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Effect of slag-based solidification material on the solidification and stabilization of sewage sludge

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ABSTRACT: Solidification/stabilization is considered to be a well-established disposal technique for reducing sludge handling and disposal obstacles. In this work, a slag-based solidification material (SBSM) was developed, using slag and dihydrate gypsum as the solidifier and sulphoaluminate cement clinker as the additive, to improve the performance of sludge solidification and thus making sludge disposal and recycling possible. The behaviour of pastes fabricated with various mass ratios of slag/sulphoaluminate cement clinker/dihydrate gypsum has been analysed in terms of mechanical strength, hydration products, microstructure, and toxicity characteristics. The results show that the strength of solidified sludge increased significantly with the addition of SBSM and the sulphoaluminate cement clinker content in SBSM. The use of sulphoaluminate cement clinker significantly improved the solidification/stabilization performance, causing a higher strength level. X-ray diffraction and scanning electron microscopy investigations revealed that a large amount of ettringite was present in the solidified sludge, leading to a crystallizing network in the solidified products and therefore the enhancement of the strength. Environmental assessment of the final products in compliance leaching tests demonstrated that the concentration of heavy metals were below the detection limits (GB5085.3-2007) set in China.

KEYWORDS: composite material, unconfined compressive strength, leachability, ettringite

INTRODUCTION

Activated sludge technology has been widely applied to treat municipal wastewater, but it has the serious drawback of producing huge amounts of excess sludge. In China, a large quantity of municipal sewage sludge is produced annually in the main cities because of the rapid progress of urbanization and industrialization[1]. Environmentally sustainable sewage sludge treatment and disposal methods are urgently required to treat and dispose increasing volumes of sludge being produced by an ever-larger number of sewage treatment plants.

Solidification/stabilization is known as one of the most popular techniques to treat hazardous waste. A major factor in applying this technique to wastes is that it improves the physical and chemical characteristics and reduces the mobility of contaminants. Currently, various binders or additive agents, such as Portland cement, calcium oxide, emulsified asphalt, or other additives, have been used[2–5]. Portland cement is considered as the most common material due to its low cost and large availability. However, it can be inferred that Portland cement is much more viable for inorganic wastes, but not suitable for the organic-high wastes such as sewage sludge. This is because organic matters has detrimental effects on the hydration reactions of cement and accordingly lowers the solidification/stabilization performance[6–8]. Therefore, recently additives have been used during the cement-based solidification/stabilization process in order to improve the influences from the organic matters in sewage sludge. Malliou et al[8] employed a Portland cement with $Ca(OH)_2$ and $CaCl_2$ as accelerators to solidify the sludge. The results showed that less than 10% increment in the compressive strength could be observed for the paste containing cement-sludge, $Ca(OH)_2$ 2% and $CaCl_2$ 3% by weight of cement with a sludge/binder ratio of 1.49/1 (m/m) at 28 days. In addition, other cementitious binders pulverized fuel ash with $Na_2SiO_3 \cdot 5\,H_2O$ and Na_2CO_3 as chemical activators[9], lime, and fly ash[10], etc. have been applied during the stabilization/solidification process. The efficiency of some of these fixing agents is however debatable since a number of the conventional solidification/stabilization processes use over 30% binders of dewatered sludge to achieve the required moisture content and compressive strength, leading to a larger volume increase, while others fail a satisfactory cost-benefit analysis[8,10].

Meanwhile, slag has received much attention as a cost-effective and efficient solidifying agent because

Table 1 Characteristics of sewage sludge used.

Sludge property			
Moisture content (%)			82.3
pH			7.07
Density (g/cm^3)			1.04
Organic matter (%)			60.2
Unconfined compressive strength (kg/cm^2)			0.067
Heavy metals (mg/kg)[a]		Chemical composition (wt. %)[b]	
Cu	2960	SiO_2	29.8
Zn	4824	Al_2O_3	25.6
Pb	112	Fe_2O_3	11.7
Cd	7.5	MgO	2.6
Cr	387	K_2O	2.1
Ni	37.8	Na_2O	1.7
As	16.9	CaO	7.8
		P_2O_5	2.2

[a] Concentration of heavy metals (mg/kg dry sludge).
[b] Dry sludge ash (ignition at 1100 °C).

of its cement-like characteristics and its abundance as a waste product from steel production plants. The study reported in this paper has attempted to develop an effective solidification binder, referred to as slag-based solidification material (SBSM) that uses the slag and dihydrate gypsum as the solidifying agent, and dihydrate gypsum sulphoaluminate cement clinker as the additive. The properties of the solidified sludge were evaluated by means of compressive strength, leaching tests and products of hydration assessed by X-ray diffraction and scanning electron microscopy.

MATERIALS AND METHODS

Materials

The sewage sludge and slag used were separately obtained from the Wastewater Treatment Plant of Hanxi and Hongda Iron and Steel Co. Ltd. in Wuhan. The sewage sludge was characterized using the standard methods of analysis[11]. The total concentrations of heavy metals were obtained using inductively coupled plasma atomic emission spectrometry analysis. The results are shown in Table 1. Meanwhile, the standard method for determining the leaching toxicity of solid wastes by horizontal vibration extraction procedure (GB5086.2, 1997)[12] was used to evaluate leaching concentrations of heavy metals from the raw sludge. The results are shown in Table 2. The chemical composition of slag, sulphoaluminate cement clinker, and dihydrate gypsum are listed in Table 3.

Table 2 Leaching concentration of sewage sludge used.

Leaching concentration of sewage sludge (mg/l)			
Cu	112.6	Zn	195.2
Pb	21.7	Cd	undetectable
Cr	47.6	Ni	8.1

Table 3 Chemical composition of slag, sulphoaluminate cement clinker, and dihydrate gypsum (wt. %).

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O	P_2O_5
slag	38.5	12.3	1.67	27.9	0.2	8.9	0.57	0.55	1.47
clinker	38.3	4.6	38.8	2.14	10.2	2.7	0.39	0.14	0.01
gypsum	42.9	4.2	0.25	0.05	44.2	1.2	0.12	0.08	0.01

Test procedures

All the samples were prepared by mixing SBSM and sewage sludge in definite ratios as listed in Table 4. The moisture content of sewage sludge was higher than 80%, hence addition of water was not required and the equal workability of all the mixtures could be obtained. The mixing procedures are as follows: the wet sludge was placed in a mixer first, all materials with a designed content were then added and the mixture stirred for 30 min. After homogenization, the mixtures were solidified in steel moulds with a size of $40 \times 40 \times 160$ mm for 24 h, and the resultant products were extruded and cured in airtight condition of (20.0 ± 0.5) °C for different times.

Samples analysis

Unconfined compression strength tested using the unconfined compression machine. And the specimens were mechanically tested in 3, 7, 14, and 28 days.

The mineralogical composition was determined by X-ray diffraction. For X-ray diffraction pretreatment, oven-dried samples were ground by mortar and pestle and passed through 200-mesh (74 µm) sieve. Then, the X-ray diffraction analysis was carried out by X-ray diffractometer with Cu Kα radiation, 30 kV

Table 4 Nomenclature and components of the samples (wt. %).

Mass ratio of slag/ clinker/gypsum	Mass ratio of SBSM/ sewage sludge	
	5%	10%
5:5:1	S(5-5)	S(5-10)
5:4:1	S(4-5)	S(4-10)
5:3:1	S(3-5)	S(3-10)
5:2:1	S(2-5)	S(2-10)

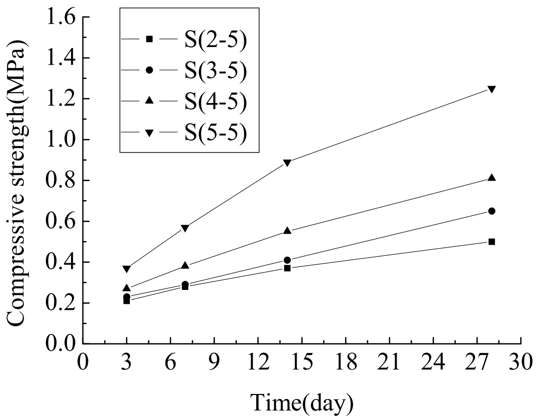

Fig. 1 Strength developments of the samples with mass ratio of SBSM/sewage sludge of 5%.

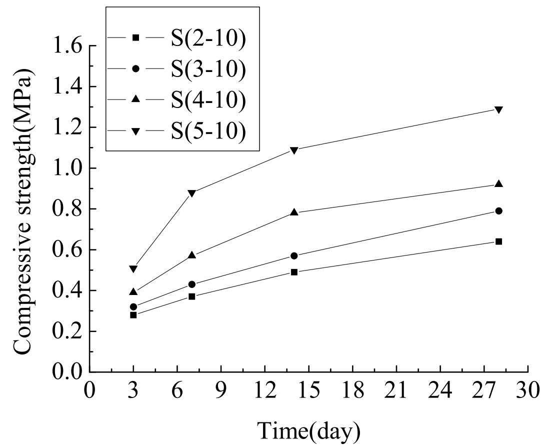

Fig. 2 Strength developments of the samples with mass ratio of SBSM/sewage sludge of 10%.

of acceleration voltage condition and 2θ scanning, ranging from 0° to 50°. Scanning electron microscopy analysis was performed on the dried samples of before and after solidification with SBSM.

Leachability of solidified sewage sludge was evaluated using standard leaching method: "Test method standard for leaching toxicity of solid wastes- horizontal vibration extraction procedure" (GB5086.2-1997)[12]. The heavy metals leaching from the samples were analysed by ICP-AES.

RESULTS AND DISCUSSION

Effect on unconfined compressive strength

Unconfined compressive strength is one of the important parameters for solidified effect. As shown in Fig. 1 and Fig. 2, with increase of the proportion of SBSM, the sludge strength increases concomitantly. At a fixed mass ratio of slag/sulphoaluminate cement clinker/dihydrate gypsum, e.g., 5:4:1, the corresponding unconfined compressive strength of S(4-5), S(4-10) series (mass ratio of SBSM/sewage sludge are 5%, 10%) is found to be 0.27 MPa and 0.39 MPa, meaning that the strength of solidified sludge increases significantly with the addition of SBSM. The same trends also occur in other mass ratio of slag/sulphoaluminate cement clinker/dihydrate gypsum. The obvious increase in strength was probably attributable to the strength of solidified product, which was influenced by the hydration degree and the amount of hydrated products.

Besides, it can be seen that the mixture ratio of slag/sulphoaluminate cement clinker/dihydrate gypsum also played an important role in strength development of solidified sludge and the increase of sulphoaluminate cement clinker content resulted in a strength increase at all ages and most importantly during the early ages. At a given addition of SBSM, e.g., 10 wt.% of sludge, the highest strength of 1.29 MPa could be obtained for paste S(5-10) after 28 days of hydration. Also the corresponding values were 0.64, 0.79, 0.92 MPa, respectively, for pastes S(2-10), S(3-10), and S(4-10). Based on the above observations, it was possibly argued that the sulphoaluminate cement clinker effectively improved the performance of solidified sludge, accelerated hydration reaction speed of binder-sludge system and transformation of hydrated products, leading to a denser microstructure and higher compressive strength.

X-ray diffraction analysis

It is apparent that the slag/sulphoaluminate cement clinker/dihydrate gypsum ratio is critical to the hydration mechanisms. In order to determine the influence of slag/sulphoaluminate cement clinker/dihydrate gypsum ratio on hydration, X-ray diffraction analysis was therefore carried out. Fig. 3 shows the X-ray diffractograms of solidified sludge pastes with the addition of 10 wt.% SBSM. Fig. 3b shows the X-ray diffractograms of solidified sludge pastes with mass ratio of slag/sulphoaluminate cement clinker/dihydrate gypsum of 5:5:1, revealing the strong presence of ettringite $((CaO)_3(Al_2O_3)(CaSO_4)_3 \cdot 32\,H_2O)$ in S(5-10) sample. In Fig. 3a, it was observed that the peak of ettringite in S(3-10) sample was lower than that of ettringite in S(5-10) sample. It can be assumed that the formation of ettringite might be responsible for the considerable strength increase in the solidified sludge with high sulphoaluminate cement clinker content. The crystalline compound

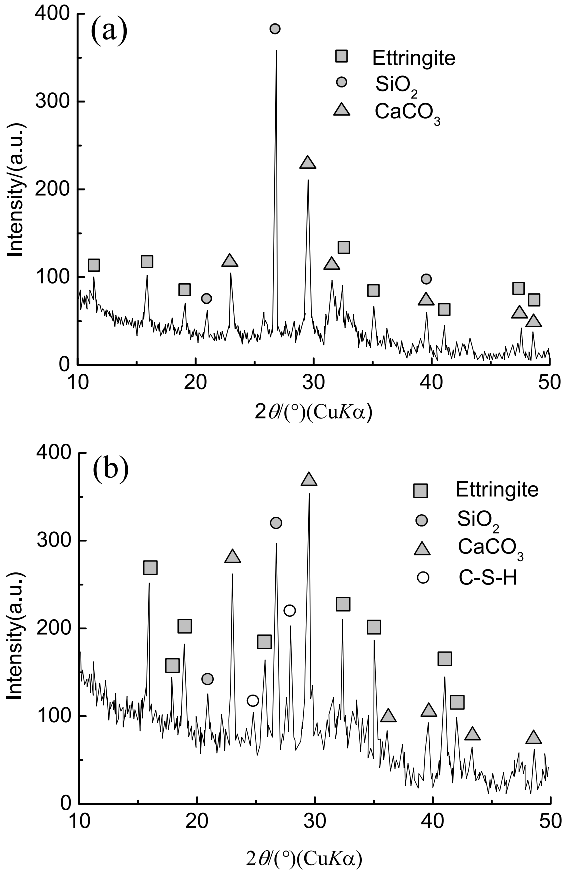

Fig. 3 X-ray diffractograms of the solidified pastes (a) S(3-10) and (b) S(5-10) cured under laboratory conditions for 28 days.

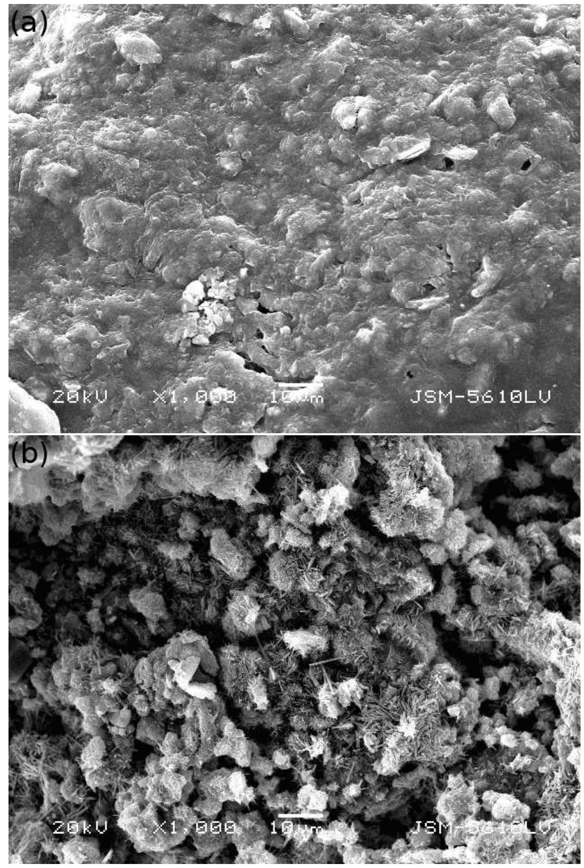

Fig. 4 Scanning electron microscopy images of the samples: (a) unsolidified sewage sludge and (b) sample S(5-10) cured under laboratory conditions for 28 days.

was able to fill the pores of the pastes making a contribution to the setting [13] and conspicuous strength development. Besides, the peaks of calcium silicate hydrate ($CaO \cdot SiO_2 \cdot nH_2O$, briefed as C-S-H) were also observed in the XRD pattern of S(5-10) sample (Fig. 3b). C-S-H phase is an important phase responsible for development of strength of cement-based materials. Thus it can be assumed that the formation of C-S-H phase in S(5-10) sample might be responsible for the considerable increase in the unconfined compressive strength of S(5-10) sample as well.

Scanning electron microscopy analysis

Scanning electron microscopy observations of the samples before and after solidification are shown in Fig. 4. The platy construct of unsolidified sewage sludge is disordered and loose in Fig. 4a. Fig. 4b shows the structure of S(5-10), with the needle-like crystals and honeycomb-like hydrated microstructures on the surface and interior of the solidified sample. Scanning electron microscopy observation confirmed the presence of a large amount of ettringite with high crystallinity. This finding corresponded well with those observed from X-ray diffraction analysis (Fig. 3b). The crystals are aggregated and connected to each other, distributed in solidified sample forming a homogeneous network. The tight connection between the sludge particles in the solidified sample might be the reason for the significant high compressive strength of S(5-10) sample.

Leaching tests

The leaching tests were conducted to examine the potential toxic heavy metal leaching hazard from the solidified sludge. The tested sample included S(4-5), S(5-5), S(4-10), and S(5-10), all samples were cured under laboratory conditions for 28 days. Table 5 presents the leaching results of Cu, Zn, Pb, Cr, Ni,

Table 5 Leaching results of heavy metals in sludge samples before and after solidification.

Sample	Heavy metal concentration (mg/l)					
	Cu	Zn	Pb	Cr	Ni	As
Raw sludge	112.6	195.2	21.7	47.6	8.1	5.4
S(4-5)	37.8	47.9	2.8	8.5	4.7	0.9
S(5-5)	15.4	38.2	2.4	2.6	3.5	0.4
S(4-10)	21.9	31.6	2.1	6.3	4.2	0.2
S(5-10)	3.8	15.7	1.7	0.3	2.6	–*
Standard†	< 100	< 100	< 5	< 15	< 5	< 5

† GB5085.3-2007.
* Undetectable.

and As analysis of all samples and the detection limits set by the standard GB5085.3-2007 [14]. It can be seen that all data in Table 5 are lower than the detection limits in China, suggesting that there were no notable hazardous effects that could cause to potential environmental and human health. The obtained leaching concentrations from S(4-5) and S(4-10) samples were 37.8 mg/l and 21.9 mg/l for Cu, 47.9 mg/l and 31.6 mg/l for Zn, 2.8 mg/l and 2.1 mg/l for Pb, 8.5 mg/l and 6.3 mg/l for Cr, 4.7 mg/l and 4.2 mg/l for Ni, 0.9 mg/l and 0.2 mg/l for As, respectively. It can be observed that at higher amounts of SBSM addition the immobilization was more efficient. A similar leaching behaviour could be observed for S(5-5) and S(5-10) samples. This may due to the inherent alkalinity of SBSM. Besides, the results improved when the sulphoaluminate cement clinker content increased. It can be inferred that ettringite was also a possible solidification matrix since it has been found the major hydration product in hydrated samples. In fact, the potential contributions of ettringite phase in fixing heavy metals had been described [15, 16].

CONCLUSIONS

The slag-based solidification material incorporating sulphoaluminate cement clinker was studied for the solidification and stabilization of sewage sludge. The addition of sulphoaluminate cement clinker played an important role in the binder-sludge solidification systems and enhanced the SBSM-based solidification/stabilization performance. X-ray diffraction and scanning electron microscopy analysis revealed that the increase of sulphoaluminate cement clinker content in SBSM facilitated the formation of crystalline phases such as ettringite, which were able to fill the pores of the solidified pastes and lead to a denser microstructure making a contribution to the strength development. In addition, assessment of environmental compatibility of the final products indicated that the concentration of heavy metals in the leachates were below the detection limits (GB5085.3-2007) set in China. It could be concluded the slag-based solidification materials incorporating sulphoaluminate cement clinker is a good binder for stabilizing the sewage sludge. Further studies are also needed to determine the effect of organic matters in sludge on mechanical and leaching behaviour during solidification process.

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