also changed into triplets as shown in Fig. 2f). These indicate that RMCu is mainly composed of T_2. In addition, the C_3S peaks of RZn (Fig. 2g) are similar to RNi, which are close to the type of M_3. After adding MSS, the C_3S polymorph of RMZn (Fig. 2h) changed obviously. 32-33° appears as triplet peaks and 51-52° is almost a singlet, indicating that the C_3S solid solution is mainly composed of M_2 in the sample of RMZn.

Generally speaking, C_3S existed in monoclinic or rhombohedral form in reference clinker samples, which is consistent with previous studies (Table 4). However, MSS changed the polymorphism of C_3S, and tended to change from rhombohedral to monoclinic and then to triclinic; for example, the C_3S polymorph changed from rhombohedral to T_2 in samples that contained Cu, and from M_3 to T_3 in samples that contained Ni. These changes indicate that C_3S tended to exist in low-temperature polymorphs because of the MSS, and that MSS caused the solubility of heavy metals in clinker to decrease.

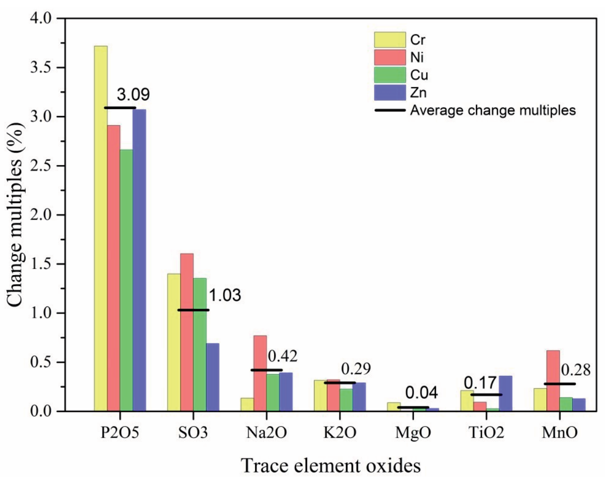


Fig. 3. Change multiples of trace elements between experiment clinkers and reference clinkers.

Impact Analysis of Municipal Sewage Sludge on Incorporating Cr, Ni, Cu, and Zn

There were no changes in SM, IM, or KH, so the effects of CaO, SiO_2, Al_2O_3, and Fe_2O_3 can be ignored. The influences caused by MSS were most likely attributed to the trace elements from MSS.

Firstly, trace element concentrations in the two clinker groups were detected by XRF, as shown in Table 5.

The concentrations of all trace elements increased after introducing MSS (Table 5). To determine which trace element changed the polymorphism of C_3S, element change multiples between reference clinkers and experimental clinkers were calculated (Eq. 2) and the results are shown in Fig. 3:

$$\text{Change multiple}_j = \frac{A_j}{B_j} - 1 \quad (2)$$

…where *j* is the trace element, *Aj* is the concentration of *j*-oxides in the experiment clinkers (with MSS), and *Bj* is the concentration of *j*-oxides in the reference clinkers (without MSS).

The results in Fig. 3 clearly demonstrate that trace elements were more abundant in clinker that contained MSS. As shown in Fig. 3, the P_2O_5 concentration increased the most after adding MSS (showing an increase of 3.09 times), followed by SO_3 (an increase of 3.09 times). The trace element irons can replace Ca^{2+} or Si^{4+} of C_3S. Due to their different ionic radius, electrovalence, and electronegativity, lattice imperfections could be generated during the replacement process. Furthermore,

Table 6. Phosphorus-containing compounds in different clinker samples.

Phosphorus-containing compounds*	Clinkers without MSS				Clinkers with MSS			
	RCr	RNi	RCu	RZn	RMCr	RMNi	RMCu	RMZn
$Ca_2P_2O_7$	√	√	√		√		√	√
$RCaPO_4$	√	√	√	√	√			√
$Fe(PO_3)_2$		√	√					
SiP_2O_7				√				√
$Al_2O_3 \cdot xP_2O_5$								√
$Ca_3(PO_4)_2$					√	√	√	
C2S-C3P					√			
$R_2MgP_2O_{7,}$						√	√	
$M_3(PO_4)_2$							√	
$R_2MP_2O_7$						√	√	

*: R means to potassium or sodium; C_2S-C_3P means to $Ca_2SiO_4 \cdot 0.05Ca_3(PO_4)_2$ and $Ca_{15}(PO_4)_2(SiO_4)_6$; M means to heavy metal.

the vacancies can cause the bond length and bond angle change of O-Si-O. Therefore, the polymorphism of C_3S changed with the introduction of a trace element. As the similar influence mechanism, maximum concentration element phosphorus should be focused on.

Secondly, in an attempt to clarify the influence of phosphorus on the C_3S polymorph, the XRD patterns of the phosphorus-containing compounds in the two groups of clinker samples were analyzed in detail. The results are shown in Table 6.

For the clinkers without MSS (see Table 6), phosphate was mainly combined with Ca, Si, and Fe (major elements of cement clinker) to generate orthophosphate, pyrophosphate, and metaphosphate, such as $RCaPO_{4,}$ $Ca_2P_2O_7$, SiP_2O_7, and $Fe(PO_3)_2$. The clinkers with MSS incorporated were quite different. Besides calcium phosphates, phosphate also existed in the form of C_2S-C_3P, alkali metal-containing compounds, and heavy metal-containing compounds.

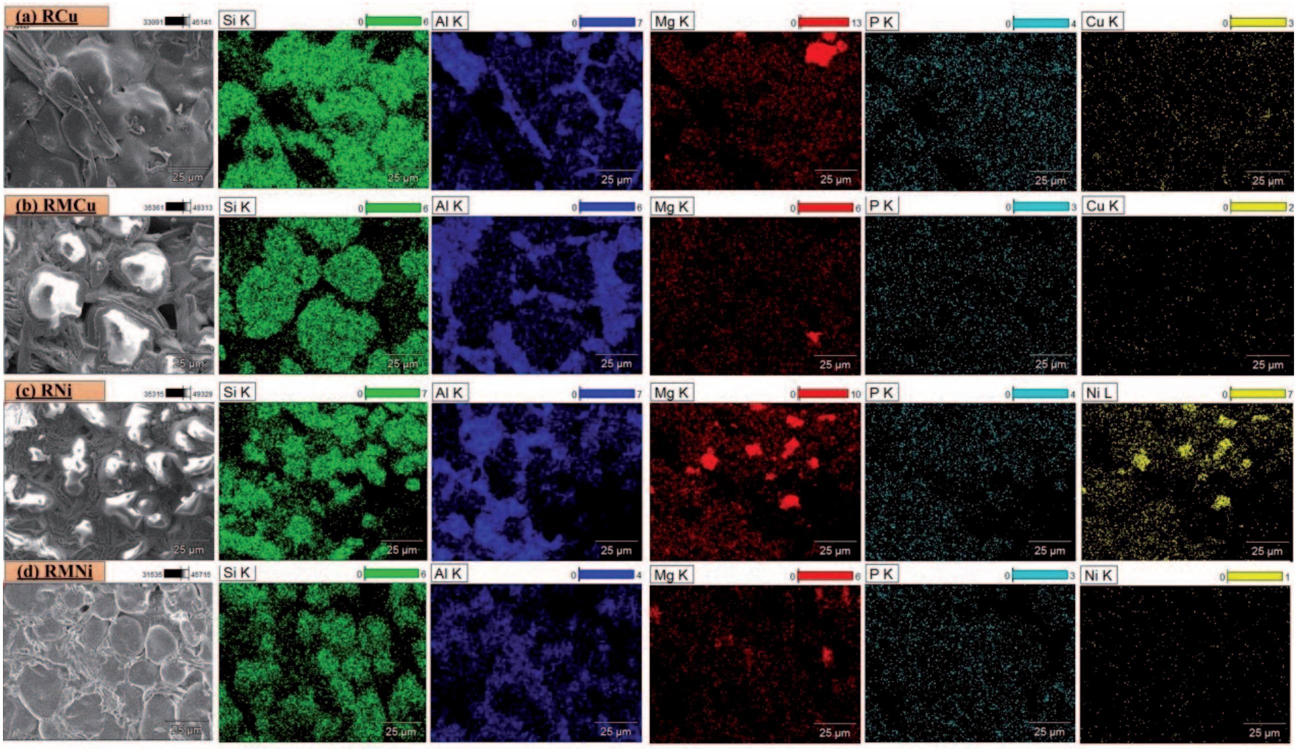
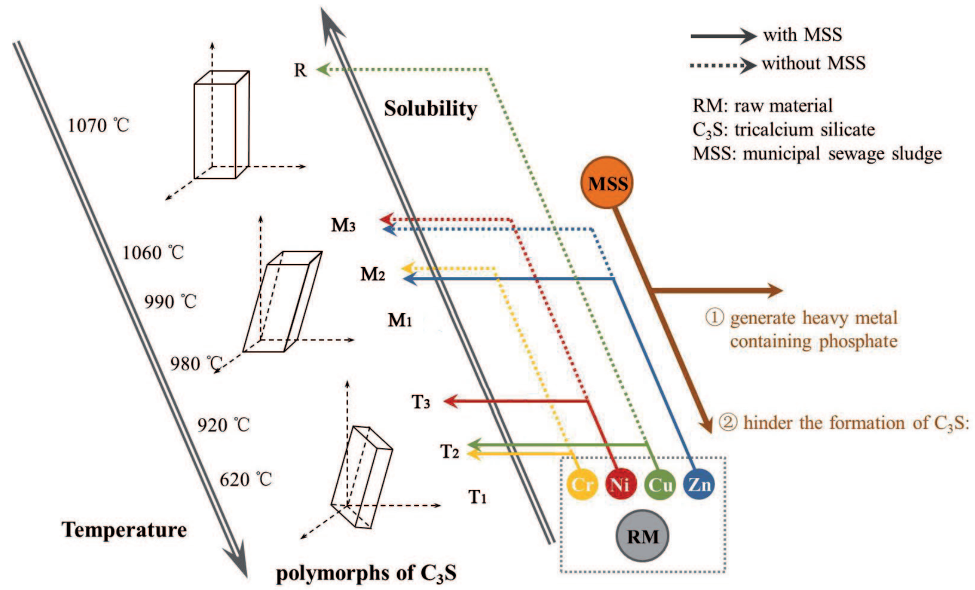


Fig. 4. SEM micrographs and elemental x-ray images of Cu- and Ni-containing clinkers: a) RCu, b) RMCu, c) RNi, d) RMNi.



Graphical Abstract

The generation of phosphorus-containing compounds is relative to the properties of P. The ionic radiuses of $P^{5+}$and Si^{4+} are 0.38 A and 0.40 A, respectively, which means that Si^{4+} that should be incorporated in clinkers and may be replaced by P^{5+}. As reported by Cédric Duée's [37], the $[SiO_4]^{4-}$ orthosilicate groups could be substituted by $[PO_4]^{3-}$ or thophosphate units in clinkers. The replacement of $[SiO_4]^{4-}$ by $[PO_4]^{3-}$ implies an excess of positive charges in the structure that occurred because of the creation of 255 Ca^{2+} vacancies, as described by the following equation:

$$2\,(SiO_4)^{4-} + Ca^{2+} \rightarrow 2(PO_4)^{3-} + V_{Ca}\ (V_{Ca} = Ca^{2+}\ \text{vacancy}) \tag{3}$$

The Ca^{2+} vacancies decreased the stability of the solid solution and hindered the generation of highly metastabile C_3S. Therefore, introducing MSS made the polymorphism of C_3S change from rhombohedral to monoclinic and to triclinic.

In addition, there were many other kinds of phosphorus-containing compounds in clinker samples. First, C_2S–C_3P solid solutions such as $Ca_2SiO_4{\cdot}0.05Ca_3(PO_4)_2$ and $Ca_{15}(PO_4)_2(SiO_4)_6$ were detected in the XRD pattern of RMCr. This phenomenon was similar to what was observed by Marie-Noe¨lle de Noirfontaine [38], who reported that adding phosphorus could cause partial decomposition of C_3S into C_2S and CaO phases, and that phosphorus was present in solid solution phases of C_2S–C_3P. Second, in the clinker samples of RMNi and RMCu, phosphorus was also present in such heavy metal-containing compounds as $K_2NiP_2O_7$, $K_2Cu(PO_3)_4$, and $Cu_4O(PO_4)_2$. This indicates that parts of Cu and Ni were not incorporated in the calcium silicate phases but that they reacted with P and alkali metals. Third, it is noteworthy that the existence the phosphorus forms changed only slightly in RMCr and RMZn, but changed considerably in RMCu and RMNi samples, which was in line with the changes in the fixation ratios in Table 1.

Therefore, the phosphate contained in MSS not only impacted the polymorphism of calcium silicates, with indirect influences on the fixation of heavy metals, but also directly impacted the fixation of heavy metals through the formation of heavy metal-containing compounds.

In addition, to examine element changes and element distribution in different clinkers in more detail, we used a scanning electron microscope with a back scatter detector (SEM-BSE). The SEM micrographs of clinkers containing Cu and Ni, and x-ray images of Si, Al, Mg, P, Cu, and Ni are shown in Fig. 4.

As shown in Figs 4(a-d), the distribution of Al in these clinkers changed from being concentrated to being relatively decentralized – most likely driven by phosphorus. As previously discussed, the presence of MSS favored substitutions of Si^{4+} for P^{5+} in the silicate phases. The valencies of Si^{4+} and P^{5+} are different and will introduce positive charges to this reaction. Normally, these positive charges can be balanced by the negative charges introduced by substituting Si^{4+} for Al^{3+} ($2Si^{4+} \leftrightarrow P^{5+} + Al^{3+}$) [24]. Therefore, part of the Al that entered the silicate phase caused the Al to decentralize and promoted the generation of Ca-Al-Metal compounds, like $Ca_6Al_4Cr_2O_{15}$ in Table 3. The species of heavy metal-containing compounds in MSS that contained clinkers were much more abundant, especially metal-Al compounds (as shown in section 3.2), which also was consistent with the distribution of Al. Moreover, increases in the P_2O_5 content can result in increases in the free CaO content and, when the P_2O_5 content in the clinker exceeds 0.5%, C_3A formation declines [39-40]. The increase in the free CaO and the decline in C_3A were conducive to the generation of Ca-Metal and Metal-Al compounds (Table 3).

X-ray images of Cu showed that Cu was basically distributed evenly in the reference samples as shown in Fig. 4a), but was transferred to interstitial phases when MSS was introduced (Fig. 4b). The distributions of Ni and Mg were well correlated as shown in Fig. 4c). The above-reported changes in the heavy metal distributions in clinkers are remarkably consistent with the results from the XRD analysis in section 3.2.

Conclusion

The role of municipal sewage sludge on the incorporation of Cr, Ni, Cu, and Zn into cement clinker was examined at the laboratory scale in our study. From the present study, we can conclude that the fixation ratios of the heavy metals Cu, Ni, Cr, and Zn decreased by 12.9%, 8.7%, 3.2%, and 1.2%, respectively, after the additions of MSS. The decreases in fixation were related to the polymorph of C_3S and the trace element composition of the MSS. The polymorphism of C_3S changed from rhombohedral to monoclinic to triclinic. More specifically, in clinker that contained Cr, Ni, Cu, and Zn, the C_3S polymorph changed from M_2 to T_2, M_3 to T_3, R to T_2, and from M_3 to M_2, respectively, after MSS was introduced. These changes were mainly caused by the trace elements, phosphorus in particular. Phosphorus from MSS caused the changes of C_3S polymorphism, and also promoted the generation of the new phases: $K_2NiP_2O_7$, $K_2Cu(PO_3)_4$, and $Cu_4O(PO_4)_2$ in cement clinker. These changes indicate a reduction in the solubility of heavy metals in cement clinker, and reductions in the fixation ratios of heavy metals.

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