Study on the emission characteristics and mechanism of sulfur-containing gas during sludge pyrolysis at low temperature

Shuo Shang
Xi'an University of Architecture and Technology
Haihong Fan (fanhaihongfu@163.com)
Xi'an University of Architecture and Technology
Binbin Li
Xi'an University of Architecture and Technology
Lin Li
Xi'an University of Architecture and Technology
Zhou Li
Xi'an University of Architecture and Technology

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Abstract

The effects of temperature, time, and calcium-based ultrafine powder on sulfur-containing gas in the sludge drying process were examined through experiments, and effective measures to control the release of sulfur-containing gases such as CS_2, H_2S, and SO_2 were proposed. Experimental results showed that the drying temperature of sludge should be controlled below 250°C, and the drying duration should be kept within 1 min. Additionally, the release amount of three gases released was small. When the addition amount of calcium-based powder added reached 20% of the original sludge mass fraction, the concentration of sulfur-containing gas released was 59.81 mg/m^3, 94% lower than that of the dry pure sludge gas. After absorption by calcium-based powder, there are almost no sulfur-containing organic compounds and sulfur-containing gases. The research results provide a direction for the selection of pyrolysis sludge treatment technology, which is conducive to control the discharge of harmful gases.

1. Introduction

With the acceleration of urbanization, the output of sludge continues to rise and reach 60–90 million tons by 2020 in China (Liu et al., 2020; Yin et al., 2019). It is crucial to find appropriate ways to reuse these wastes to reduce their impacts on environment. The most common disposal options of sewage sludge are landfill, land diffusion, and incineration (Kelessidis, A and Stasinakis, A. S., 2012; Svanström, M et al., 2005).As the moisture content of sludge is ~ 80%, a drying process is required for the harmless reduction and resource treatment of sludge (Lu et al.,2014; Liu et al.,2012). However, the inevitable odor emissions that are unavoidable during drying may raise concerns about environmental pollution and human health. There are eight kinds of odorous gases that must be strictly controlled and detected in the emission standard for odor (GB 14554-93). Five of them are sulfur-containing compounds, namely, H_2S, CH_3SH, C_2H_6S, CS_2, and $C_2H_6S_2$. The influence of sulfur on sludge in the treatment and disposal process should not be underestimated, such as the corrosion of infrastructure caused by sulfur gas emission, the speciation regulation of metals (such as Cu, Zn and Ag), and the undesirable gases produced in the biological treatment process (Luo et al., 2014; Donner et al., 2011; Zhang et al., 2008). Therefore, we need to pay attention to the release and control of sulfur gas in sludge pyrolysis.

S in wasted sludge is primarily constituted of S-containing biomolecules (e.g., amino acids with S-containing side chains), inorganic sulfides, and insoluble sulfate (Lin et al., 2014; Du and Parker, 2013; Dewil et al.,2008; Svanström et al., 2005). Compared with most biomass, the characteristics of sludge related to thermochemical conversion during pyrolysis are more complex and different (Thipkhunthod et al., 2007). Liu et al. (2015) showed that the release of sulfur-containing odor gases from sludge comes from two processes: the first is mainly the inorganic sulfur release process of free sulfur-containing gas molecules from inorganic sulfur, and the second is the decomposition of sulfur-containing organic matter caused by the heating of sludge and the release of organic sulfur, which produces sulfur-containing polluting gases. During pyrolysis, aliphatic-S and sulfonate were preferentially degraded at low temperature (below 350°C) and sulfate was thermochemically reduced at a temperature above 450°C,

while metal sulfides (up to 27%) and thiophenes (up to70%) were increasingly formed (Huang et al.,2021). If these sulfur-containing gases are directly discharged without control and treatment, it will cause great harm to human health and life. It is reported that the main sulfur-containing gases released during a sludge drying process were H_2S and SO_2, and they accounted for 82.4% of the total gas released (Liu et al., 2012). Cheng et al. (2017) selected two representative organic sulfides—BS and DHS—to conduct pyrolysis experiments of sludge and NaOH at different temperatures. They discussed the organic sulfide model after adding alkali and analyzed its transformation effect. In particular, Liu et al. (2014a) proposed that CaO could significantly improve the conversion of sludge into coke and combustible gases (especially H_2 and CO) and explained the effect of CaO on sulfur conversion during pyrolysis. It is found that adding CaO to sludge will result in deoxidation reaction, reducing O-containing compounds in organic matter and adsorbing CO_2 from noncondensable gas (Udayanga et al., 2019).

Several scholars are currently interested in the release mechanism of sulfur gas produced during a drying process; however, the absorption and inhibition mechanism of sulfur gas release have not been studied in-depth, and there are no effective control methods for the odor gases released in a drying process. This study focuses on the production technology of “Using a cement kiln tail system to atomize and dry sludge—cement rotary kiln to incinerate and dry sludge” (proposed by Powder Engineering Institute of Xi’an University of Architecture and Technology) and explores how different factors influence odor emission. The research results have a new understanding of the release characteristics of sulfur-containing gas in the process of sludge low-temperature pyrolysis, and the measures to control the emission of sulfur-containing gas have been proposed.

2. Experimental

2.1. Experimental materials and properties

Table 1 shows the elemental composition of the sludge and Table 2 shows the chemical composition of calcium-based powder used in the experiment. CBP is obtained from the flue gas produced by the kiln of a cement plant. The maximum particle size of CBP is 12 μm, the average particle size is 3.12 μm, and the particle size of 90% of the powder is less than 6.88 μm.

Table 1
Element Composition of Sludge (RS)%

Element	C	H	O	N	S	Si	Ca	Al	Fe	K	Mg
Composition	30.65	6.14	20.13	3.96	1.81	14.45	6.25	5.7	8.84	3.24	2.18

Table 2
Chemical Composition of Calcium Based Powder (CBP)%

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Loss	Sum
13.87	2.52	1.74	42.56	2.18	0.68	0.06	0.48	35.02	99.11

2.2. Experimental instruments and methods

The experimental system shown in Fig. 1(a) was used to study the effect of sludge temperature and time on the release of sulfur gas.N_2 is used as a carrier for gas transport gas. After the sludge is dried, the content of CS_2, H_2S, and SO_2 in the absorption solution is measured by a spectrophotometer method, and the total amount of each gas released by the quantitative sludge is calculated. The experimental schemes of temperature and time are as follows:

1. Temperature effect experiment: 0.5 g of sludge was put into a 250 ml three-port flask, and the temperature of the heating jacket was controlled at 150°C, 200°C, 250°C, 300°C, and 350°C, respectively, for 10 min.
2. Time effect experiment: 0.5 g sludge was put into a 250 ml three-port flask, the temperature of the heating jacket was adjusted to 250°C, and the heating time was 0.5, 1, 1.5, 2, 3, 4, 5, and 10 min, respectively.

The influence of calcium-based ultrafine powder on sulfur-containing gas is shown in the sludge drying experimental system in Fig. 1(b). CVT-1600PC sintering analyzer is the main equipment used to test and record the change of sludge quality during the drying process. The system temperature is controlled by the control system operated by the PC. The dried gas is collected and stored in a gas sampling bag for detecting gas concentration, except for NH_3. Specific experimental steps are as follows:

The material RS and CBP were mixed in order of 0, 20:1, 10:1, and 5:1 and then put into the sintering analyzer for testing. At a room temperature of 20.8°C, the air in the furnace is pumped to 0.06 MPa using a vacuum system and then heated to 200°C and 250°C at a heating rate of 5°C/min for 60 min. The high-temperature mixed gas is transferred through the upper exhaust valve of the sintering analyzer and collected after cooling and drying. The concentration of H_2S gas is determined using gas chromatography. Additionally, the gas released from pure sludge heated and dried at 300°C was collected and adsorbed using CBP. The concentration of H_2S gas was determined and the change of raw material quality was recorded.

3. Results And Discussion

3.1. Effect of temperature on odor emission

As shown in Fig. 2, the release characteristics of main sulfur-containing odors CS_2, H_2S, and SO_2 with drying temperature were measured via the spectrophotometer method.

It shows that although the release of CS_2 is not large during the drying process, the growth rate with increasing temperature is large because CS_2 is produced by the reaction of CH_4 and FeS and the reaction rate increases with increasing temperature; however, the peak temperature of CS_2 formation is 500°C. In the temperature range of 150°C–350°C and 10 min, the release of CS_2 increased from 17 to 27.2 μg/g,

which is an increase of 62.5%. When the temperature is lower than 200°C, the release amount of H_2S gas released is less than 50 μg/g, whereas when the temperature is higher than 200°C, the release amount of the gas released rapidly increases sharply, reaching 386.25 μg/g at 250°C. This is because of the large amount of organic acids produced in this temperature range, which transforms inorganic sulfides into H_2S or decomposes a large amount of organic sulfides(Ros et al., 2006). When the temperature rises above 250°C, the growth of H_2S becomes more gradual and, eventually, constant. According to the influence of drying temperatures on SO_2 emission, when the temperature is less than 250°C, SO_2 release is slow and less intense. When the temperature reaches 300°C, SO_2 emission increases from 88.74 to 307.81 μg/g, an increase of ~300%. This is because a large amount of SO_2 is produced by the decomposition of sulfur-containing aliphatic compounds at 300°C, and then, with the increase in temperature, the release amount of SO_2 increases growth is extremely slow.

To conclude, controlling the drying temperature of sludge should be controlled below 250°C reduces the release of the three gases is less.

3.2. Effect of time on odor emission

It can be seen from Fig. 3 that the release characteristics of the main sulfur gases CS_2, H_2S, and SO_2 with drying time were measured via the spectrophotometer method. The figure shows that as time passes, the amount of the three gases released increases continuously, with the gas release amount of gas released increasing significantly at 30 s and tending to be constant at 10 min, and there is almost no gas was released afterward. This is due to heat transfer between the materials as the sludge is stacked in the three beakers. It takes a certain amount of time to heat the sludge to be heated from room temperature to 250°C. The sludge release rate is low during this time. When the sludge temperature reaches 250°C, the gas release rate increases continuously, releasing a large amount of gas. Fig. 3 shows that the release of CS_2 and H_2S is mainly concentrated in the first 3 min, with the release of C_2S and H_2S being 20.84 and 339.42 μg/g, respectively, accounting for 93.2% and 93.4% of the total release. At this temperature for CS_2, most CH_4 produced by sludge pyrolysis reacts with FeS within 3 min and is consumed completely. For H_2S, this is mainly due to the complete decomposition of most sulfur-containing organic acids. When the time is 2 min, the SO_2 release amount of SO_2 released can reach 77.58 μg/g, accounting for 92.4% of the total release, and then, the release rate rapidly decreases. This is because the sulfur-containing aliphatic group that can be decomposed in the sludge decomposes almost completely in 2 min at a temperature of 250°C.

3.3. CBP inhibits the release of sulfur gas

Fig. 4 shows the variation of H_2S concentration during sludge drying with different CBP contents. The concentration of H_2S in the waste gas decreases significantly as CBP content increases. The concentration of H_2S increases with increasing temperature. The concentration of H_2S in the gas produced by the drying of pure sludge is 1038.62 mg/m^3 at a temperature of 250°C. When 10 wt% CBP

was added, the concentration of H_2S was reduced by 85%; when the mass ratio of CBP to sludge was 1:5, the concentration of H_2S was only 59.81 mg/m^3, which was 94% lower than that of dry sludge gas (1038.62 mg/m^3) without CBP. Additionally, the mixed CBP and pH value of sludge were determined. When the amount of CBP was 10 wt% (CBP:sludge = 1:10), the pH value of sludge increased from 6.5 to 11.1, whereas the concentration of H_2S in the tail gas decreased significantly decreased. The concentration of H_2S was 50.57 mg/m^3 when dried at 200°C.

Previous studies have shown that heat decomposed aliphatic sulfur and aromatic sulfur in sludge, and then, C–S bonds were broken, producing sulfur-containing gas (Zhang et al.,2017a). Additionally, alkali can inhibit the release of sulfur-containing gas during sludge drying, and the stronger the alkalinity, the better the effect (Cheng et al., 2017; Liu et al.,2014b). This is because, at a certain temperature, alkali can promote the oxidation of aliphatic sulfur and aromatic sulfur to sulfoxide and sulfone in sludge, respectively, and eventually sulfonic acid may be produced (Cheng et al., 2017;Tang et al., 2017; Liu et al., 2012) . Moreover, sulfoxide and sulfone almost do not produce sulfur-containing gas during the drying process, and their properties are more stable. Fig. 5 shows that R–S–R uniformly represents aliphatic sulfur and aromatic sulfur. Sulfoxide, sulfone, and sulfonate can be labeled as R–SO–R, R–SO_2–R, and R–SO_3–R, respectively. Because of the low bond dissociation energy of the C–S bond in R–S–R compounds, the C–S bond is easy to cleave at low temperatures to form sh-radical and then form H_2S. Following the addition of alkali, a series of reactions, as shown in Fig. 5, occur because of the action of OH^-. Finally, hexavalent sulfur sulfonic acids are formed through nucleophilic addition, which greatly inhibits the release of H_2S and other gases. Some scholars have proposed that the active components of the conditioner added in the sludge can react with some free groups in the sludge to form precipitation, so that most of the sulfur elements are fixed in various solid compounds, and the relative ratio of sulfates and inorganic sulfides is rapidly increased sharply (Lens et al., 1998). Thus, the addition of CaO can cause a series of complex physical and chemical reactions of sulfur-containing substances in sludge, forming chelates with high stability and nonpolar calcium salts.

Additionally, alkalinity inhibits the growth of sulfate-reducing bacteria (SRB). SRB are anaerobic bacteria that can reduce elemental sulfur or sulfate to H_2S and other sulfur-containing gases. Thus, SRB activity is crucial for sulfate, sulfite, and organic sulfide in sludge to produce sulfur-containing gas (Dias et al., 2008). Weng et al. (2015) found that the optimal PH value for SRB growth is 7.0. Hence, the release of H_2S and SO_2 can be inhibited by controlling the pH value of the sludge drying process and inhibiting the growth of SRB. To conclude, the addition of calcium-based ultrafine powders, on one hand, uses the strong oxidizing hydroxyl group to change the proportion of all types of organic sulfur in the sludge; on the other hand, it provides an alkaline environment and changes its internal biochemical conditions, thereby inhibiting the release of sulfur-containing gases.

3.4. Absorption and adsorption of sulfur-containing gas by CBP

Some characteristic gases collected in the airbag are shown in Tables 2 and 3. Tables 2 and 3 show that a large number of alkanes, alkenes, alkynes, CH compounds, alkanes, and alkanols are produced when the sludge is decomposed at 300°C. According to the chemical composition of gases in Table 3, the sludge is decomposed without any treatment to produce various amino acids, organic compounds containing nitrogen and sulfur, and various sulfur-containing gases, such as H_2S, CS_2, and COS. Comparing the gas composition in Table 3, there are almost no sulfur-containing organic compounds and sulfur-containing gases. After CBP adsorption, the types of gas collected in the airbag did not significantly change much, but the substances containing S and N in Table 3 were reduced compared with those in Table 3, indicating that the adsorption of sulfur-containing gas in sludge using calcium-based ultrafine powder was very obvious, which helped control the emission of odor gas. The odor of sludge particles is obvious, but when the particles are completely coated by CBP, the odor is hardly emitted. This is because the odor is covered by a large amount of powder on the surface of the sludge particles, preventing it from passing through the surface fly ash layer.

Calcium-based desulfurizers commonly used in the market now include CaO, $Ca(OH)_2$, and $CaCO_3$ (Zhang et al., 2017b), and the main component of CBP is CaO, which can absorb sulfur gases such as H_2S and SO_2. Second, CaO reacts with SO_2 to form $CaSO_4$ to realize desulfurization and sulfur fixation . The chemical reactions that occur are as follows:

$SO_2+CaO \rightarrow Ca\ SO_3$	(1-3)
$SO_2+H_2O \rightarrow H_2SO_3$	(1-4)
$CaO+ H_2SO_3 \rightarrow CaSO_3+ H_2O$	(1-5)
$CaSO_3 + 1/2O_2 \rightarrow CaSO_4$	(1-6)

Because of the evaporation of aliphatic compounds in the process of sludge drying at 200°C–450°C, water in the sludge drying process is not easily lost. The produced H_2S can be partially ionized in the presence of water, and H^+ and HS^- can be generated by one-step ionization, and a small amount of HS^- can be ionized in two steps to form S^{2-}; with CaO, the amount of H_2S can be ionized to form S^{2-}, and by increasing its content, it reacts with water to release heat and form $Ca(OH)_2$. The alkalinity in the system increases gradually, neutralizing more H^+, thus promoting the ionization of H_2S and producing more S^{2-}, which can react with CaO to produce CaS or react with hydrated $Ca(OH)_2$ to form CaS; SO_2 produced from organic sulfur decomposition will also react with $Ca(OH)_2$ to form $CaSO_3$, and $CaSO_4$ is more stable under oxidation conditions (Karatepe et al., 1998). Other experimental results (Liu et al., 2012)also showed that when the sludge was dewatered with CaO as a conditioning agent, alkaline CaO promoted the conversion of most H_2S and SO_2 to CaS and $CaSO_4$, resulting in a rapid increase in the relative ratio of sulfate to inorganic sulfide. In particular, the addition of CBP, on one hand, produces sludge in an alkaline environment, and the acid-free H_2S and SO_2 molecules can react with CaO and $Ca(OH)_2$ to form stable calcium salt, thus reducing the inorganic sulfur release process in the subsequent drying process;

on the other hand, the alkaline calcium materials can absorb the release of sulfur-containing organic matter during the sludge drying process. Acid gases such as H_2S and SO_2 can further reduce the sulfur released during the drying process.

Generally, the chemical process of absorption must be accompanied by the adsorption process. Calcium-based superfine powder can absorb and adsorb sulfur-containing gas at the same time. The main components of CBP powder are SiO_2 and $CaCO_3$, and it also contains a lot of amorphous SiO_2 and Al_2O_3, which can be regarded as a type of pozzolanic ash. In the presence of water at normal temperature, properly crushed pozzolan can react with an alkali metal and alkaline earth metal hydrate.

These newly formed hydrated aluminosilicates are usually incomplete crystals, mostly fibrous, with large specific surface area and high-water holding capacity (Deng and Su, 2014). The results show that the reaction of (2-1)–(2-4) changes the surface structure of the powder, increases the specific surface area, improves the pore structure, and improves the pore structure and the gas adsorption effect, whereas the high-water holding capacity increases the humidity of the powder particles and accelerates the reaction on the surface (Sanders et al., 1995). CBP powder may also play a catalytic role, especially the high content of silicon, iron, magnesium, and aluminum, and some trace elements can also promote the absorption of gas (Gong et al., 2019). Additionally, a large number of studies have shown that the potentially active powder and CaO can be digested to form calcium silicate hydrates and form loose porous structure, thus greatly improving the adsorption of sulfur-containing gas.

$Ca(OH)_2 + SiO_2 + H_2O \rightarrow (CaO)_x(SiO_{2)y}(H_2O)_z$	(2-1)
$Ca(OH)_2 + A1_2O_3 + H_2O \rightarrow (CaO)_x(A1_2O_3)_y(H_2O)_z$	(2-2)
$Ca(OH)_2 + A1_2O_3 + SiO_2 + H_2O \rightarrow (CaO)_x(A1_2O_3)_y(SiO_2)z(H_2O)_w$	(2-3)
$Ca(OH)_2 + A1_2O_3 + SO_3 + H_2O \rightarrow (CaO)_x(A1_2O_3)_y(CaSO_3)z(H_2O)_w$	(2-4)

Table 3. Representative gas released by sludge at 300°C

Number	Type	Appearance time (min)	Name	Chemical formula	Molecular weight
1	Hydrocarbon organic matter	0.392	Ketene	C_2H_2O	42.011
		0.815	Oxalic acid	$C_2H_2O_4$	89.995
		2.258	Methanol-D4	CD_4O	36.051
		11.729	(R,R)-Tartaric acid	$C_4H_6O_6$	150.016
		11.729	Butanedioic acid, 2,3-dihydroxy-, [S-(R*,R*)]-	$C_4H_6O_6$	150.016
2	Nitrogenous compounds	0.620	Diazirine	CH_2N_2	42.022
		0.620	Pyrazine, methoxy-, 1-oxide	$C_5H_6N_2O_2$	126.043
		0.815	Dimethylamine	C_2H_7N	45.058
		0.815	Epinephrine	$C_9H_{13}NO_3$	183.09
		0.815	2-Hexanamine, 4-methyl-	$C_7H_{17}N$	115.136
		0.815	2-Propanamine, 1-methoxy-	$C_4H_{11}NO$	89.084
		3.798	2-Amino-1,3-propanediol	$C_3H_9NO_2$	91.063
		6.214	Methyl isocyanide	C_2H_3N	41.027
		10.133	Butane, 1-isocyano-	C_5H_9N	83.073
3	Sulfur-containing substances	0.620	2-Pyrrolidinethione	C_4H_7NS	101.03
		2.258	Hydrogen sulfide	H_2S	33.988
		3.798	Carbonyl sulfide	COS	59.967
		3.798	Ethanone, 1-(5-methylfur-2-yl)-, Thiosemicarbazone	$C_8H_{11}N_3OS$	197.062
		11.729	Carbon disulfide	CS_2	42.011
		11.729	4,4'-Diisothiocyanatostilbene-2,2'-disulfonic acid	$C_{16}H_{10}N_2O_6S_4$	453.942
		11.729	Thiourea	CH_4N_2S	76.01
		11.729	Monoethyl	$C_3H_6S_3$	137.963

	carbonotrithioate		
11.729	Mono-sec-butyl carbonotrithioate	$C_5H_{10}S_3$	165.994
11.729	Mecysteine	$C_4H_{10}ClNO_2S$	151.979
22.729	Monoisopropyl carbonotrithioate	$C_4H_8S_3$	151.979

Table 3. Representative gas components collected by sludge 300°C heating sampling bag

Number	Type	Appearance time (min)	Name	Chemical formula	Molecular weight
1	Hydrocarbon organic matter	22.153	Cyclobutanol	C_4H_8O	72.058
		22.379	Phthalan	C_8H_8O	120.058
			Benzene, (butoxymethyl)-	$C_{11}H_{16}O$	164.12
2	Nitrogen oxide organic matter	22.379	2-Propanamine, 1-methoxy-	$C_4H_{11}NO$	89.084
		22.153	l-Guanidinosuccinimide	$C_5H_7N_3O_2$	141.054
			l-Alanyl-l-alanyl-l-alanine methyl ester	$C_{10}H_{19}N_3O_4$	245.138
			dl-Alanine ethyl ester	$C_5H_{11}NO_2$	117.079
			Acetic acid, hydroxy[(1-oxo-2-propenyl) amino]-	$C_5H_7NO_4$	145.038
			L-Alanine, methyl ester	$C_4H_9NO_2$	103.063
			Cathinone	$C_9H_{11}NO$	149.084
			Benzenemethanol, 3-hydroxy-.alpha.-[(methylamino) methyl]-, (R)-	$C_9H_{13}NO_2$	167.095
3	Nitrogenous compounds	22.153	n-Hexylmethylamine	$C_7H_{17}N$	115.136
			Amphetamine-3-methyl	$C_{10}H_{15}N$	149.12
			N-Dodecylmethylamine	$C_{13}H_{29}N$	199.23
			2-Heptanamine, 5-methyl-	$C_8H_{19}N$	129.152
			1-Octadecanamine, N-methyl-	$C_{19}H_{41}N$	283.324
		22.397	1-Propanamine, N,2-dimethyl-	$C_5H_{13}N$	87.105
			sec-Butylamine	$C_4H_{11}N$	73.089
			Benzeneethanamine, N-methyl-	$C_9H_{13}N$	135.105

4. Conclusion

Experimental results showed that as the sludge drying temperature increased, more CS_2, H_2S, and SO_2 were released from the sludge, and the release of H_2S and SO_2 rapidly increased at 200°C and 250°C, respectively, indicating that the amount of gas released could be effectively reduced when the temperature was controlled below 250°C. By increasing the sludge drying time, the amount of CS_2, H_2S, and SO_2 released from the sludge increased continuously, and the gas release rate increased first and then decreased. The amount of gas released began to increase significantly at 30 s, and a large amount of gas was released within 3 min, indicating that reducing the drying time can effectively decrease the amount of gas released.

Furthermore, the experimental results show that when the amount of calcium-based ultrafine powder added reached 20% of the original sludge mass fraction, the concentration of sulfur gas released was only 59.81 mg/m^3, which was 94% lower than that of the dry sludge gas without CBP. This is because the CBP provides an alkaline environment, which promotes the conversion of more organic compounds in the sludge into more stable sulfoxides and sulfoxides, and inhibits the growth of sulfuric acid-reducing bacteria, thereby inhibiting the release of H_2S and SO_2. Additionally, the experiment showed that after adding CBP, the number and damage degree of harmful gases in the sludge drying process decreased. H_2S and SO_2 molecules are neutralized by calcium-based ultrafine powder, forming stable calcium salts. Hence, using CBP and sludge to form a coating ball to inhibit and absorb the sludge dry sulfur odor is an effective way to control the emission of odor gases.

Declarations

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Conflicts of interest/Competing interests (include appropriate disclosures)

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

Availability of data and material (data transparency)

All data generated or analysed during this study are included in this published article (and its supplementary information files).

Code availability (software application or custom code)

Not applicable

Authors' contributions

Haihong Fan and Binbin Li contributed to the conception of the study;

Shuo Shang, Lin Li and Zhou Li performed the experiment;

Haihong Fan and Shuo Shang contributed significantly to analysis and manuscript preparation;

Shuo Shang performed the data analyses and wrote the manuscript;

Binbin Li helped perform the analysis with constructive discussions.

Ethics approval (include appropriate approvals or waivers)

Not applicable

Consent to participate (include appropriate statements)

The Author confirms :

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References

1. Cheng S, Qiao Y, Huang J, Cao L, Yang H, Liu H, … Xu M (2017) Effect of alkali addition on sulfur transformation during low temperature pyrolysis of sewage sludge. Proceedings of the Combustion Institute, 36(2), 2253–2261.https://doi.org/10.1016/j.proci.2016.06.124
2. Dewil R, Baeyens J, Roels J, Steene BVD (2008) Distribution of sulphur compounds in sewage sludge treatment. Environ Eng Sci 25(6):879–886. https://doi.org/10.1089/ees.2007.0143

3. Dias M, Salvado JC, Monperrus M, Caumette P, Amouroux D, Duran R, Guyoneaud R (2008) Characterization of Desulfomicrobium salsuginis sp. nov. and Desulfomicrobium aestuarii sp. nov., two new sulfate-reducing bacteria isolated from the Adour estuary (French Atlantic coast) with specific mercury methylation potentials. Syst Appl Microbiol 31(1):30–37. https://doi.org/10.1016/j.syapm.2007.09.002
4. Donner E, Howard DL, Jonge MDD, Paterson D, Cheah MH, Naidu R, Lombi E (2011) X-ray absorption and micro X-ray fluorescence spectroscopy investigation of copper and zinc speciation in biosolids. Environ Sci Technol 45(17):7249–7257. https://doi.org/10.1021/es201710z
5. Du W, Parker W (2013) Characterization of sulfur in raw and anaerobically digested municipal wastewater treatment sludges. Water environment research 85(2):124–132. https://doi.org/10.2175/106143012X13407275694671
6. Deng W, Su Y (2014) Experimental study on agitated drying characteristics of sewage sludge under the effects of different additive agents. J Environ Sci 26(7):1523–1529. https://doi.org/10.1016/j.jes.2014.05.019
7. Gong Z, Wang Z, Wang Z, Fang P, Meng F (2019) Study on the migration characteristics of nitrogen and sulfur during co-combustion of oil sludge char and microalgae residue. Fuel 238:1–9. https://doi.org/10.1016/j.fuel.2018.10.087
8. Huang R, Tang Y, Luo L (2021) Thermochemistry of sulfur during pyrolysis and hydrothermal carbonization of sewage sludges. Waste Manag 121:276–285. https://doi.org/10.1016/j.wasman.2020.12.004
9. Karatepe N, Mericboyu AE, Küçükbayrak S (1998) Effect of hydration conditions on the physical properties of fly ash-Ca (OH) 2 sorbents. Energy Sources 20(6):505–511. https://doi.org/10.1080/00908319808970075
10. Kelessidis A, Stasinakis AS (2012) Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. Waste management 32(6):1186–1195. https://doi.org/10.1016/j.wasman.2012.01.012
11. Lens PNL, Visser A, Janssen AJH, Pol LH, Lettinga G (1998) Biotechnological treatment of sulfate-rich wastewaters. Crit Rev Environ Sci Technol 28(1):41–88. https://doi.org/10.1080/10643389891254160
12. Lin RB, Shih SM (2003) Characterization of Ca (OH) 2/fly ash sorbents for flue gas desulfurization. Powder technology 131(2–3):212–222. https://doi.org/10.1016/S0032-5910(03)00003-2
13. Liu H, Luo GQ, Hu HY, Zhang Q, Yang JK, Yao H (2012) Emission characteristics of nitrogen-and sulfur-containing odorous compounds during different sewage sludge chemical conditioning processes. J Hazard Mater 235:298–306. https://doi.org/10.1016/j.jhazmat.2012.07.060
14. Lu S, Chen L, Huang Q, Yang L, Du C, Li X, Yan J (2014) Decomposition of ammonia and hydrogen sulfide in simulated sludge drying waste gas by a novel non-thermal plasma. Chemosphere 117:781–785. https://doi.org/10.1016/j.chemosphere.2014.10.036

15. Luo L, Xu C, Ma Y, Zheng L, Liu L, Lv J, Zhang S (2014) Sulfur speciation in an arable soil as affected by sample pretreatments and sewage sludge application. Soil Sci Soc Am J 78(5):1615–1623. https://doi.org/10.2136/sssaj2013.11.0506
16. Lin H, Ye C, Lv L, Zheng CR, Zhang S, Zheng L, … Yu X (2014) Characterization of extracellular polymeric substances in the biofilms of typical bacteria by the sulfur K-edge XANES spectroscopy. J Environ Sci 26(8):1763–1768. https://doi.org/10.1016/j.jes.2014.06.017
17. Liu H, Zhang Q, Hu H, Xiao R, Li A, Qiao Y, … Naruse I (2014) Dual role of conditioner CaO in product distributions and sulfur transformation during sewage sludge pyrolysis. Fuel 134:514–520. https://doi.org/10.1016/j.fuel.2014.06.020
18. Liu H, Liu P, Hu H, Zhang Q, Wu Z, Yang J, Yao H (2014) Combined effects of Fenton peroxidation and CaO conditioning on sewage sludge thermal drying. Chemosphere 117:559–566. https://doi.org/10.1016/j.chemosphere.2014.09.038
19. Liu S, Wei M, Qiao Y, Yang Z, Gui B, Yu Y, Xu M (2015) Release of organic sulfur as sulfur-containing gases during low temperature pyrolysis of sewage sludge. Proceedings of the Combustion Institute, 35(3), 2767–2775.https://doi.org/10.1016/j.proci.2014.06.055
20. Liu Y, Ran C, Siddiqui AR, Siyal AA, Song Y, Dai J, … Zhang T (2020) Characterization and analysis of sludge char prepared from bench-scale fluidized bed pyrolysis of sewage sludge. Energy 200:117398. https://doi.org/10.1016/j.energy.2020.117398
21. Ros A, Montes-Moran MA, Fuente E, Nevskaia DM, Martin MJ (2006) Dried sludges and sludge-based chars for H2S removal at low temperature: influence of sewage sludge characteristics. Environ Sci Technol 40(1):302–309. https://doi.org/10.1021/es050996j
22. Sanders JF, Keener TC, Wang J (1995) Heated fly ash/hydrated lime slurries for SO2 removal in spray dryer absorbers. Ind Eng Chem Res 34(1):302–307. https://doi.org/10.1021/ie00040a032
23. Svanström M, Fröling M, Olofsson M, Lundin M (2005) Environmental assessment of supercritical water oxidation and other sewage sludge handling options. Waste management research 23(4):356–366. https://doi.org/10.1177/0734242X05054324
24. Thipkhunthod P, Meeyoo V, Rangsunvigit P, Rirksomboon T (2007) Describing sewage sludge pyrolysis kinetics by a combination of biomass fractions decomposition. J Anal Appl Pyrol 79(1–2):78–85. https://doi.org/10.1016/j.jaap.2006.10.005
25. Tang S, Tian S, Zheng C, Zhang Z (2017) Effect of calcium hydroxide on the pyrolysis behavior of sewage sludge: reaction characteristics and kinetics. Energy Fuels 31(5):5079–5087. https://doi.org/10.1021/acs.energyfuels.6b03256
26. Udayanga WC, Veksha A, Giannis A, Lisak G, Lim TT (2019) Effects of sewage sludge organic and inorganic constituents on the properties of pyrolysis products. Energy Conv Manag 196:1410–1419. https://doi.org/10.1016/j.enconman.2019.06.025
27. Weng H, Dai Z, Ji Z, Gao C, Liu C (2015) Release and control of hydrogen sulfide during sludge thermal drying. J Hazard Mater 296:61–67. https://doi.org/10.1016/j.jhazmat.2015.04.037

28. Yin Q, Liu M, Ren H (2019) Biochar produced from the co-pyrolysis of sewage sludge and walnut shell for ammonium and phosphate adsorption from water. Journal of environmental management 249:109410. https://doi.org/10.1016/j.jenvman.2019.109410
29. Zhang L, De Schryver P, De Gusseme B, De Muynck W, Boon N, Verstraete W (2008) Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: a review. Water Res 42(1–2):1–12. https://doi.org/10.1016/j.watres.2007.07.013
30. Zhang J, Zuo W, Tian Y, Chen L, Yin L, Zhang J (2017) Sulfur transformation during microwave and conventional pyrolysis of sewage sludge. Environ Sci Technol 51(1):709–717. https://doi.org/10.1021/acs.est.6b03784
31. Zhang J, Tian Y, Yin L, Zuo W, Gong Z, Zhang J (2017) Investigation on the removal of H 2 S from microwave pyrolysis of sewage sludge by an integrated two-stage system. Environ Sci Pollut Res 24(24):19920–19926. https://doi.org/10.1007/s11356-017-9637-6

Figures

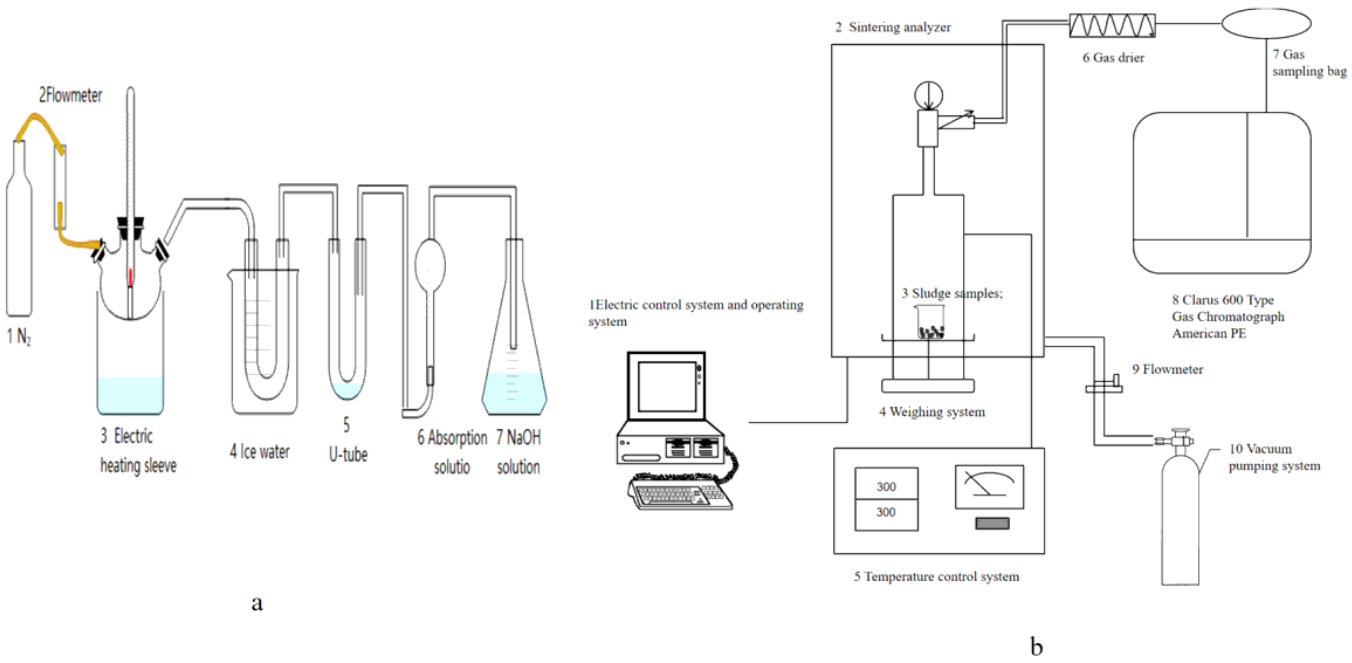

Figure 1

(a) Gas absorption experiment device; (b) Experimental diagram of drying sludge system

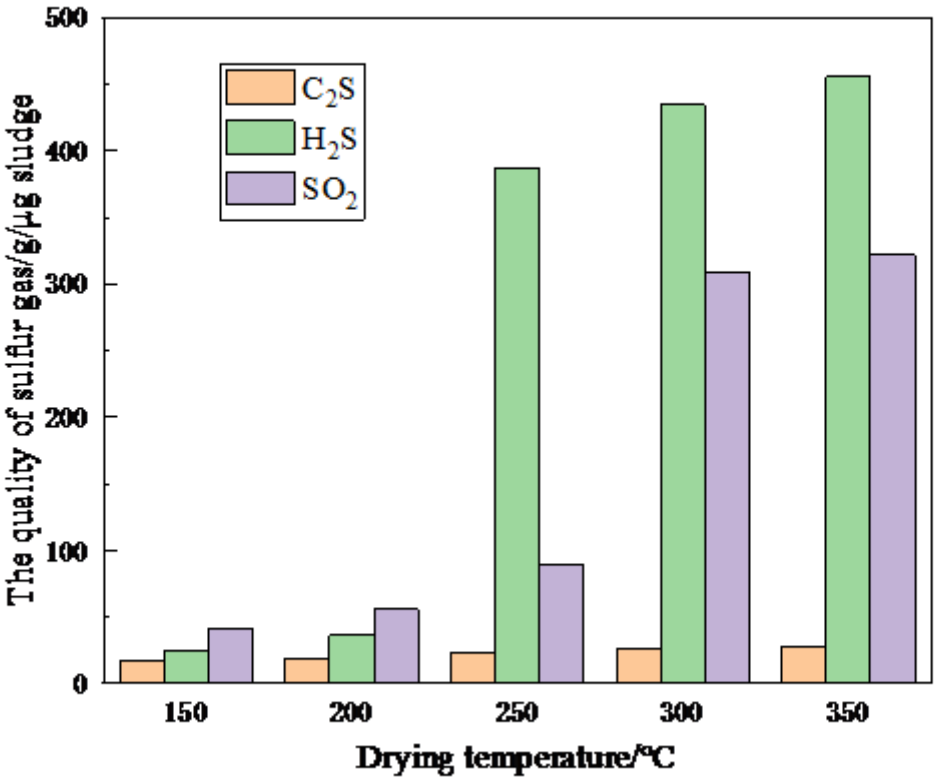

Figure 2

Influence of drying temperature on the amount of releasion of the gas released

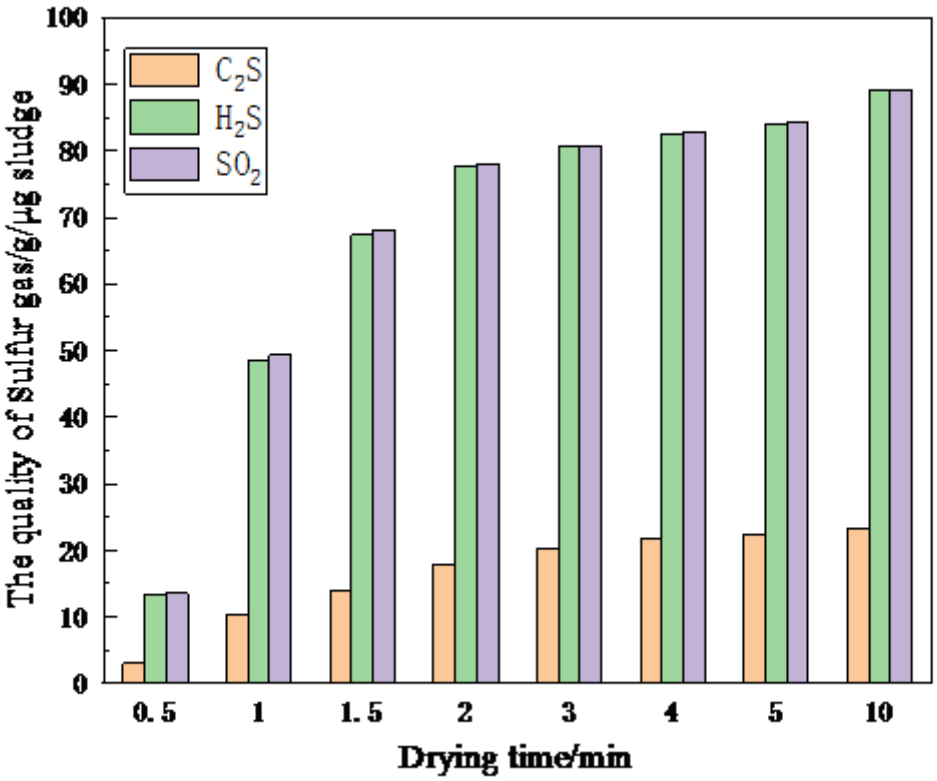

Figure 3

Influence of drying time on the amount of releasion of the gas released

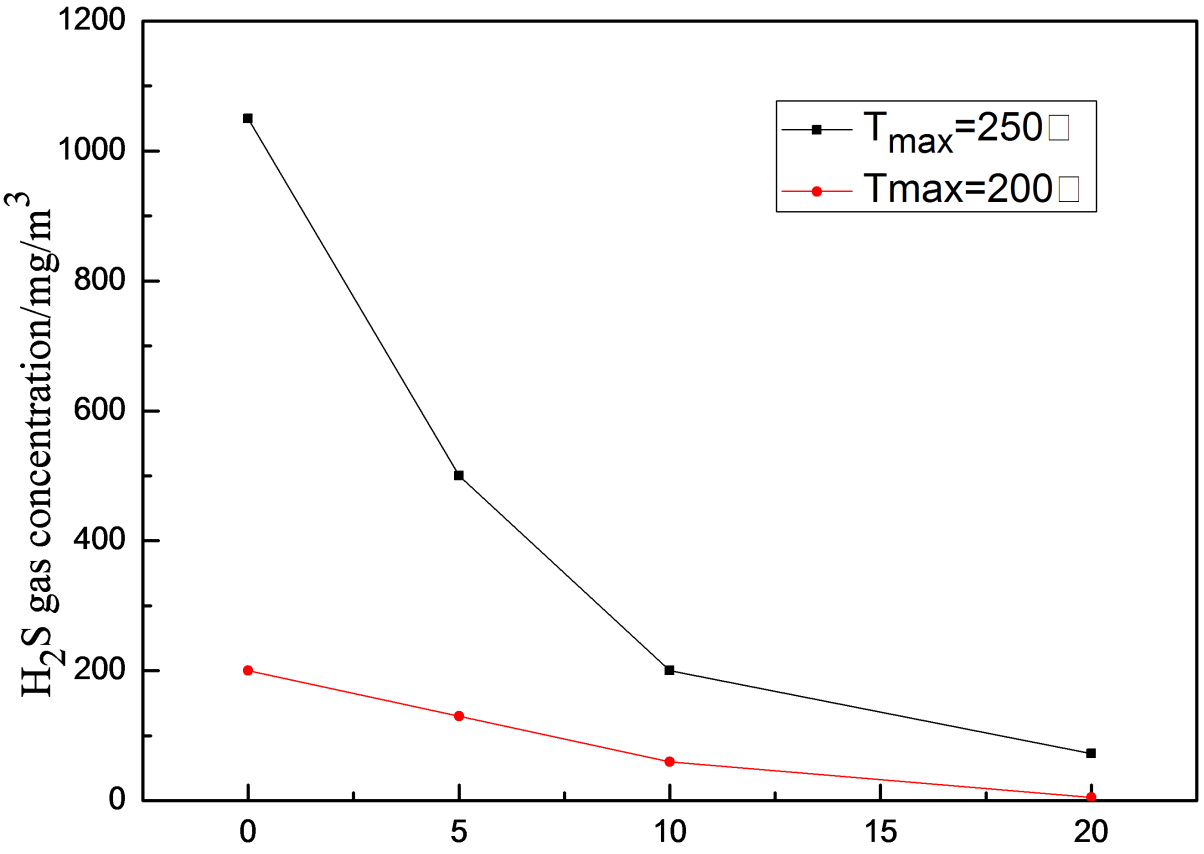

Figure 4

variation of H2S concentration in sludge drying process with different CBP content

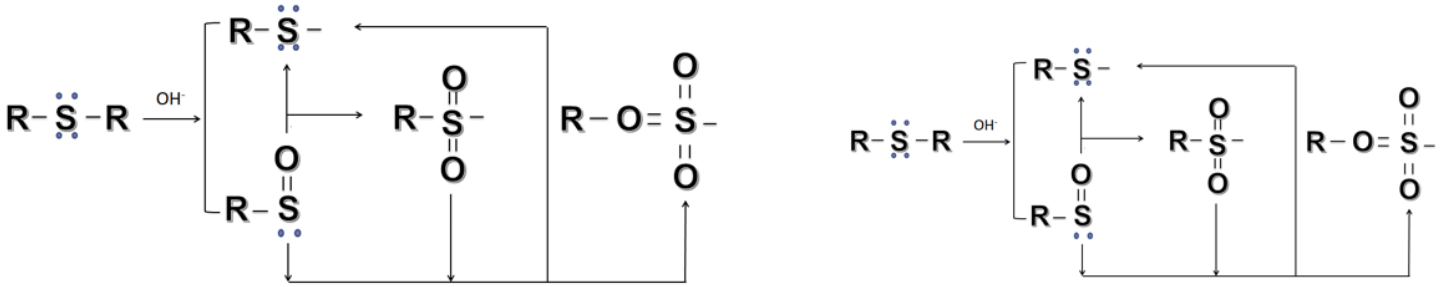

Figure 5

Diagram of organic matter transformation

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