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Combined effects of Fenton peroxidation and CaO conditioning on sewage sludge thermal drying

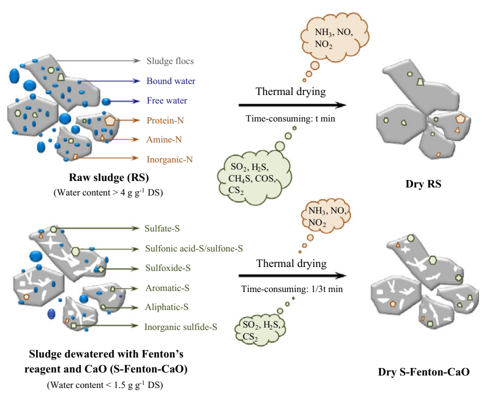
Huan Liu [a], Peng Liu [a], Hongyun Hu [a], Qiang Zhang [a], Zhenyu Wu [a], Jiakuan Yang [b], Hong Yao [a,*]

[a] State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China
[b] School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

HIGHLIGHTS

- Joint application of Fenton's reagent and CaO improves sludge drying performance.
- Conditioners reduce the amounts of both free and bound water in dewatered sludge.
- Conditioners create porous structure and efficiently promote sludge heat transfer.
- Emissions of S- and N-containing gases during sludge drying are greatly suppressed.
- Decreased odor emissions are related to the variations in sludge-S and -N species.

GRAPHICAL ABSTRACT



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ABSTRACT

Joint application of Fenton's reagent and CaO can dramatically enhance sludge dewaterability, thus are also likely to affect subsequent thermal drying process. This study investigated the synergistic effects of the two conditioners on the thermal drying behavior of sewage sludge and the emission characteristics of main sulfur-/nitrogen-containing gases. According to the results, Fenton peroxidation combined with CaO conditioning efficiently promoted sludge heat transfer, reduced the amounts of both free and bound water, and created porous structure in solids to provide evaporation channels, thus producing significant positive effects on sludge drying performance. In this case, the required time for drying was shortened to one-third. Additionally, joint usage of Fenton's reagent and CaO did not increase the losses of organic matter during sludge drying process. Meanwhile, they facilitated the formation of sulfate and sulfonic acid/sulfone, leading to sulfur retention in dried sludge. Both of Fenton peroxidation and CaO conditioning promoted the oxidation, decomposition, and/or dissolution of protein and inorganic nitrogen in sludge pre-treatment. As a consequence, the emissions of sulfurous and nitrogenous gases from dewatered sludge drying were greatly suppressed. These indicate that combining Fenton peroxidation with CaO conditioning is a promising strategy to improve drying efficiency of sewage sludge and to control sulfur and nitrogen contaminants during sludge thermal drying process.

* Corresponding author. Tel./fax: +86 27 87545526 (O).
E-mail address: hyao@mail.hust.edu.cn (H. Yao).

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1. Introduction

Wastewater treatment process generates large amounts of sewage sludge, which is a complex mixture of moisture, inorganic compounds, microorganism and certain undigested substances (Manara and Zabaniotou, 2012; Tyagi and Lo, 2013). Without proper treatment and disposal, this byproduct will cause serious environmental pollution. It is generally acknowledged that thermal drying represents an essential intermediate stage (Bennamoun et al., 2013). Through this process, the water content of mechanical dewatered sludge was further lowered, so as to meet the requirements of final disposal (Hassebrauck and Ermel, 1996; Vaxelaire et al., 2000). Simultaneously, costs for storage, transport and operation were also reduced sharply (Bennamoun, 2012; Bennamoun et al., 2013). Many researchers have tried to improve sludge drying efficiency by upgrading equipment or optimizing parameters. For example, Chun and Lee (2004) obtained satisfactory results through combining a contact dryer and a fluidized bed dryer together. Arlabosse et al. (2004) developed an experimental methodology to design efficient paddle dryers with vertical agitator. Yan et al. (2009) and Deng et al. (2009a) investigated the influences of system pressure, stirrer speed as well as dryer load both experimentally and theoretically. Zhu et al. (2012) examined thermal drying efficiency of sludge with various shapes at different temperatures.

Actually, by comparison to these external factors, sludge characteristics, e.g. the contents and types of water, thermal conductivity and textural properties of solid substances, are even more important to its drying behavior (Dewil et al., 2005; Léonard et al., 2003, 2004; Peeters et al., 2013). In traditional wastewater treatment plant, sludge was usually subjected to polyelectrolyte conditioning and belt press or centrifugal dewatering. After this procedure, bound water and partial free water are still tied to solid residual, and the water content decreases from 93–99.5% to 75–80% (Neyens et al., 2003; Tyagi and Lo, 2013). Subsequently, a lot of energy needs to compensate for latent heat of moisture evaporation during sludge drying process. A good way to solve this problem is to reduce initial water content of dewatered sludge (Peeters et al., 2013). Our previous studies (Liu et al., 2012b,2013b,2014) have found that joint application of Fenton's reagent (Fe^{2+}/H_2O_2) and lime (mainly presented as CaO) could significantly enhance sludge dewaterability. Deep dewatering (water content $\leqslant$1.5 g g^{-1} DS, 60%) can then be realized directly by using filter press, which will contribute to low energy consumption in followed thermal drying. Furthermore, these conditioners may also change solids properties, and play other role in this process. By calculating, Dewil et al. (2005) demonstrated that Fenton peroxidation is effective in improving sludge thermal conductivity. Huron et al. (2010) deduced that CaO conditioning exerts a positive influence on heat and mass transfer. However, the mechanism of Fenton peroxidation and CaO addition affecting sludge drying is still enigmatic, and little research has touched upon the synergies of Fenton's reagent and CaO on thermal drying behavior of sewage sludge.

Besides, it should not be ignored that the emissions of odorous compounds, especially nitrogen- and sulfur-containing ones, pose great challenges to environment and public health, which will hinder the practical application of sludge thermal drying. According to our previous work (Liu et al., 2012a), Fenton oxidation facilitates the generation of H_2S, SO_2 and COS in conditioning process. CaO treatment reduces the release amount of each sulfurous gas, but increases that of NH_3. Unfortunately, there is a lack of relevant literatures having illustrated the individual or combined effects of the two types of conditioners on odor emission from sludge drying.

Considering the problems mentioned above, this study aims to (1) clarify the mechanism of Fenton peroxidation and CaO conditioning influence sludge thermal drying behavior; (2) elucidate the synergistic effects of composite conditioner on emissions of main S- and N-containing gases by speciation analysis; and (3) propose possible strategies for reducing energy consumption as well as polluting gases formation during sludge thermal drying.

2. Experimental

2.1. Materials

Raw sludge (RS) was collected after mechanical dewatering with cationic polymeric flocculants as conditioner from a municipal wastewater treatment plant in Wuhan, China. To ensure sample comparability, partial of this sludge was subjected to mixing with water, and the sludge slurry was treated by one or both of Fenton's reagent (Fe^{2+} 40 mg g^{-1} DS, H_2O_2 32 mg g^{-1} DS) and CaO (0.3 g g^{-1} DS) followed by filter press dewatering. Three obtained sludge were named as S–Fenton, S–CaO, and S–Fenton–CaO, respectively. The detailed sample preparation procedures and specific dosages of conditioners have been described in our earlier reports (Liu et al., 2012b, 2013a, 2014).

It can be seen from Table 1 that, Fenton treatment reduced the content of fixed carbon and increased that of volatile matter, since strong oxidation was able to destroy many stable organics (Neyens and Baeyens, 2003; Tony et al., 2008). Moreover, H_2SO_4 and $FeSO_4$ were used for adjusting pH and providing Fe^{2+}, thus S–Fenton comprised of a little more sulfur than RS. CaO addition enhanced the relative ratio of ash from 40.8% to 53.3%, resulting in reductions of 7.5%, 2.5%, and 0.2% in carbon, nitrogen, and sulfur content. It is not difficult to find that the absolute loss of carbon is only about 1%, probably due to the dissolution of some organics in alkaline condition. For the case of S–Fenton–CaO, the results of proximate and ultimate analysis were very close to that for S–CaO.

2.2. Sludge drying procedure

Experiments were performed in a specific horizontal quartz reactor (500 mm length, 36 mm i.d.) which is similar to that in our previous study (Liu et al., 2014). A commonly used drying temperature, 473 K (Zhu et al., 2012), was selected in this study. Prior to each test, the reactor was electrically heated to the set value with 2 NL min^{-1} high purity N_2 passing through. When the system had stabilized, a quartz boat carrying 2 g of sample (based on DS)

Table 1
Characteristics of different sludge samples.

Materials	Proximate analysis (wt%) (dry basis)			Ultimate analysis (wt%) (dry basis)					Water content (g g^{-1} DS)			LHV (kJ kg^{-1}) (dry ash-free basis)	
	Volatile matter	Ash	Fixed carbon	C	H	O[a]	N	S	Total	Free	Bound	Before drying[b]	After drying[c]
RS	51.4	40.8	7.8	29.2	5.0	18.3	5.7	1.0	4.4	3.6	0.8	19206	19038
S–Fenton	57.6	40.8	1.6	27.3	4.7	20.3	5.3	1.6	1.9	1.5	0.4	18250	18198
S–CaO	46.5	53.3	0.2	21.8	4.1	16.2	3.8	0.8	2.1	1.6	0.5	17111	16963
S–Fenton–CaO	47.0	52.7	0.3	20.1	4.0	17.9	3.5	1.8	1.1	0.7	0.5	15245	15178

[a] Calculated by difference.
[b] Freeze-dried sample.
[c] Sample collected from the drying experiments.