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Experimental study on the modified dehydration and solidification/stabilization for desulfurization sludge

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ABSTRACT

Desulfurization sludge is generally characterized by high moisture content and high heavy metal content, leading to difficulty in co-landfilling treatment. This study presents a new type of sludge modification to reduce the moisture content of desulfurization sludge and a new type of curing agent to reduce the leaching concentrations of heavy metals. The moisture content could be reduced to less than 60%. The leaching concentrations of all heavy metals measured by the acetic acid buffer solution method could be reduced less than the standard limits.

Keywords: Desulfurization sludge; Modified dehydration; Solidification/stabilization

1. Introduction

Power plants use flue gas desulfurization (FGD) systems to control sulfur dioxide emissions from the flue gas generated in the plants' boilers. Wet flue gas desulfurization (WFGD) scrubbers are the most common type of FGD system with a share of more than 80% of the total installed FGD capacity worldwide [1], and limestone is definitely the predominant sorbent because of the ease of obtaining and its low cost [2]. Limestone and water react with sulfur dioxide to produce calcium sulfite. Given that the disposal of sulfite sludge is problematic, the plant injects air into the reaction tank and vigorously mixes the slurry to oxidize the calcium sulfite to gypsum [3]. The scrubber recycle pumps pump the slurry from the reaction tank to various spray levels within the FGD scrubber. The plant continuously recirculates the slurry in the FGD scrubber. When the percent solids or the chlorides concentration in the slurry reach a certain high set point in the reaction tank, WFGD must use the scrubber blowdown pumps to remove some of the wastewater from the scrubber [4]. Therefore, desulfurization wastewater, which is typically acidic, highly saline solutions containing varying quantities of suspended solids, chlorides, and heavy metals, is the most important waste generated by the WFGD system.

Desulfurization wastewater must be treated before discharge or recycling. Chemical precipitation is the most widely used process for desulfurization wastewater treatment [5]. Chemicals are added to the wastewater to alter the physical state of dissolved and suspended solids to facilitate settling and removal of the solids. $Ca(OH)_2$, organic sulfur reagent (TMT-15), and flocculants (such as PAM or $FeCl_3$) are the most commonly used chemicals. Heavy metals in the desulfurization wastewater are transferred to the sludge in the form of precipitates of hydroxides and sulfides. Then, the wastewater is transported into the clarification tank, where it is settled down by gravity. The supernatant liquid is adjusted to pH 6–8 by acid and discharged. The sludge is the terminal waste in the WFGD system [6,7].

Desulfurization sludge is a typical inorganic sludge, whose main component is gypsum, including traces of heavy metals such as mercury (Hg), copper (Cu), zinc (Zn), chromium (Cr), lead (Pb), nickel (Ni), and cadmium (Cd). These heavy metal elements restrict the use of desulfurization sludge in agriculture, because their

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accumulation is harmful to the environment, particularly to the food chain [8]. The most common treatment is disposal in landfills with strict environmental standards. Leaching concentrations of heavy metals regulated by the Chinese national standard [9] are shown in Table 1. Furthermore, desulfurization sludge contains a high moisture content, which significantly increases the transportation difficulty. The moisture content of the sludge must be less than 60% for co-landfilling regulated by the Chinese national standard GB/T 23485-2009 [10].

Therefore, this paper presents several new types of sludge modification and curing agent to reduce the moisture content and leaching concentrations of heavy metals. These chemicals could be added to the flocculating clarifier during the current chemical precipitation processes. The addition of a small amount of chemicals could reduce the binding force between sludge particles and water molecules so that the sludge dehydration capability is improved. The results showed that the moisture content could be reduced to less than 60%. The leaching concentrations of all heavy metals measured by the acetic acid buffer solution method could be reduced less than the standard limits.

2. Experimental method

2.1. Sampling and measuring

Two kinds of desulfurization sludge were used in the experiment, which were taken from two power plants in Nanjing and Guangzhou, namely NJ sludge and GZ sludge, respectively. Chemical precipitation methods were used to treat the desulfurization wastewater in the two plants. However, the sludge dehydration equipment used in Nanjing's plant was a frame filter press, and that in Guangzhou's plant was a spiral machine.

The physical and chemical properties of the sludge samples were mainly analyzed by the following methods:

(1) Moisture content was measured according to the method proposed in the Chinese industry standard CJ/T221-2005 [11]. The sample was dried to a constant weight at 103°C, and the reduced weight was calculated as the sludge moisture weight.
(2) Crystal water content was measured according to the method proposed in the Chinese national standard GB/T5484-2012 [12]. The sample was dried to a constant weight at 45°C, and the reduced weight was calculated as the crystal water weight.
(3) The specific resistance to filtration (SRF) and capillary suction time (CST) were measured by a professional measuring instrument.
(4) Chemical structure and composition were analyzed by X-ray diffractometry (XRD) and X-ray fluorescence.
(5) Morphology was observed by scanning electron microscopy (SEM).
(6) The leaching concentrations of heavy metals were measured by two methods: (1) the sulfuric acid and nitric acid method proposed in the Chinese industry standard HJ/T299-2007 [13] and (2) the acetic acid buffer solution method proposed in the Chinese industry standard HJ/T300-2007 [14]. The sulfuric acid and nitric acid method simulated the effect of acid rain on the leaching of heavy metals, whereas the acetic acid buffer solution method simulated the effect of leachate on the leaching of heavy metals under the condition of co-landfilling with organic municipal waste. Most concentrations of heavy metals were determined by inductively coupled plasma mass spectrometry. The concentration of Hg was determined by atomic absorption spectrometry.

Table 1
Leaching concentrations of heavy metals regulated by the Chinese national standard GB8978-1996 [9] (mg/L)

Heavy metals	Discharge limits
Hg	0.05
Cu	0.5
Zn	2.0
Pb	1.0
Cd	0.1
As	0.5
Ni	1.0
Cr	1.5

2.2. Modified dehydration method

The sludge samples were diluted with water and reverted to the original state with moisture content of 90%. Then, the modification agents were added to the diluted sample. The weight of the agents was 5% to 55% of the weight of sludge sample. The modified samples were pressure-filtered using a laboratory frame filter press. The dehydration capability of the sludge before and after modification was measured by the methods described in section 2.1.

The modification agents were prepared by the grinding method and were mainly composed of slag, and a small amount of gypsum, clinker and active stimulant. The raw materials were easily available and at low cost. The modification agents could adsorb and bridge the sludge particles, causing the fine sludge particles to agglomerate and form more gaps, such that the water dispersed in the sludge particles could be easily detached.

2.3. Solidification/stabilization method

The sample sludge, curing agent and water were stirred and mixed uniformly. Then, the mixture was added to a cube mold (4 cm * 4 cm * 4 cm) to be cured for 7 and 28 d. Given the weak water absorption of the NJ sludge, the high water ratio increased the fluidity of mixture and the solidification/stabilization (S/S) solid was difficult to mold. Given the strong water absorption of the GZ sludge, the low water ratio causes premature condensation and decreased the passivation effect on heavy metal. Therefore, the NJ sludge, curing agent and water were mixed at mass ratios of 52%, 15%, 33%, respectively, whereas the GZ sludge, curing agent and water were mixed at mass ratios of 43%, 13%, 44%, respectively.

Three kinds of curing agents were used in this study, namely, Ordinary Portland Cement 32.5, self-developed HAS curing agent (composed of 80% power plant fly ash, 3% activator and a certain amount of excipients), and self-developed M curing agent (composed of slag, clinker, master batch, etc.).

3. Result and discussion

3.1. Sample analysis

The physical and chemical properties of the NJ sludge and GZ sludge are summarized in Tables 2 and 3. The organic and gypsum contents (detected as CaO and SO_3) of the two samples were high, which was different from that of municipal sludge. The moisture content of the NJ sludge was low, which could be attributed to the lower content of Cl^-, reducing the blockage between gypsum and other grains. By contrast, the moisture content of the GZ sludge was high and exceeded the limits for co-landfilling.

Figs. 1 and 2 show the SEM images of the NJ sludge and GZ sludge, respectively. The particle size of the NJ sludge was smaller than that of the GZ sludge. The structure of the NJ sludge was compact with a few voids and had a large number of sheet-shaped particles. The structure of the GZ sludge was relatively loose and had a large number of rod-shaped particles. The loose crystal structure led to an increase in the contents of interstitial and crystal water, which in turn led to high moisture content.

The leaching concentrations of heavy metals measured by the sulfuric acid and nitric acid method and the acetic acid buffer solution method are summarized in Table 4. The concentrations measured by the sulfuric acid and nitric acid method were lower than by the acetic acid buffer solution method. This finding indicates that the heavy metals in the desulfurization sludge were difficult to leach out under the natural rainfall condition. However, some heavy metals, such as Hg, Zn, Cd, Ni and Cr, might leach out and exceed the standard limits under the condition of co-landfilling with organic municipal waste. In particular, the concentration of Cd measured by the lattice method was 10 times higher than the standard limit for the NJ sludge, whereas the concentration of Hg is 10 times higher than the standard limit for the GZ sludge.

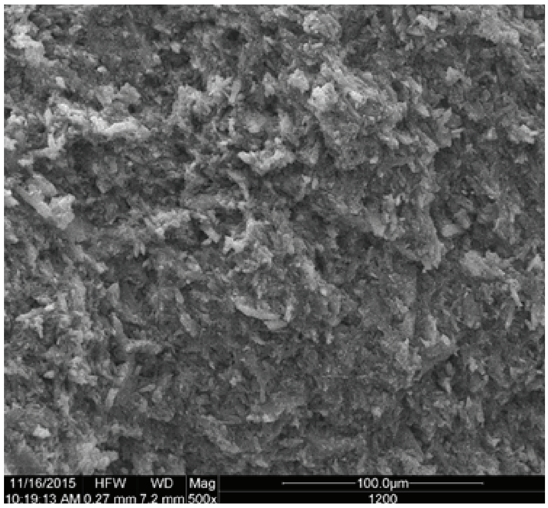


Fig. 1. SEM image of the NJ sludge.

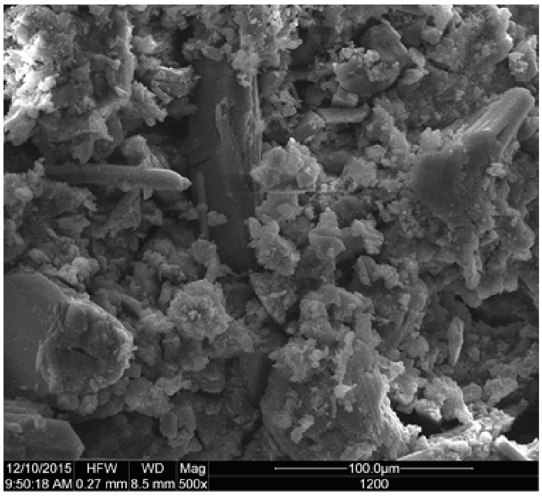


Fig. 2. SEM image of the GZ sludge.

Table 2
Physical and chemical properties of NJ sludge and GZ sludge

Properties	Moisture	Density	Organic	pH	Crystal water
NJ sludge	43.43%	1.53 g/cm^3	2.62%	8.236	1.44%
GZ sludge	76.21%	1.33 g/cm^3	9.34%	8.434	5.61%

Table 3
Analysis of the chemical composition of the samples

Component	CaO	SO_3	MgO	Al_2O_3	SiO_2	K_2O	Cr_2O_5	MnO
NJ sludge	37.50	49.04	1.10	2.59	5.47	0.352	0.014	0.505
GZ sludge	21.61	33.59	9.293	5.63	9.14	0.106	0.049	0.075
Component	Fe_2O_3	NiO	CuO	ZnO	CO_2	Cl	F	
NJ sludge	1.04	0.007	0.037	0.031	–	0.878	2.07	
GZ sludge	2.13	0.007	0.032	0.021	0.73	1.14	15.1	

Table 4
Leaching concentrations of heavy metals measured by the sulfuric acid and nitric acid method and acetic acid buffer solution method

Heavy metal	Sulfuric acid and nitric acid method		Acetic acid buffer solution method	
	NJ sludge (mg/L)	GZ sludge (mg/L)	NJ sludge (mg/L)	GZ sludge (mg/L)
Hg	0.016	0.043	0.012	0.122
Cu	<0.01	<0.01	0.25	0.088
Zn	<0.01	<0.01	7.14	3.53
Pb	<0.01	<0.01	0.12	0.038
Cd	<0.01	0.038	1.13	0.21
As	<0.01	<0.01	0.03	0.048
Ni	<0.01	<0.01	1.33	1.57
Cr	0.030	<0.01	0.21	1.98

3.2. Modified dehydration

Fig. 3 shows that the SRF and CST of the GZ sludge change with the addition of the modification agent. The SRF was reduced with the addition of the modification agent. However, the downward trend was not obvious when the amount added was more than 40% of sludge sample. The CST reached its minimum value when the amount added was approximately 30%. Thus, the most suitable amount of addition was approximately 30%–40%.

The effects of the addition of the modification agent and the filter pressure on the moisture contents of the GZ sludge are summarized in Table 5. The moisture content of the sludge without the addition of modification agent was 66.8%, which was slightly lower than that of the sampled sludge. The dehydration capability of the high-pressure frame filter was more efficient than of the spiral machine used in the GZ power plant, but it exceeded the limits for co-landfilling. The moisture content of the sludge decreased significantly with the addition of the modification agent and decreased with the filter pressure. The minimum could be reduced to 52.8% to meet the requirement for co-landfilling.

Fig. 4 shows the SEM image of the modified GZ sludge. Compared with that shown in Fig. 2, the particle structure of modified sludge was more suitable for dehydration. The sludge particles were cemented because of the amorphous glassy colloid produced by the hydration reaction, resulting in a compact particle structure with only a few voids and a uniform particle size.

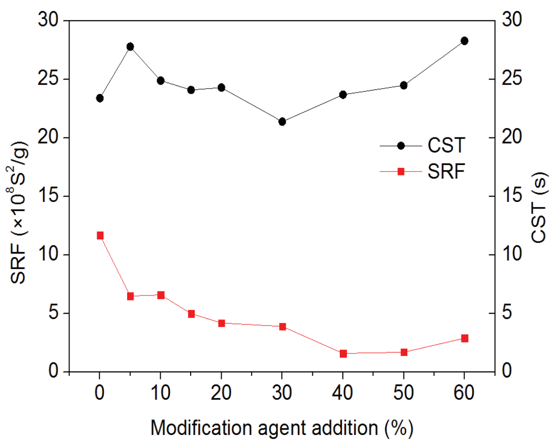


Fig. 3. SRF and CST of the GZ sludge change with the addition of modification agent.

Table 5
Effects of the addition of the modification agent and the filter pressure on the moisture contents of the GZ sludge

Filter pressure (kPa)	700	260	500	700
Addition of the modification agent (%)	0	30	30	30
Filter (min)	100	100	100	100
Moisture (%)	66.8	59.4	55.3	52.8

3.3. Solidification/stabilization

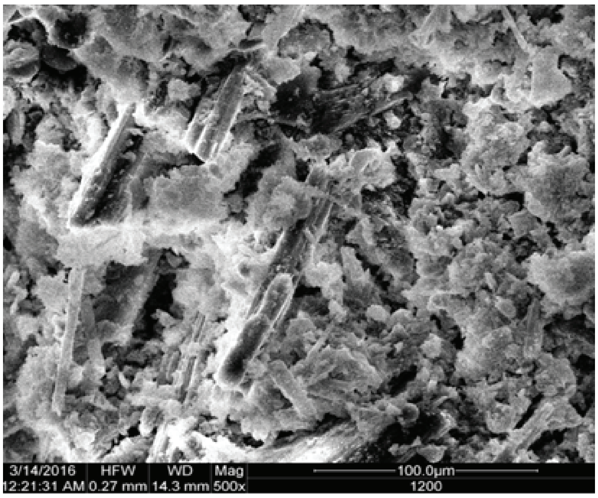
The compressive strength of S/S solid using different curing agents is summarized in Table 6. A high compressive strength, which is beneficial to backfilling and resource utilization, could be obtained using the cement and HAS.

The leaching concentrations of heavy metals measured by the acetic acid buffer solution method are summarized in Tables 7 and 8. The concentrations of heavy metals were reduced significantly. HAS was the most effective curing agent for the solidification of heavy metals. The leaching concentration of Ni for the S/S solid of the NJ sludge could be reduced to less than the standard limit after curing for 7 d with HAS, and the leaching concentrations of Zn and Cd were close to the standard limits. The leaching concentrations of all heavy metal for the S/S solid of the GZ sludge could be reduced to less than the standard limit after curing for 7 d with HAS.

As shown in Table 9, the leaching concentrations of all heavy metal for the S/S solid of the NJ sludge could be reduced to less than the standard limits after curing for 28 d with HAS.

The XRD spectra of the S/S solid of the NJ sludge and GZ sludge after curing with HAS are presented in Figs. 5 and 6, respectively. Most heavy metals could combine with aluminosilicates to form stable aluminosilicate compounds.

The S/S mechanism included a variety of physical and chemical process, such as physical encapsulation, physical adsorption, metathesis precipitation and isomorphous



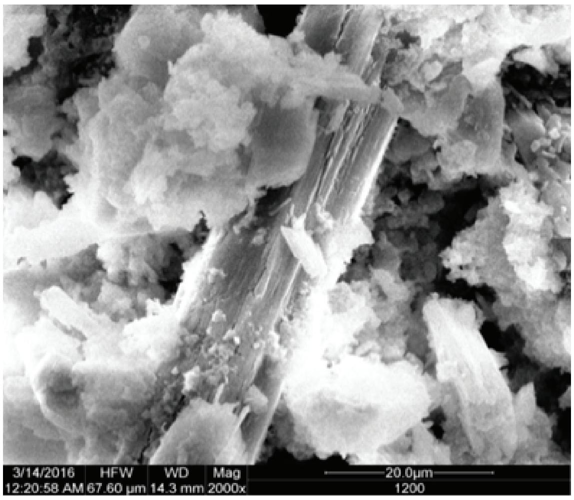


Fig. 4. SEM image of modified GZ sludge.

Table 6
Compressive strength of S/S solid using different curing agents

Curing agent	NJ sludge (MPa)	GZ sludge (MPa)
Cement	1.53	0.83
HAS	1.41	0.94
M	0.98	0.31

substitution. The hydration reaction of the curing agent during solidification produced a large amount of ettringite and hydrated calcium silicate. Ettringite was a stomatal structure with a high specific surface area and could adsorb heavy metal ions. Moreover, the mineral had a stable crystal structure, which could inhibit the leaching of heavy metals through isomorphous substitution. The S/S mechanism of Ni and Zn was the typical isomorphous substitution. The Ni or Zn ions could replace the calcium ions in the crystals of calcium aluminosilicate and calcium carbon aluminate and produce nickel aluminosilicate, nickel carbon aluminate, zinc aluminosilicate, or zinc carbon aluminate.

Table 7
Leaching concentrations of heavy metals measured by the acetic acid buffer solution method for the S/S solid of the NJ sludge after curing for 7 d (mg/L)

Curing agent	None	Cement	HAS	M
Zn	7.14	2.43	2.21	2.83
Cd	1.13	0.57	0.24	0.58
Ni	1.33	0.86	0.89	0.91

Table 8
Leaching concentrations of heavy metals measured by the acetic acid buffer solution method for the S/S solid of the GZ sludge after curing for 7 d (mg/L)

Curing agent	None	Cement	HAS	M
Zn	3.53	1.31	0.53	2.53
Cd	0.21	0.201	0.054	0.102
Ni	1.57	0.865	0.62	0.91
Cr	1.98	0.65	0.61	1.27
Hg	0.122	0.083	0.041	0.00036

Table 9
Leaching concentrations of heavy metals measured by the acetic acid buffer solution method for the S/S solid of the NJ sludge after curing for 28 d (mg/L)

Curing agent	None	HAS
Zn	7.14	1.03
Cd	1.13	0.06
Ni	1.33	0.52

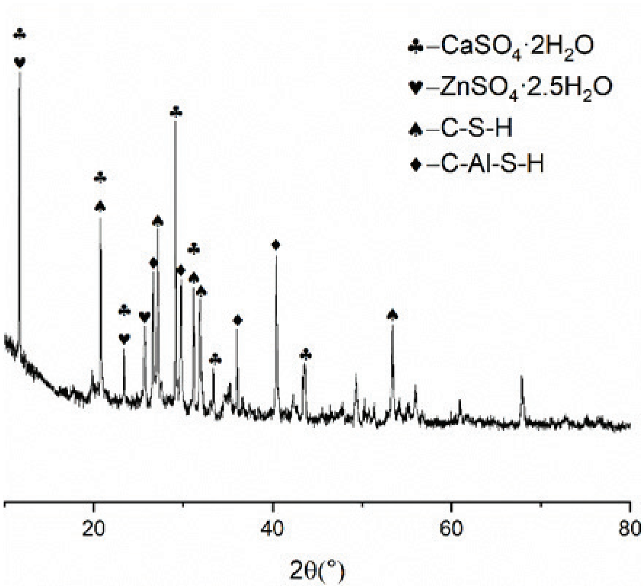


Fig. 5. XRD spectra of the S/S solid of the NJ sludge after curing with HAS.

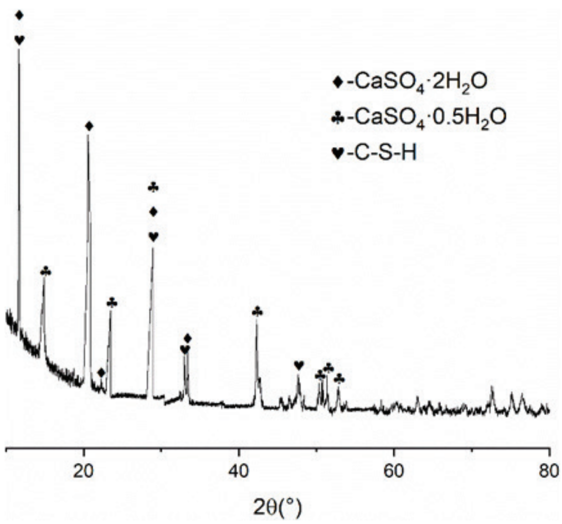


Fig. 6. XRD spectra of the S/S solid of the GZ sludge after curing with HAS.

4. Conclusion

(1) The leaching concentrations of heavy metals from desulfurization wastewater measured by the sulfuric acid and nitric acid method were lower than that measured by the acetic acid buffer solution method. Some heavy metals, such as Hg, Zn, Cd, Ni and Cr, might leach out and exceed the standard limits for the acetic acid buffer solution method.
(2) The modification agent mainly composed of slag could significantly reduce the moisture content of desulfurization sludge to less than 60%.
(3) HAS was the most effective curing agent for the solidification of heavy metals. The leaching concentrations of all heavy metals measured by the acetic acid buffer solution method could be reduced to less than the standard limits.

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