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Hydration process of the aluminate $12CaO \cdot 7Al_2O_3$-assisted Portland cement-based solidification/stabilization of sewage sludge

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ABSTRACT

The high organic content in sewage sludge is the main obstacle to Portland cement-based solidification/stabilization (S/S). A novel aluminate $12CaO \cdot 7Al_2O_3$ was prepared as accelerator in order to improve the performance of cement-based S/S making the sludge disposal and recycling possible. The behavior of pastes fabricated with various mass ratios of aluminate/cement has been analyzed in terms of mechanical strength, hydration products, microstructure and leaching characteristics. The incorporation of aluminate significantly improved the cement-based S/S performance. The solid matrix obtained with the aluminate/cement ratio of 4/6 and binder addition of 10 wt.% presented 28 day-strength of 157.2 kPa, in contrast, 25.1 kPa or so obtained for the cement only-sludge mix. X-ray diffraction (XRD), thermogravimetry–differential scanning calorimetry (TG-DSC) and scanning electron microscopy (SEM) analysis revealed that the presence of aluminate counteracted the interference from organic matters, favored the formation of crystalline phases viz. ettringite $C_6A\overline{S}_3H_{32}$, calcite $CaCO_3$ and quartz, and therefore the strength development. Environmental assessment of the final products in compliance leaching tests demonstrated that the concentration of heavy metals were below the certain legal limits (GB 5085.3-2007) set in China, though the addition of aluminate slightly fell the resistance of solidified mortars to acidic environments.

1. Introduction

The increasing number of waste sludge devoted to waste immobilization reflects a genuine need for cost-effective solutions for restoring a safe and green environment. Solidification/stabilization (S/S) technologies are expected to increase in treating hazardous wastes, like heavy metal-contained wastes before land disposal. A major factor in applying this process to wastes is that it improves the physical and chemical characteristics and reduces the mobility of contaminants. In this process, the identification of binders able to assume the fixation of contaminants is essential for the success of the technique [14]. Portland cement (PC) is considered as the most common amendment media due to its low cost and large availability [3,6,10,22].

However, a potential concern is that the PC-based formulations are much more viable for inorganic wastes, but not suitable for the organic-high wastes such as waste activated sludge. It is because organic matters had detrimental effects on the hydration reactions of cement and accordingly lowered the S/S performance [12,16,18]. A study by Minocha et al. [16] on the impact of grease, oil, hexachlorobenzene, trichloroethylene and phenol on the geotechnical properties of solidified sludge revealed that the grease, oil and phenol had the significantly negative effect on binders. The presence of 8 wt.% grease and oil resulted in 50% reduction in the 28 day-strength of cement-fly ash samples, also 54% and 92% decrement were observed for the cement only and cement-fly ash pastes with 8 wt.% phenol addition, respectively.

Therefore, recently various additives have been utilized during the cement-based S/S process in order to counteract the influences from the organic matters in activated sludge. Researchers have studied the feasibility of using bentonite as the additive due to its high adsorbability to organic substances [12]. Yet no apparently positive effect on the strength development was observed. In contrast, the strength of specimens solidified by cement–bentonite mixture was similar to, and in some cases, 52–68% lower than those obtained with cement only. Another study by Luz et al. [14] employed sulfoaluminate cement and bottom ash as the blended binder to modify a galvanic sludge. They observed that the introduction of bottom ash induced the increased porosity of solidified matrixes, which was more detrimental than beneficial to the strength development. Furthermore, Malliou et al. [18] utilized Portland cement with both $CaCl_2$ and $Ca(OH)_2$ as accelerators to solidify sludge. Results showed that 10% or so increment in the

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28-day strength was achieved when adding 3 wt.% $CaCl_2$ and 2 wt.% $Ca(OH)_2$ of cement. But the presence of chloride ion retarded the reuse of final products in some fields, especially in building industries attributed to chloride-induced steel corrosion in reinforced concrete structures [13]. In addition, other pozzolanic additives like jarosite, alunite [3], $Na_2SiO_3{\cdot}5H_2O$, Na_2CO_3 [1], as well as lime and fly ash [20] have also been added to or partially replaced PC for sludge S/S, however, the published data were less satisfactory.

Mayenite ($12CaO{\cdot}7Al_2O_3$), one among aluminates, can be detected in some high performance cement [7,14]. It owns the outstanding pozzolanic and rapid hardening activity, which makes it sufficiently possible to be employed as the accelerator of PC to enhance its resistance to organics. Whereas very few attentions have been paid to the possibility thanks to the exiguity of mayenite, as thus to date there have been no comprehensive studies in the pertinent literature on how the Portland cement–mayenite systems function.

The specific objective of the present study was to investigate the potentials of mayenite as the modifier for PC, and also the PC-mayenite systems as a binder for sludge S/S. This involved varying the mix design (aluminate/PC ratios and the binder content), evaluating the mechanical and microstructural properties as well as leachability based on pH, also exploring the mechanisms of sludge S/S.

2. Materials and methods

2.1. Characterization of the sludge

The dewatered sludge of test was a biological sludge from a sewage treatment plant with a daily scale of 2.2 million ton in Shanghai, China, and its physicochemical properties are depicted in Table 1, with a moisture content of approximately 81.2 wt.%, pH 6.7, total organic matters content of 45.7 wt.%, and a low concentration of heavy metals. In addition, the chemical composition of sludge was determined by X-ray fluorescence. The main elements present in dry sludge ash were silica (SiO_2), calcium oxide (CaO) and alumina (Al_2O_3).

2.2. Binders

The binders used for S/S of dewatered sludge were PC type CEM II 32.5 and mayenite. Standard procedure for synthesizing mayenite was detailed elsewhere [27]. In brief, $CaCO_3$ and $Al(OH)_3$ were calcined at 950–1000 °C for 2.5 h in a SX2-10-12 muffle furnace (Shanghai Chongming Electric Co., Ltd., China) to produce reactive CaO and Al_2O_3, respectively, followed by the mixing of these two chemicals with a stoichiometric ratio of 12/7 after ground to a size of 74 μm. Thereafter, the binary system was mixed with tap water at a liquid–solid ratio of 1:1 (mL/g), hydrothermally heated to boiling for 1–1.5 h, and dried at 65 °C for 24 h. The product thus obtained was sintered in a muffle furnace at a rate of 10–20 °C/min to 1180 °C and soaked at the maximum temperature for 2 h. The calcined product finally obtained was ground into the sizes below 80 μm and employed as the modifier for PC during S/S of dewatered sludge.

The mineralogical analysis of PC and synthesized aluminate were done by X-ray diffraction, and the results are presented in Fig. 1. The diffractogram of PC showed the presence of quartz, tricalcium silicate (C_3S), tricalcium aluminate (C_3A). In reference to the aluminate, mayenite $12CaO{\cdot}7Al_2O_3$ was identified as the primary phase, with the main ray at the 18.82° and 33.48° of 2θ.

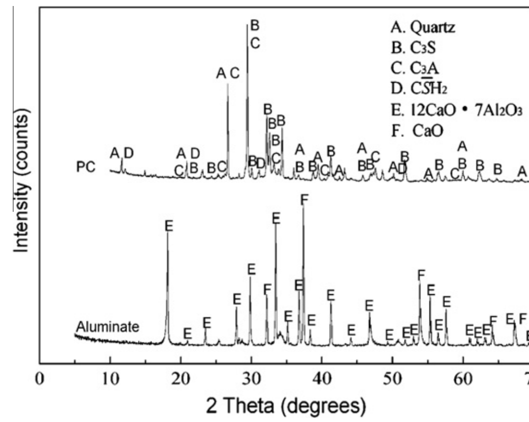

Fig. 1. X-ray diffractograms of the PC and aluminate.

Table 2
Nomenclature and components of the pastes (wt.%).

Mass ratios of aluminate/PC	Mass ratios of binder/sludge	
	10%	20%
0:10	$AC_{0/10-10}$	$AC_{0/10-20}$
2:8	$AC_{2/8-10}$	$AC_{2/8-20}$
3:7	$AC_{3/7-10}$	$AC_{3/7-20}$
4:6	$AC_{4/6-10}$	$AC_{4/6-20}$
5:5	$AC_{5/5-10}$	$AC_{5/5-20}$

2.3. Preparation of specimens

All pastes were prepared by mixing dewatered sludge and solidifier in definite ratios as listed in Table 2. After thoroughly mixed using a high speed blender for 5–10 min, the sludge-laden samples were immediately transferred into the molds with a size of 39.1 mm in diameter and 80.0 mm in height and pre-cured under air-tight condition at 25 ± 0.5 °C for 24 h. The specimens obtained from the molds were then cured at room temperature until the strength tests.

2.4. Analytical methods

2.4.1. Unconfined compressive strength (UCS)

UCS was measured in compliance with SL237-020-1999 (China). And the specimens were mechanically tested in 3, 7, 14 and 28 days. For each mortar and curing age, three specimens were tested.

2.4.2. X-ray diffraction (XRD) analysis

The hydrations of samples were stopped by immersion in acetone solution for 24 h, followed by drying at 65 °C. Then a D8 Advance powder diffractometer (Bruker AXS Inc., Germany) was employed to identify the crystalline products present. The accelerating voltage was 40 kV and the current was 40 mA. The samples (<5 μm) were examined at room temperature over the 2θ range 2–70° using graphite monochromated Cu Kα radiation. The step scan was 0.02° and the measuring time 0.1 s/step. The diffractograms were obtained with Diff-plus and analyzed using MDI Jade 5.0 software.

Table 1
Physicochemical properties of dewatered sludge used.

Property	Value							
Moisture content (%)	18.81							
pH	6.70							
Organic matter content (*wt.%*)	45.67							
Heavy metal (g/kg dry sludge)								
Cu	Zn	Pb	Cd		Cr		Ni	
0.20	1.00	0.04	Undetectable		0.10		0.03	
Chemical composition (wt.%[a])								
SiO_2	MgO	Al_2O_3	Na_2O	K_2O	CaO	Fe_2O_3	TiO_2	Others
46.40	3.97	10.30	1.76	3.19	7.85	5.66	0.79	20.08

[a] Dry sludge ash (ignition at 1100 °C).