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Original Research Paper

Research on the thermal decomposition and kinetics of byproducts from MgO wet flue gas desulfurization

L.Y. Yan [a],*, X.F. Lu [a],*, Q. Guo [a], Q.H. Wang [a], X.Y. Ji [b]

[a] *Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Ministry of Education, Chongqing University, Shapingba, Chongqing 400044, PR China*
[b] *College of Mechanical and Power Engineering, Chongqing University of Science & Technology, Chongqing 401331, PR China*

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ABSTRACT

This paper was aimed at the thermal decomposition and kinetics of the byproducts from MgO flue gas desulfurization. The effects of particle size and charcoal on thermal decomposition of the byproducts were investigated by the thermogravimetric analysis method, and the non-isothermal kinetic parameters of the byproducts were evaluated with the Coats–Redfern method. The results showed that the mass loss increased with the decrement of the particle size. However, the effect of the particle size on the mass loss of each thermal decomposition stage was different. Increasing the amount of charcoal powder in the byproducts had an obvious effect on the temperature characteristics of the thermal decomposition of magnesium sulfate, resulting in a reduced thermal decomposition temperature which could facilitate the thermal decomposition process. The equations $G(\alpha) = 1-(1-\alpha)^{1/2}$, $G(\alpha) = [-\ln(1-\alpha)]^2$, and $G(\alpha) = 1-(1-\alpha)^{1/3}$ were the quite appropriate kinetic mechanisms describing the thermal decomposition process of $MgCO_3$, $MgSO_3$, and $MgSO_4$, respectively.

1. Introduction

The energy consumption of China in 2012 reached 3.62 billion tons of standard coal equivalent [1]. Coal resources in China are characterized by low heat value and high sulfur content. Coal combustion leads to high SO_2 annual emission, although the tougher control has been enacted in China. It is a fact that the emission of SO_2 contributes to acid rain, solid acidification, forest degeneration, and human diseases, which should be harmlessly treated before it can be released into the atmosphere. Therefore, the desulfurization system must be employed in coal-fired units, and more than two hundred kinds of flue gas desulfurization (FGD) technologies have been studied, of which dozens have already been in operation. The wet FGD (WFGD) technologies account for about 85% for control technology of SO_2 all over the world and desulfurization based on limestone accounts for 90% for the control technology of SO_2 in China [2,3]. However, the desulfurization basing on limestone results in the following questions in China. First, the desulfurization technology of China relies on imports, lacking self-owned intellectual property rights, which leads to high cost for desulfurization. Second, the natural gypsum is rich in China, and the method used to disposal desulfurization byproducts in Europe and the United States is not for China [4–6], which leads to lots of desulfurization byproducts being piled up as solid waste [7], although government vigorously supports the application of the byproducts.

Therefore, a kind of desulfurization technology suiting China's actual conditions should be developed. MgO WFGD technology has been paid close attention as a highly efficiency technology without solid byproducts waster problem for the desulfurization byproducts can be calcined to generate MgO for desulfurization and SO_2 for acid-making. China has abundant resources of magnesium and poor resources of sulfur. The development of this technology is suitable for China's national conditions and can be regarded as a reference to the development of this technology for other similar developing country.

This technology has been widely used in Japan, Taiwan and Southeast Asia, and also in 330 × 2 MW and 225 × 2 MW power plants in China. Some studies about MgO WFDG such as the investment [8], the characteristics of the $MgSO_3$ and $MgSO_3{\cdot}6H_2O$ [9–11], SO_2 absorption in desulfurization system [12,13], the oxidation inhibition of the byproducts [14,15], the byproduct recovering process [16,17], the magnesium-based WFGD process[18,19], and the activity of MgO generated from the decomposition of the by-products [20] have been carried out. Besides, a series of patents have been applied in this area [21–25].

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* Corresponding authors. Tel./fax: +86 23 65102475.
E-mail addresses: yanziyly@sina.cn (L.Y. Yan), xf_luke@163.com (X.F. Lu).

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Nomenclature

FGD	flue gas desulfurization
WFGD	wet flue gas desulfurization
TG	thermogravimetry
DTG	differential thermogravimetry
T	heating temperature (°C)
m_{i0}	mass at initial (mg)
m_i	mass at t (mg)
$m_{i\infty}$	mass at final (mg)
t	time (min)
k_i	temperature-dependent constant
$f(\alpha_i)$	reaction model
A_i	pre-exponential factor (s^{-1})
E_i	activation energy ($kJ\ mol^{-1}$)
R	gas constant, 8.314 $J\ mol^{-1}\ k^{-1}$
$G(\alpha_i)$	integral reaction
C	$MgCO_3$ thermal decomposition
D	$MgSO_3$ thermal decomposition
E	$MgSO_4$ thermal decomposition
T_i	initial thermal decomposition temperature (°C)
T_f	final thermal decomposition temperature (°C)
V_{max}	maximum rate of mass loss (wt/min)
V_{mean}	mean rate of mass loss (wt/min)
n	the ratio of carbon to byproduct

Greek letter

α	conversion degree at stage i (%)
β	heating rate (°C/min)

Sub-scripts

i	C, D or E

To date, the thermal decomposition and kinetics characteristic of the byproducts of MgO FGD from thermal power plant were reported rarely. These characteristics of the byproducts mixed with charcoal powder have not been reported. They are the key technologies for the recycling MgO and SO_2 from MgO WFGD byproducts. It is necessary to know the particle characteristic and calcination temperature for designing test and adjusting operation parameters. Therefore, the characteristics of thermal decomposition and kinetics of these byproducts were studied by thermogravimetric method and Coats–Redfern method in this paper. It is expected that these will provide guidance to thermal decomposition reactions of the by-products of MgO WFGD for the recoveries of SO_2 and MgO.

2. Experiments

2.1. Materials

The magnesia FGD byproducts were received from a 300 MW coal fired power plant in China. The samples were smashed to a small particle size by a pulverizer, then were dried in an oven under room temperature, finally were sieved by the different size of the sieves for experiment. The charcoal for experiment was milled to powder by grinding, and then mixed with byproducts. The component analysis of the byproducts is shown in Table 1.

2.2. Thermogravimetric measurements

Using a NetzschSTA-409 PC thermal analyzer, approximately 10.874 mg samples of different particle sizes were placed in an alumina crucible and heated from 40 °C to 1160 °C at 20 °C/min in 50 ml/min nitrogen flow. The average particle size distributions (d) are 60 μm, 82.5 μm, and 107.5 μm, respectively. Approximately 30 ± 0.05 mg sample of byproducts with charcoal were placed in an alumina crucible and heated to 1160 °C from 40 °C at 20 °C/min in 50 ml/min nitrogen flow. The mass ratios (n) of charcoal to byproducts are 0, 1:8, 1:4, 1:2, respectively. The charcoal is mainly composed of C (86.1%), H (4.6%), O (5.2%), and N (2.8%).

Table 1
Component analysis of byproducts.

Component	$MgSO_3$	$MgSO_4$	Crystal water	$MgCO_3$	MgO
Content (wt%)	28.7	21.39	25.65	9.59	4.2

Before the experiments, pure N_2 was supplied into the thermogravimetric analyzer for 60 min to eliminate the initial air in the system. During the experiments, it is necessary to supply N_2 to produce an inert atmosphere for the thermal decompose process, to take away the generated gas products, and to prevent reflux of the outside air into the heating furnace which would lead to the occurrence of reverse reactions and oxidation of the product or sample.

3. Results and analysis

3.1. Analysis of thermal decomposition

The TG and DTG curves of the byproducts with different particle sizes are shown in Figs. 1 and 2, respectively. As shown in Figs. 1 and 2, it could be observed that five phases of the thermal decomposition. The surface water and the crystal water were removed in the temperature range 90–300 °C, and the final three decomposition reactions occurred in the temperature range 480–1160 °C which forms compounds in the sequence of $MgCO_3$, $MgSO_3$, and $MgSO_4$, as determined by the component analysis in Table 1 and the different decomposition temperatures after dehydration [26–27].

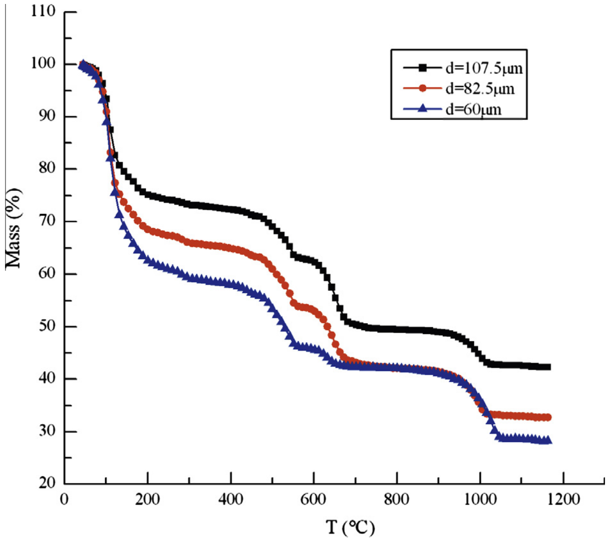

Fig. 1. TG curves of different particle size.