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Reuse of water purification sludge as raw material in cement production

HuXing Chen [a], Xianwei Ma [b,c,*], HengJie Dai [a]

[a] College of Material Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China
[b] Cement-based Material Institute, Tongji University, Shanghai 200092, China
[c] Henan University of Urban Construction, Pingdingshan 467000, China

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ABSTRACT

The feasibility of partial replacement of siliceous raw material for cement production with water purification sludge (WPS) was investigated by X-ray diffraction, free-lime analysis, compressive strength testing and toxicity characteristics leaching procedure (TCLP). It is found that WPS has no negative effects on the consumption of free lime and the formation of clinker minerals. The samples with WPS from 4 to 10 wt.% have higher 3 days and 7 days strengths than the control. After 28 days, however, only WPS replacements <7% increased the strength of samples. It is noteworthy that heavy metals in WPS were almost completely incorporated into the clinkers, and up to 28 days the heavy metals were not detected in the leachates. From the above results of clinker minerals, compressive strength and leaching tests, it can be concluded that WPS has the potential to be utilized as an alternative raw material in cement production.

1. Introduction

In modern society, much sludge including industrial sludge (tannery sludge, sludge from the paper industry, electroplating sludge, etc.) and domestic sludge is produced everyday. Formerly, sludge was often landfilled without any special treatment, even though it often contains heavy metals that may be released under acidic conditions and cause environmental hazards. Consequently, landfilling is being substituted by other practices, such as physical/chemical/biological treatments, incineration and stabilization/solidification methods [1]. Most of the treatment processes, however, are either too expensive or not practically available at this stage. Therefore, the reuse of sludge containing heavy metal may be a better alternative than that of treatment processes.

On the other hand, Portland cement clinker production consumes massive amounts of raw materials (limestone, clay, etc.), and large amounts of energy (850 kcal/kg of clinker) and increases the emissions of greenhouse gases (around 0.85 kg of CO_2/kg of clinker). Therefore, looking for other new, economical raw materials is also becoming an immediate concern.

The main chemical compounds of sludge are Al_2O_3, Fe_2O_3 and SiO_2, which are also the main chemical compounds of some raw materials in cement production. Thereby, at least in theory, it can be used as an alternative for raw materials in cement production. Moreover, there are several advantages of using a cement kiln for sludge treatment. The high temperature (above 1400 °C) kiln can decompose the toxic organic materials and the bacteria; most of the heavy metal can be incinerated into the clinker [2–4]; fuel use can be reduced due to its high calorific value [5,6]. Thus, reusing sludge as raw material in cement production can offer savings in other raw materials and fuels. In recent years, some researchers have tried to use some types of sludge as raw materials in cement production [4,7,8].

In China, water purification sludge (WPS) from water supply companies is different from other industrial sludge. Since the water sources of many water supply companies come from rivers, WPS contains much silt, but lower amounts of heavy metals and organic matter. Therefore, if WPS is used as cement raw materials, it should be more easily accepted by cement plants compared with other sludge.

The potential threat of sludge has also caught the Chinese government's attention and many related programs are being carried out. This study, which is one of those programs, consists of two stages. The early-stage work is carried out in laboratory and the later-stage in a cement rotary kiln.

In this study, the burnability of raw materials was evaluated in terms of the free lime amount in clinker glycol–ethanol method. The crystalline phases of the resultant cement clinkers were identified by X-ray powder diffraction. 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

* Corresponding author. Address: Cement-based Material Institute, Tongji University, Shanghai 200092, China. Tel.: +86 571 87952258; fax: +86 571 88843560.
E-mail addresses: chenhx@zju.edu.cn (H. Chen), feitian7799@163.com (X. Ma).

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hydrated clinkers were also tested by toxicity characteristics leaching procedure (TLCP).

2. Experimental

2.1. Material

WPS was obtained from a water supply company. Limestone, shale, sand, copper waste and gypsum were industrial raw materials and aluminum hydroxide (analytically pure, >99 wt.%) was used to adjust the amount of Al_2O_3 in the cement raw mixture. WPS and other raw materials were, respectively, dried at 105 °C to constant weight, crushed by a jaw crusher and ground to ASTM 200 mesh size with a centrifugal ball mill. Chemical compositions of raw materials and WPS and Heavy metal contents in WPS were shown in Tables 1 and 2. It can be found from Table 2 that the concentrations of Zn and Cr in WPS are higher than those of Pb, Ni and Cu.

2.2. Cement raw material preparation

The compositional parameters in cement chemistry, listed as follows (Eqs. (1)~(3)), should be fulfilled in advance. Typically, the composition parameters of Chinese cement clinkers are controlled at SR values around 1.7~2.7, AR values around 0.9~1.9, and KH values around 0.87~0.96 [9].

$$\text{Lime saturation ratio} \quad (\text{KH}) = \frac{\text{CaO} - 1.65\text{Al}_2\text{O}_3 - 0.35\text{Fe}_2\text{O}_3}{2.80\text{SiO}_2} \quad (1)$$

$$\text{Silica ratio (SM)} = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \quad (2)$$

$$\text{Alumina ratio (IM)} = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3} \quad (3)$$

According to a similar set of parameters (KH = 0.94, SM = 2.37, IM = 1.30), all the raw materials were blended. The difference was that WPS replaced shale with different percentages. OPC, PI, PII, PIII, PIV and PV represent, respectively, the mixtures with 0, 4, 5.5, 7, and 8.5 wt.% WPS. The chemical compositions and parameters of all the mixtures are listed in Table 3.

All the mixtures were prepared with appropriate water, and pressed into 10 mm × 40 mm × 40 mm cuboids with a pressure of 200 MPa. And then those cuboids were heated to 1400 °C at the rate of 10 °C/min, maintained for 40 min in the furnace, cooled in air to room temperature and ground to ASTM 200 mesh for future analysis. Clinker that was sintered with raw mixture added WPS is called eco-clinker, and the corresponding cement is eco-cement.

Table 1
Chemical composition of WPS and cement materials (by wt.%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	MgO
WPS	52.18	19.90	6.29	1.68	0.97	2.9	1.38
Shale	68.10	14.69	6.23	1.35	0.24	0.89	1.33
Limestone	3.65	0.81	0.42	52.37	0.02	0.01	0.73
Sand	88.88	5.40	2.88	0.67	0.07	0.09	0.73
Copper waster	30.51	6.06	52.71	8.76	0.08	0.07	5.57

Table 2
Heavy metal in WPS (mg/kg).

	Cd	Cr	Cu	Ni	Pb	Zn
WPS	ND	76.4	43.9	37.6	29.3	144

ND: not detected (<0.005 mg/g).

Table 3
Composition (by wt.%) and parameters of the raw mixes.

	OPC	PI	PII	PIII	PIV	PV
Shale	15.5	9.6	7.4	5.0	2.5	0
WPS	0	4.0	5.5	7.0	8.5	10.0
Limestone	81.5	81.3	81.2	81.1	81.0	80.9
Sand	0	2.1	2.9	3.8	4.8	5.8
Copper waster	2.5	2.6	2.6	2.7	2.8	2.9
Aluminum hydroxide	0.5	0.4	0.4	0.4	0.4	0.4
LSF	0.942	0.942	0.942	0.942	0.942	0.943
IM	1.30	1.30	1.31	1.30	1.30	1.29
SM	2.37	2.37	2.37	2.36	2.36	2.36

Compressive strength tests were carried out according to GB/T 17671-1999 (which is equivalent to ISO679: 1989). Mortars were prepared by mixing cement with deionized water at a water-to-cement weight ratio of 0.27 and cement-to-sand ratio of three, cast in 40 mm × 40 mm × 160 mm molds and vibrated at the time of casting to remove air bubbles. The molded pastes were kept at 20 ± 2 °C and relative humidity exceeding 90% for 24 h, and then removed from the molds. The demoulded samples were cured in a water tank at 20 ± 2 °C for the set ages and then their strengths were measured.

2.3. Testing method

The content of f-CaO in clinker was analyzed by the glycerol–ethanol method. Clinker minerals were identified by XRD. A Siemens D500 diffractometer and Kristalloflex 810 generator using monochromatic Cu Kα radiation operating at a voltage of 30 kV and current of 15 mA was used. Scanning speed was 10° 2θ/min. The tolerable heavy metal concentration in clinker and leachability of metals from the hydrated sample was evaluated using US Environmental Protection Agency toxicity characteristic leaching procedure (TCLP) (Method 1311) to determine their hazardous characteristics [10]. PV clinker and leachates of PV hydrated sample were analyzed by microwave-assisted digestion followed by inductively coupled plasma spectrometry (ICP-OES, Perkin Elmer Optima 2000).

3. Results and analysis

3.1. Burnability of cement raw mixture

Raw mix burnability is related to the rate at which CaO combines during the thermal process and is generally evaluated according to the amount of free lime in clinker. The analysis result of free lime is given in Fig. 1. The results show that WPS improves the burnability of raw mixes. To be noticed, when the amount of WPS in raw mixture is <5.5 wt.%, the free lime content decreases rapidly, but above 5.5 wt%, the trend becomes slow. The effect of WPS on burnability may be related to the presence of minor elements in WPS, but compared with the amount of those metals (>1%) generally added to raw mixture, their contents in raw mixture are smaller and the extent of burnability to improve is not more remarkable.

3.2. Main clinker mineral

XRD patterns of the sintered clinkers are shown in Fig. 2. With different WPS replacement, from 4% to 10%, XRD patterns of the clinkers are almost the same as that of the control (OPC), and no new phase is detected. The major components of OPC clinker, Alite (C_3S), Belite (C_2S), Tricalcium aluminate (C_3A) and Celite (C_4AF) are also present in the clinkers from PI to PV. The slight differences are

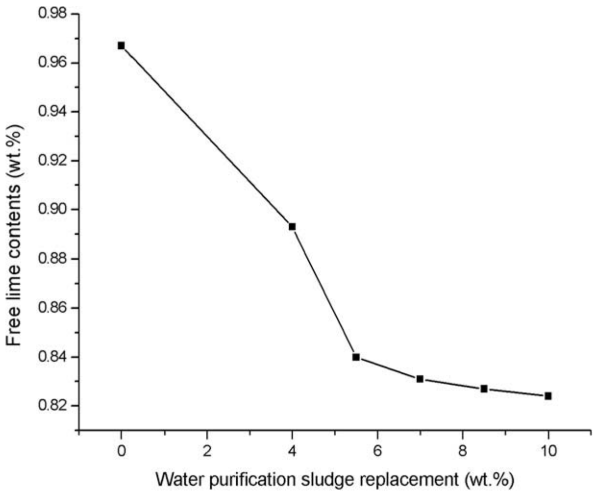

Fig. 1. Free lime contents of the OPC and eco-cement clinkers at 1400 °C.

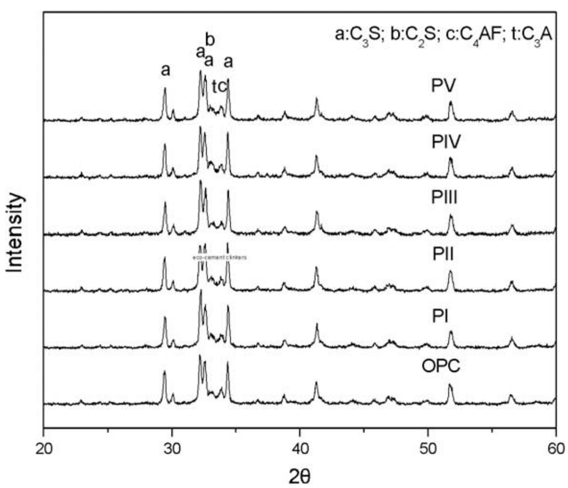

Fig. 2. XRD patterns of the OPC and eco-cement clinkers.

that the intensity of the C_3S peak in PII clinker is slightly greater than those in other clinkers and the C_3A/C_4AF rate increases with increasing the WPS replacement. These results, however, are not in agreement with those of Shih et al. who found that the relative amounts of C_3S increased by 39% as the percentage of electroplating sludge (EPS) added to raw mixture was 10 wt.% [4]. The difference of results may be the different amount of minor elements in EPS and WPS.

3.3. Compressive strength development of eco-cement

Fig. 3 shows compressive strength of the OPC and eco-cement. It can be observed that the strengths of all the eco-cements at 3 days and 7 days are greater than those of the OPC. Even when WPS is totally substituted for shale (10% WPS), the strengths of the PV at 3 days and 7 days are 13.0% and 5.6% higher than those of the OPC. At 28 days, however, the eco-cements have slightly higher strengths when the WPS replacement is below 7%, but much lower strengths above 7% WPS compared with the OPC. It is worth mentioning that compressive strength increases significantly when the WPS replacement is below 5.5%, but the strength begins to decrease above that amount (5.5%). The trend of decrease is more obvious at 3 and 28 days than at 7 days. Therefore, for compressive strength there might be a better WPS replacement rate, which needs further study.

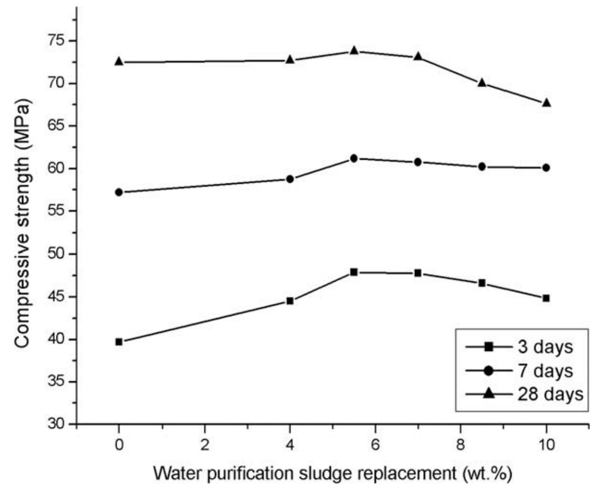

Fig. 3. Compressive strength development of the OPC eco-cement.

3.4. Heavy metal in clinkers

The concentrations of heavy metals in clinker are related to their volatility during the burning process. According to their volatility, minor elements could be divided into three groups, highly volatile (<20% remained in clinker, such as Cd, Pb), moderately volatile (such as Ni and Cr), and lowly volatile (almost 100% remained in clinkers, such as Cu and Zn) [11]. The concentrations of heavy metals in PV clinker were measured as shown in Table 4. Cu and Zn elements in PV clinker have higher contents than Pb, Cr and Ni, but Cr and Zn elements in WPS have higher contents than Pb, Cu and Ni. Due to addition of copper slag, however, it can not be deduced that Cu and Zn have lower volatility while Cr has higher volatility. Moreover, in practical rotary kiln operations, the volatility of heavy metal might be affected by composition of raw meal, burning conditions and atmosphere which are not considered in this study.

3.5. Toxicity leaching characteristics of heavy metal

When the eco-cement is used in engineering, the heavy metals incorporated into the clinkers might be released in an acidic environment and cause environmental hazards. To investigate this possibility, TCLP was performed. The heavy metal contents, including Cd, Cr, Cu, Ni, Pb, and Zn, in the PV hydrated sample at different curing ages are shown in Table 5. No heavy metal could be detected in the leachates. This indicates that the heavy metals in clinker are almost all incorporated into clinker minerals and well fixed

Table 4
Heavy metal concentrations in clinker PV (mg/kg).

	Cd	Cr	Cu	Ni	Pb	Zn
PV clinker	ND	43.4	180	18.5	10.0	321

ND: not detected (<0.005 mg/g).

Table 5
Concentrations of heavy metal in TCLP leachates from hydrated sample PV (mg/L).

	Cd	Cr	Cu	Ni	Pb	Zn
3 days	ND	ND	ND	ND	ND	ND
7 days	ND	ND	ND	ND	ND	ND
28 days	ND	ND	ND	ND	ND	ND
GB 5085.3-2007	<1	<15	<100	<5	<5	<100
USEPA,1997	<1	<5	–	–	<5	–

ND: not detected (<0.005 mg/L).

Table 6
Content of R_2O in clinkers.

Clinkers	OPC	PI	PII	PIII	PCIV	PV
R_2O (%)	0.473	0.583	0.628	0.664	0.707	0.748

R_2O (%) = $Na_2O + 0.658K_2O$.

by the hydration products. Therefore, the eco-cement would present no immediate threat to the environment, but the long-term threat needs to be further studied.

3.6. Discussion

From the above results of chemical analysis, XRD and compressive strength, it is found that addition of WPS has some positive influences on the consumption of free lime, the formation of clinker mineral and the development of strength. The effect of WPS is closely related to the minor elements in WPS. When WPS is added to raw mixture, Cu, Zn, Cr, Ni, K, Na, etc., are also introduced. It is known that some minor elements can reduce the melting point of burning, increase the content of liquid phase, reduce liquid phase viscidity, and accelerate the rate of diffusion of particle greatly so that the reactivity of raw materials is increased and especially the formation of C_3S is accelerated. In addition, the test result of leachate indicates that the heavy metals in clinker were almost all incorporated into clinker minerals. Incorporation of minor element into mineral structure would lead to lattice distortion which would alter clinker mineral reactivity with water.

The influences of minor elements, however, are closely related to their amount. Cr, Ni, and Zn have no influence on the formation of the clinker phases, compressive strength and the initial setting or hydration when their concentrations are very low in raw mixture. Only very high intakes ($\geqslant$0.1%) of Cr, Ni, and Zn can cause changes in the clinker mineral and hydration properties [12,13]. In our research, the total concentration of heavy metals in PV clinker is far below 0.1%. Therefore, their effects would be limited, which is confirmed by variance in the amount of free lime and the results of XRD. Compressive strength, however, has an obvious change that may be related to amount of potassium and sodium elements in clinker. Their contents ($R_2O = Na_2O + 0.658K_2O$) in clinkers are shown in Table 6. It is generally accepted that potassium and sodium ions (in the form of either sulfates or hydroxides) can accelerate the early hydration of cement, but cause the strength to decrease at later ages [14]. This trend is similar to our results that the eco-cements made from WPS have much higher 3 days and 7 days strengths than the OPC but the 28 days strength slightly increases, or even decreases.

4. Conclusions

From the above results of chemical analysis, XRD, compressive strength and TLCP tests, it is feasible to use water purification sludge (WPS) as a substitute of siliceous material in cement production. The following major conclusions may be drawn:

1. Additions of WPS to the raw mixture can lower the free lime contents, and increase the amount of C_3S, and the ratio of C_3A and C_4AF. The effects, however, are limited due to low concentrations of Cu, Cr, Zn, and Ni in the raw mixture.
2. WPS contributes positively to compressive strength during days. Even when the amount of WPS added to raw mixture is 10%, the 3 days and 7 days strengths increased by 13.0% and 5.6%, respectively. At 28 days, however, only WPS replacements <7% resulted in sample strengths that were higher than that of the control. Therefore, the amounts of WPS should have an appropriate value, which is between 4% and 7% in this study.
3. The heavy metals (Cr, Cu, Ni, Pb, Zn) in WPS were almost completely incorporated into clinkers, and the heavy metals were not detected in the leachates up to 28 days. Therefore, the eco-cement would present no immediate threat of heavy metals to the environment.

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