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Effect of calcium magnesium acetate on the forming property and fractal dimension of sludge pore structure during combustion

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HIGHLIGHTS

- The changes in pore structure of sludge with increasing Ca/S ratio are nonlinear.
- The growth and expansion of pore structure changes at different combustion stage.
- The mechanisms of pore structure during blended fuel combustion are obtained.
- The fractal dimension increases with Ca/S ratio, indicating improved combustion.

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ABSTRACT

The changes in pore structure characteristics of sewage sludge particles under effect of calcium magnesium acetate (CMA) during combustion were investigated, the samples were characterized by N_2 isothermal absorption method, and the data were used to analyze the fractal properties of the obtained samples. Results show that reaction time and the mole ratio of calcium to sulfur (Ca/S ratio) have notable impact on the pore structure and morphology of solid sample. The Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) of sample increases with Ca/S ratio, while significant decreases with reaction time. The fractal dimension D has the similar trend with that of S_{BET}, indicating that the surface roughness of sludge increases under the effect of CMA adding, resulting in improved the sludge combustion and the desulfurization process.

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1. Introduction

In 2014, approximate 30 million tons municipal sewage sludge with moisture content of 80% is generated in China, and the sludge discharge increases by 10% annually (Cong et al., 2013). Incineration is considered to be one of the effective technologies to make it possible to achieve the targeted decreasing sewage sludge and is a promising method to realize the energy utilization of sludge. However, the pollutant emissions from sewage sludge incineration may be inevitable and serious harm could be done to urban residents. Using new methods to dual remove these pollutant emissions attracts widespread attention. Currently, extensive experiments in test rigs and power plants have been made to investigate the effect of organic calcium compound on the pollutant removal from coal combustion (Nimmo et al., 2004; Patsias et al., 2005; Shemwell et al., 2000; Tayyeb Javed et al., 2009). Results showed organic calcium compound has the superior SO_2 and NOx capture ability with reductions greater than 75%. In these studies, calcium magnesium acetate is one of the organic calcium compounds which is most used, and it has best sulfur removal efficiency (Adánez et al., 1999; Nimmo et al., 2004; Shuckerow et al., 1996). Therefore, using calcium magnesium acetate as additive to removal SO_2 and NOx simultaneously will be helpful to the development, popularization and application of sludge incineration technique (Niu et al., 2011; Zhang et al., 2015b).

Sludge structure including micropore area, total pore volume, micropore volume, pore size distribution and pore diameter, etc., represents a key factor that dominates its important transport properties such as porosity and permeability (Zou et al., 2013). Low-pressure nitrogen gas adsorption (LP-N2GA) analysis has been verified to be an effective method to characterize the pore structure of porous medium. Many researchers studied the pore characteristics of sludge during combustion, pyrolysis, and gasification using LP-N2GA analysis method (Jindarom et al., 2007; Wu et al., 2013;

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Zou et al., 2013). Results indicate that total pore volume and specific surface area increase with the increasing final temperature.

However, CMA can release plenty of carboxylic and hydrocarbonyl radical during the thermal decomposition process and these intermediates can reduce NO emission (Shemwell et al., 2000; Zhang et al., 2015a). CMA is rich in organic matters which can be burned, and it is sometimes known as the fuel. Besides, calcium oxide as the residual solid products can react with SO_2, H_2S, HCl, and Cl_2 to form $CaSO_4$ and $CaCl_2$. Meanwhile, commercially available CMA is expensive (about $1300/ton) due to the relatively high cost of producing acetic acid from natural gas and due to its limited markets (Zhang et al., 2015b). Therefore, we used low-cost raw materials in this study to produce CMA by chemical synthesis. The total cost of raw materials for MCMA is about $400/ton in China at present, which is about one third of the cost of commercially available CMA. This significantly decreases the costs of CMA, and maybe helps to using CMA in industrial application. Nevertheless, CMA has relatively high volatile matter (VM) compared with other calcium-based sorbents, resulting in more complex pore characteristic. Therefore, when blended CMA with sludge, the complicated microscopic pore structure of CMA samples not only affects sludge physical properties (i.e., mechanical properties and adsorption properties) but also controls the desulfurization reaction during sludge thermal decomposition process. Therefore, accurately and quantitatively describing the microscopic pore structure of sludge blended with CMA is important. Until now, there is still a lack of experimental studies especially concerning this topic. It is of great significance to investigate the pore characteristic of sludge under effect of CMA adding.

Besides, the traditional Euclidean geometry is limited by its theory in describing irregular samples, and it fails to analyze the irregularity of surface morphology and pore structure. Although the solid samples structure parameters can be quantitatively obtained by N_2 adsorption isotherm, it is still difficult to build the correlation with the surface chemical reactivity of samples. The initial concepts and possible applications of fractals were popularized by Mandelbrot in 1975 (Pfeifer and Avnir, 1983). Nowadays, fractal model is widely used in many fields and is also proven to be a powerful and reasonable tool that quantitatively describes disordered self-similar fractals in coal and sludge (He et al., 1998; Jin et al., 2004; Zhang et al., 2014). To quantitatively illustrate the changes in the pore structure of solid samples in the processing of chemical reaction under the effect of CMA adding, the fractal model was also employed in this study.

In this work, the pore structure characteristics of sewage sludge particles under effect of CMA adding during combustion were investigated. Based on the LP-N2GA data, PSDs in solid samples are quantitatively analyzed together with the pore shape, S_{BET}, average pore diameter (APD) and pore volume (PV). Besides, the data were also used to analyze the fractal properties of the obtained samples.

2. Methods

2.1. Test facility

Fig. 1 shows the process flow diagram of the experiment system in this study. This system consists of a tube furnace, gas supply, electrical heating system, flue gas treatment and data sampling. A digital mass flow meter is used to control the air flow rate. To decreases the diffusion resistance of the solid fuels, the samples with the total weight of 200 mg are placed in the bottom of the porcelain boat uniformly. The concentrations of the flue gas, such as SO_2, CO_2, NO, and O_2 were continuously recorded by ecom-J2KN flue gas analyzer. In this test, the reaction temperature is fixed at 800 °C and air flow rate is fixed at 450 ml/min. After the furnace temperature and the flow rate attained the setting values and the system stabilized for 2 min, the porcelain boat with solid samples were pushed into the center of the tube furnace. And after that, the gas analyzer was started to record the flue gas concentration for about 200 s.

2.2. Materials

Dried sewage sludge was obtained from the Nanjing Waste Water Treatment Plant, which had been stockpiled outdoors and exposed to weathering for approximately 5 days. The proximate analysis data of dried sludge such as volatile, fixed carbon and ash are 46.05, 4.51, and 49.44%, respectively. The ultimate analysis data of dried sludge such as C, H, O, N, and S are 28.71, 4.36, 12.12, 4.43, and 0.94%, respectively. Synthesis CMA was chemically synthesized from magnesium oxide (MgO), calcium hydroxide ($Ca(OH)_2$) and acetic acid at a determined mole ratio. For preparation of synthesis CMA, a quantity of acetic acid is determined at an excess mole ratio of 50% and it is expected that MgO and $Ca(OH)_2$ could be mostly transformed into organic radical based compounds under the effect of acetic acid. To guarantee a uniform distribution of CMA in sludge, according to the Ca/S ratio, CMA and dried sludge were well dispersed in water using magnetic stirring bar at 500 rpm for 2 h under room temperature. Afterwards, the blended fuels were oven dried at 105 °C for 24 h and ground into less than 0.15 mm.

During this test, the solid samples are obtained at the time of $t = 60$ s and $t = 200$ s. Two numbers "60" and "200" represent the sample time, s, respectively. To easily identify these samples, they were designated as MR0-60, MR1-60, MR3-200, and so on. Specifically, M represent blended fuels, respectively. "R" represents the Ca/S ratio, and the number after "R" stands for different Ca/S ratios (i.e. "1", "2", and "3" represents 1:1, 2:1, and 3:1, respectively, and "0" represents sludge separate combustion). Besides, samples-60 and samples-200 are also used to represent the total samples at the time of $t = 60$ s and $t = 200$ s, respectively.

2.3. Pore characteristic analysis

The residual samples were weighted 1–2 g, and they were degassed at 105 °C for 12 h under vacuum to a final pressure of 0.33 Pa. The physical characteristics of the co-combustion residues, including specific surface area, micropore area, total pore volume, micropore volume, pore size distribution and pore diameter were measured with N_2 (g) adsorption (ASAP 2010 Pore Structure Analyzer, Micromeritrics Inc., USA) at 77 K with liquid N_2. The isotherms were measured for the relative pressure (P/P_0) range from 0.01 to 0.99. N_2 gas adsorption/desorption isotherms were used to measure the specific surface area and average pore diameter according to the Brunauer–Emmett–Teller (BET) method and the pore volume. Pore size distribution was calculated according to the Barrett–Joiner–Halenda (BJH) method.

2.4. Fractal dimension calculation

The multimolecular adsorption of nitrogen on the solid surface is weak when the relative pressure (P/P_0) is smaller than 0.37. It is considered that the main adsorption in the micropores is monolayer adsorption, and this process can reflect the solid pore surface structure. Therefore, the fractal characteristics of solid samples were investigated based on the monolayer adsorption process in this study. Different methods, such as fractal BET, fractal Langmuir, and fractal Frenkel–Halsey–Hill (FHH), have been used to calculate fractal dimension based on gas adsorption isotherm (Vaimakis et al., 1995). Among these, the widely used fractal FHH method

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