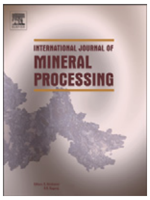
International Journal of Mineral Processing 98 (2011) 145–149

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro



Degradation behavior of high surface area calcium hydroxide sorbent for SO_2 removal

Hyun-Gyoo Shin [a,1], Hwan Kim [a,*], Taimin Noh [b,2], Dowan Kim [b,2], Yong-Nam Kim [c,*]

[a] Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, Republic of Korea
[b] School of Materials Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea
[c] Material Testing Center, Korea Testing Laboratory, Seoul 152-848, Republic of Korea

ARTICLE INFO

Article history:
Received 2 April 2010
Received in revised form 26 October 2010
Accepted 7 November 2010
Available online 22 November 2010

Keyword:
Calcium hydroxide sorbent
Durability test
Degradation behavior
Crystal growth

ABSTRACT

The degradation behavior of a calcium hydroxide sorbent for SO_2 removal was investigated in terms of microstructure and crystal phase change. Hydrated lime sorbents with a high surface area were prepared by hydration of Diethylene glycol-coated quicklime. A durability test for sorbents was carried out in a consistent chamber condition at a temperature of 50 °C and a humidity level of 60% relative humidity for 168 h. With respect to SO_2 reactivity, the deteriorated sorbents showed lower reactivity toward SO_2 gas than an as-prepared sorbent. And the longer degradation time the hydrated lime sorbents were exposed to a humid atmosphere, the lower their SO_2 reactivity became because the specific surface area of sorbents decreased from 41.23 m^2/g to 15.23 m^2/g. The calcite crystals formed in the deteriorated sorbents due to carbonation and the calcite crystals were grown with the elapse of degradation time. Accordingly, the SO_2 removal efficiency of the deteriorated sorbents was lower than that of the as-prepared sorbent. It could be concluded that the degradation behavior of calcium hydroxide sorbents originated from the formation and growth of calcite in them.

1. Introduction

The flue gas desulfurization (FGD) process is one of the current state-of-the-art technologies used for removing SO_2 in exhaust gas discharged from a power plant and incinerator. It is based on the injection of slurries or solid sorbents which are sprayed into ducts situated between an air pre-heater and a particulate collection system. From the point of view of the phases in the sulfation medium, a general classification of FGD processes leads to a wet process and a dry process. The wet FGD process shows higher SO_2 removal efficiency of sorbent than the dry process and can reduce 90% or higher of SO_2 emission. With regard to systems or facilities, however, the wet FGD process is more complicated than the dry FGD process and has problems of secondary contamination and waste disposal.

On the other hand, the dry FGD systems are more easily retrofitted onto existing combustion facilities (Bigham et al., 2005; Wang and Teng, 2009). The dry sorbent injection control technology, which is among the dry FGD methods, has been widely accepted by reasons of being simple with less equipment, lower capital and operating costs, limited secondary waste generation and fewer problems of corrosion and scaling-up. In this process, suitable alkaline sorbent particles are normally introduced into temperature-controlled and humidified flue gas in the duct between the air pre-heater and the particulate control device (Karatepe et al., 1999, 2004). As an alkaline sorbent for SO_2 removal, limestone (calcium carbonate, $CaCO_3$), quicklime (calcium oxide, CaO) and hydrated lime or slaked lime (calcium hydroxide, $Ca(OH)_2$) are commonly used. Among them, hydrated lime is the most widely utilized in the humidified duct injection processes (Siagi et al., 2007). Generally, it has been well known that calcium hydroxide is reacted with SO_2 in the desulfurization process through the following steps:

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \cdot 1/2H_2O + 1/2H_2O$$

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$Ca(OH)_2 + H_2SO_3 \rightarrow CaSO_3 + 2H_2O$$

$$CaSO_3 + H_2SO_3 \rightarrow Ca(HSO_3)_2$$

$$Ca(OH)_2 + Ca(HSO_3)_2 \rightarrow 2CaSO_3 + 2H_2O$$

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[*] Corresponding authors. Hwan Kim is to be contacted at the Department of Materials Science and Engineering, Seoul National University, Seoul 151-742, Republic of Korea. Tel.: +82 2 860 1575; fax: +82 2 860 1579. Yong-Nam Kim, Material Testing Center, Korea Testing Laboratory, Seoul 152-848, Republic of Korea. Tel.: +82 2 860 1577; fax: +82 2 860 1649.

E-mail addresses: hgshin@ktl.re.kr (H.-G. Shin), hwan94@snu.ac.kr (H. Kim), nohtm@pusan.ac.kr (T. Noh), kolet@nate.com (D. Kim), ynkim@ktl.re.kr (Y.-N. Kim).

[1] Tel.: +82 2 860 1575; fax: +82 2 860 1579.

[2] Tel.: +82 51 510 3225; fax: +82 51 512 0528.

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doi:10.1016/j.minpro.2010.11.002

In order to increase the desulfurization efficiency of these systems, hydrated lime sorbents must have smaller particle size, higher surface area, higher pore volume and larger pore diameter (Shin et al., 2009). Previous studies have shown that most of all, the reactivity of hydrated lime toward SO_2 gas depends strongly on its specific surface area (Siagi et al., 2007). However, the reactivity of hydrated lime toward SO_2 gas tends to be highly reduced in a humid environment. In general, as-produced hydrated lime sorbent, in industries, can be preserved in silo or storage facilities before it is sprayed into the dry FGD systems. For the period of storage, its reactivity toward SO_2 gas is decreased and so its performance for SO_2 removal is deteriorated. Therefore, hydrated lime sorbent with performance decay cannot be used for SO_2 removal or more quantity of degraded sorbent must be sprayed into the dry FGD system than that of normal sorbent.

Previous investigations of hydrated lime or sorbents have been performed on SO_2 removal efficiency, while it is not enough to study the performance decay and the degradation behavior of hydrated lime sorbents. In order to prolong high SO_2 removal efficiency of hydrated lime sorbent and improve its durability, the study for the degradation behavior of hydrated lime sorbent should be carried out. In our study, the performance decay of hydrated lime sorbent degraded in a humid environment was examined through a durability test and the analysis for degraded hydrated lime sorbent was performed to investigate its degradation behavior.

2. Experimental procedure

Limestone as a starting material was calcined at 1100 °C for 3 h to obtain quicklime. Table 1 shows the composition of limestone analyzed by X-ray fluorescence analysis (RIGAKU, ZSX100e). Hydrated lime sorbents were prepared using a hydration method. Quicklime powder coated with 5 wt.% Diethylene glycol (DEG) was hydrated using distilled water. Through the reaction between DEG-coated quicklime and DI-water of 1.8 times stoichiometric amount, hydrated lime sorbents were obtained. This preparation method for hydrated lime sorbents with high specific surface area was previously studied (Shin et al., 2009).

A durability test for as-prepared hydrated lime sorbents was carried out under atmospheric pressure using a chamber maintaining a consistent temperature at 50 °C and humidity at 60% relative humidity (RH) for up to 168 h.

After the durability testing, the SO_2 reactivity of hydrated lime sorbents was measured using a thermo-gravimetric (TG) analyzer (SHIMADZU, TMA-60H). N_2 gas including 2000 ppm SO_2 gas was used as a standard reaction gas to analyze the sulfation reactivity of hydrated limes. The flow rate of gas was 100 ml/min and the sulfation reaction was held at 350 °C for 4 h.

Crystal phase and crystalline size of hydrated lime sorbents were analyzed using an X-ray diffractometer (Bruker, D8 Advance). XRD patterns were recorded in the 2θ range of 20–60° using Cu Kα (1.5406 Å) radiation. Crystalline size was calculated from XRD data using Scherrer's Eq. (1) (Cullity, 1978):

$$t = \frac{0.9\lambda}{B\ \cos\theta} \tag{1}$$

where λ is the wavelength of X-ray (1.5406 Å for Cu Kα), B is the broadening of diffraction peak measured at half-height of diffraction peak, and θ is the angle of diffraction peak. Specific surface areas of hydrated lime sorbents were measured by a Brunauer–Emmett–Teller method (Micromeritics, ASAP 2010) and morphological analysis was performed by a FE-SEM (Field emission-scanning electron microscope, Hitachi S-4800). In addition, transmission electron microscope (TEM, JEN 2100F) analysis was carried out to confirm the crystal growth and crystalline size.

Table 1
Chemical composition of limestone analyzed by X-ray fluorescence.

Component	Content (wt.%)
$CaCO_3$	99.1279
SiO_2	0.2724
MgO	0.1747
Fe_2O_3	0.1563
Al_2O_3	0.1359

3. Results and discussion

The reactivity towards SO_2 gas of a hydrated lime sorbent can be derived from the weight gain of the sorbent because the higher its reactivity is, the more largely its weight gain increases due to the reaction with more SO_2 gas. Therefore, the reactivities toward SO_2 gas of hydrated lime sorbents were measured using thermo-gravimetric analysis. Fig. 1 shows the TG data of three kinds of hydrated lime sorbents. Hydrated lime sorbents as-prepared and exposed to the humid environment of 50 °C and 60% RH for 48 h and for 168 h showed the weight change of 120 wt.%, 113 wt.%, and 104 wt.%, respectively. The weight of hydrated lime sorbents increased because the formation of calcium sulfate occurred due to the reaction between calcium hydroxide and SO_2 gas. As shown in Fig. 1, the hydrated lime sorbents exposed to the humid environment acquired less weight gains than the as-prepared one. In addition, the longer time the hydrated limes were exposed to the humid environment, the less their weight gains became. This result indicates that while hydrated lime sorbents were exposed to the humid environment, they became degraded and their performance of SO_2 removal was decayed.

It is well known that the SO_2 reactivity of hydrated lime depends strongly on its specific surface area (Karatepe et al., 1999, 2004). To verify the relation between the decrease in specific surface area and its performance decay, the specific surface areas of hydrated limes were measured as a function of degradation time and shown in Fig. 2. In Fig. 2, as-prepared hydrated lime shows the specific surface area of 41.23 m^2/g and hydrated limes degraded in the humid environment for 48 h and 168 h show the specific surface area of 22.15 m^2/g and 15.23 m^2/g, respectively. From these results in Figs. 1 and 2, it is suggested that the exposure of hydrated lime sorbent to a humid environment decreased its surface area and so its performance of SO_2 removal was reduced.

XRD patterns of hydrated lime sorbents as-prepared and exposed to the humid environment for 24–168 h are shown in Fig. 3. As shown in Fig. 3, as-prepared hydrated lime sorbent has only the crystal phase

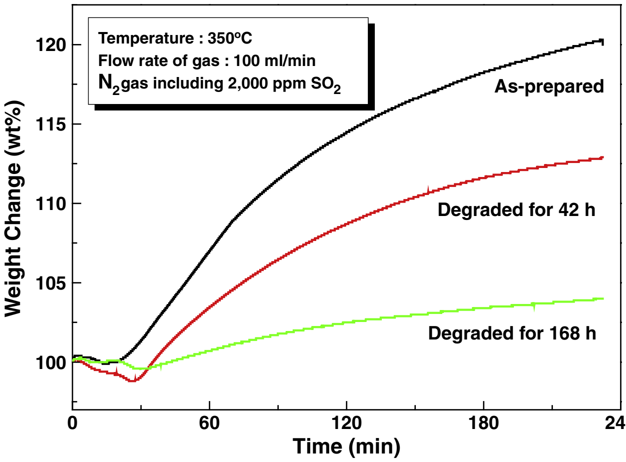

Fig. 1. Thermo-gravimetric curves of as-prepared sorbent and degraded sorbents reacted with SO2 gas at 350 °C for 4 h.