

Full Length Research Paper

Microstructure contradistinction for indirect/direct desulfurization product layer of limestone particle in coal-fired flue gas

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Accepted 25 October 2013

The micro morphology of limestone sorbent is a key for improving the SO₂ removal efficiency in the coal-fired power plant. The tube furnace system was built for imitating the indirect desulfurization reaction in traditional boiler atmosphere (65%N₂, 15%CO₂, 4.7%O₂, 15%H₂O, 0.3%SO₂) and the direct desulfurization reaction in oxygen-fired atmosphere (80%CO₂, 4.7%O₂, 15%H₂O, 0.3%SO₂). The reacted limestone particle samples were observed by SEM and are analyzed by Fourier transformation 3-D reconstruction technique. It is shown that the sizes of internal pore within sorbent particle in two kind atmospheres differ by an order of magnitude, one is about 200 nm for indirect desulfurization, and the other is about 20 nm for direct desulfurization. The CaSO₄ products of indirect desulfurization are chaotic derivatives with serious blockage, and the direct desulfurization product layer belongs to uniform honeycombed micro-structure without blockage. Those numerous micro-porous passages can guarantee continuous reactive substance transmission.

Key words: Limestone powder, SO₂ removal, particle surface, 3-D reconstruction, product layer.

INTRODUCTION

The hazards to human survival from free SO₂ gas molecules in the atmosphere continue to get the attentions of scientists from various countries (Sipila et al., 2010; Mihaela et al., 2010; Ramirez et al., 2008). The limestone powder sorbent is widely used in the dry SO₂ removal system in many large coal-fired power plants. Especially in recent years, the circulating fluidized bed (CFB) boiler oxy-fuel combustion technology is emerging rapidly in many countries including china, which can effectively control the emissions of three gaseous pollutions (NO_x, SO₂, CO₂) at O₂/CO₂ atmosphere (Ramon and Carmen, 2008; Krzywanski et al., 2010). The SO₂ removal efficiency of this technology, which still takes the

limestone as sorbent, should be higher than that of the dry limestone injection pattern in the traditional coal-fired boiler, and the latter is 40% (Winaya and Basu, 2001; Avila et al., 2012). The reason for this difference in the desulfurization efficiency is that the researchers tried to find, especially its microscopic mechanism (Sınırkaya et al., 2012). In the traditional coal-fired boiler, air is the fuel accelerant, and the partial pressure of CO₂ in its flue gas is low about 14 to 16%. So from the chemical point of view under such a low partial pressure of CO₂, the limestone will be firstly decomposed thermally at very high temperature, and then take part in the desulfurization reaction (Ramón and Carmen, 2009).

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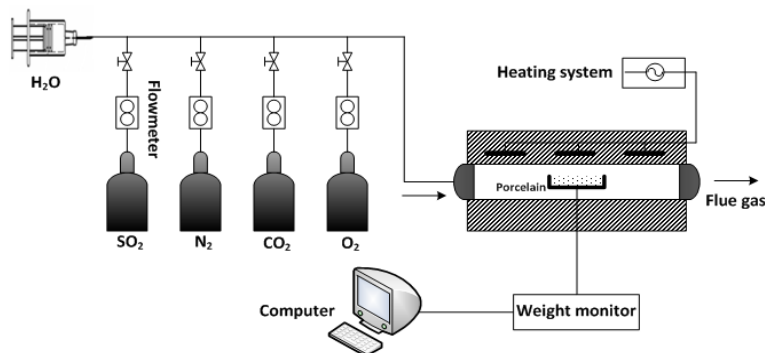


Figure 1. Schematic diagram of tube furnace system.

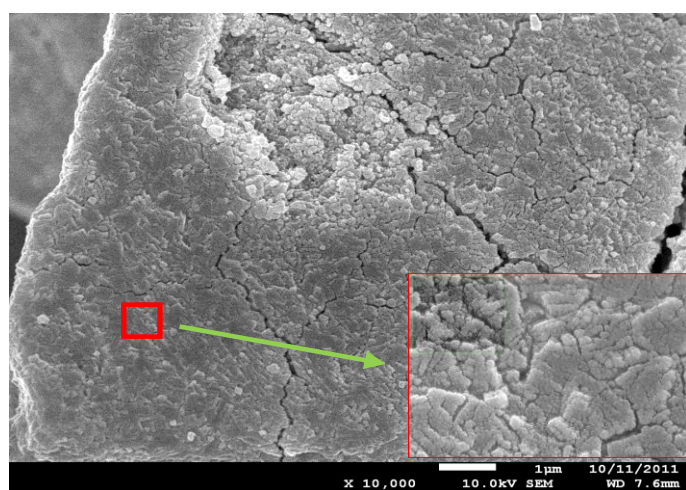
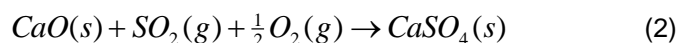
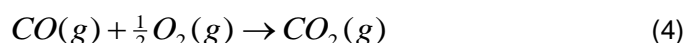


Figure 2. The indirect desulfurization particle morphology in the reaction atmosphere of 65%N₂, 15%CO₂, 4.7%O₂, 15%H₂O, 0.3%SO₂.

The chemical reaction equation is as follows:



According to above equations, the limestone does not directly involve in the desulfurization reaction, and the desulfurization reaction cannot happen without intermediate CaO, so it is called indirect desulfurization (De Diego et al., 2011; Pisani De Moraes 2004). However in the CFB oxy-fuel boiler, pure oxygen (O₂) is the fuel accelerant, and the partial pressure of CO₂ in its flue gas is high about >80% (Wu et al., 2011; De Joannon et al., 2012). Under such a high partial pressure of CO₂, the thermal decomposition of limestone particle like Equation (1) cannot occur anyhow. So recently, some researchers include us consider that its reaction in this case should be as follows (Scala et al., 2010; Stewart et al., 2012).



Because CaO does not appear in this reaction, it is also called direct desulfurization. The reports on the direct desulfurization are rarely, especially for the evidence on CO. As we all know, any reaction mechanism is closely related to its reactant microstructure, so those limestone powder's surface micro-structure properties may be different between two cases, and some clues were found by us as following.

EXPERIMENTAL SETUP

In order to verify that indeed some differences exist, the tube furnace system was built for indirect/direct desulfurization reaction experiments as shown in Figure 1, by which the aforementioned two reactions could be simulated for getting the limestone desulfurization samples. It includes: (1) In first test, the indirect desulfurization atmosphere was make up by N₂(65%), CO₂(15%), O₂(4.7%), H₂O(15%), SO₂(0.3%). (2) In second test, the direct desulfurization atmosphere was make up by CO₂(80%), O₂(4.7%), H₂O(15%), SO₂(0.3%). At above two tests, the working temperatures were both 850°C, the gas flows were both 60 ml/min, the limestone particles were both sieved by 15.6 μm, the limestone powder were put into the porcelain and sent into the furnace by a track, the reaction times were both 40 min. After tests, the samples were removed and kept under seal. Both of above samples were observed by scanning electron microscope (SEM; KYKY3800, China).

RESULTS AND DISCUSSION

Figure 2 is the sample particle from the first test in the flue gas of traditional coal-fired boiler, and its magnification is 10000 times. It is shown that the surface

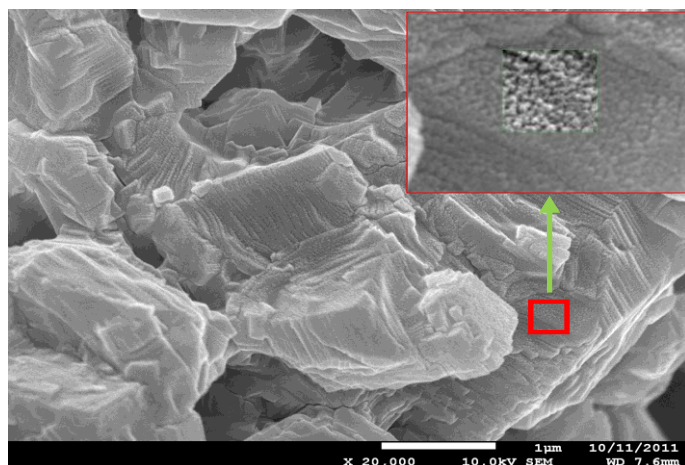


Figure 3. The direct desulfurization particle morphology in the reaction atmosphere of 80%CO₂, 4.7%O₂, 15%H₂O, 0.3%SO₂.

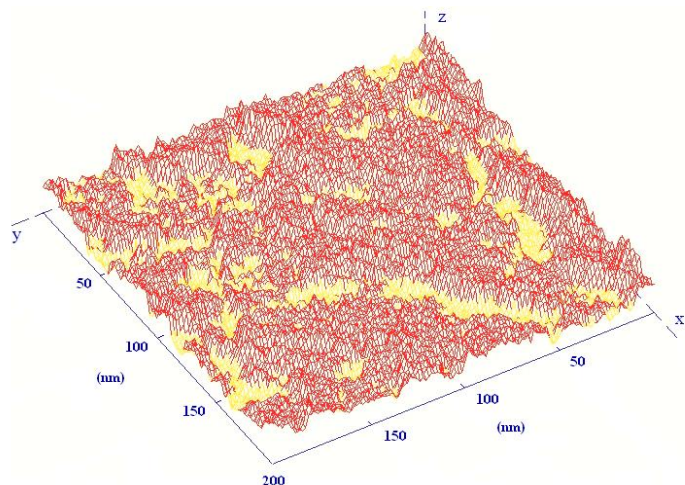


Figure 4. The indirect desulfurization micro-morphology reconstruction by Fourier transformation.

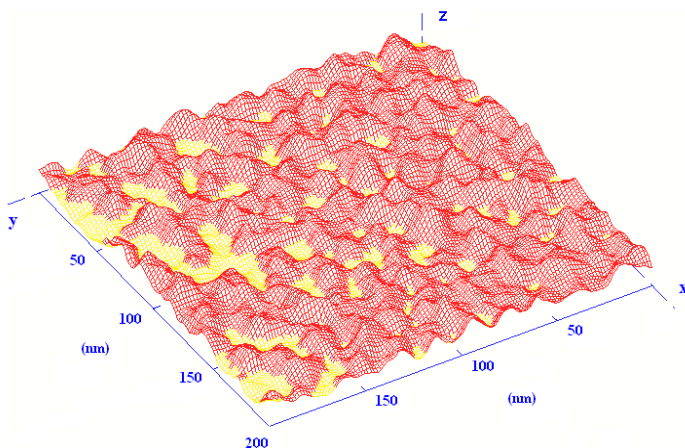


Figure 5. The direct desulfurization micro-morphology reconstruction by Fourier transformation.

of sample particle is covered by dark desulfurization product layer, on which there is a breakpoint. At the breakpoint, a large number of smaller un-reacted grains appear to agglomerate together, the grain sizes are about 200 nm. Pores between those grains should be same size order of magnitude with those grains. The origin for those pores is that CO₂ gas fully precipitates according to Equation 1 during the pre-calcination process before the beginning of indirect desulfurization reaction. Obviously, the blockage phenomenon is serious on the surface of sulfide layer. In the enlarged image as shown in the red-region, the product of CaSO₄ is cotton-shaped and this shape may be caused by the outward diffusion (Hsia et al., 1995) of Ca²⁺. Figure 3 is the particle morphology in the second test simulated the flue gas of CFB oxy-fuel boiler. There is an obvious structural difference with Figure 2 that CaO grains do not appear anywhere and those larger pores like Figure 2 inside particle do not exist yet. However we have found that there are a lot of extremely smaller micro-pores on the surface of product layer in Figure 3. For example in the red region, those pore's quantity is great, and their size and their growth law are that we care about. In the enlarged region in Figure 3; the surface of product layer is honeycombed with extremely smaller pores, which should also be a large number below the surface. For the above two experimental samples, their morphologies are different. In order to deeply and microscopically get their structural properties, the mathematical analysis is necessary by Fourier transformation (Solookinejad et al., 2011; Szloch et al., 2012) which can transform the image pixel into frequency height at 3-D space as shown in Figures 4 and 5.

In Figure 4, the 3-D morphology is reconstructed from the red region in Figure 2. The sulfide products are chaotic derivatives like numerous cluster mountains, in which outward growth heights are very uneven. Any valuable pore cannot be found; it may be two reasons, one is that CO₂ does not continue to separate out from the dense internal of grains, the other is that many pores between grains are blocked by those outward growth sulfide products (Vieille et al., 2012; Adnadjecic and Popovic., 2008). From the point of gas diffusion theory, such topography is not conducive to the reaction mass diffusion, and therefore it will result in lower desulfurization efficiency. In Figure 5, the 3-D morphology is reconstructed from the red region in Figure 3. The product growth heights are uniform; the distribution of those pores is also uniform and pore sizes are about 20 nm, any blockage cannot be found, the active sites for adsorption are very rich. So, we may reasonably conclude that gaseous reactive substances can constantly and uniformly precipitate through those micro pores during the reaction process of desulfurization. Because the partial pressure of CO₂ in this reaction atmosphere is high about >80%, the gaseous precipitated product should not be CO₂ (Yu et al., 2013). During the process of desulfurization reaction as shown in Figure 6, Ca²⁺ combines SO₂ molecule into

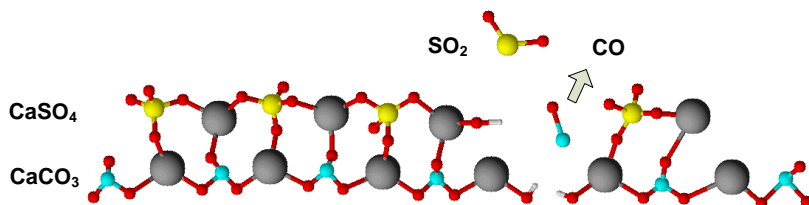


Figure 6. The precipitation of CO from CaSO₄ product layer leads to micro-porous passages.

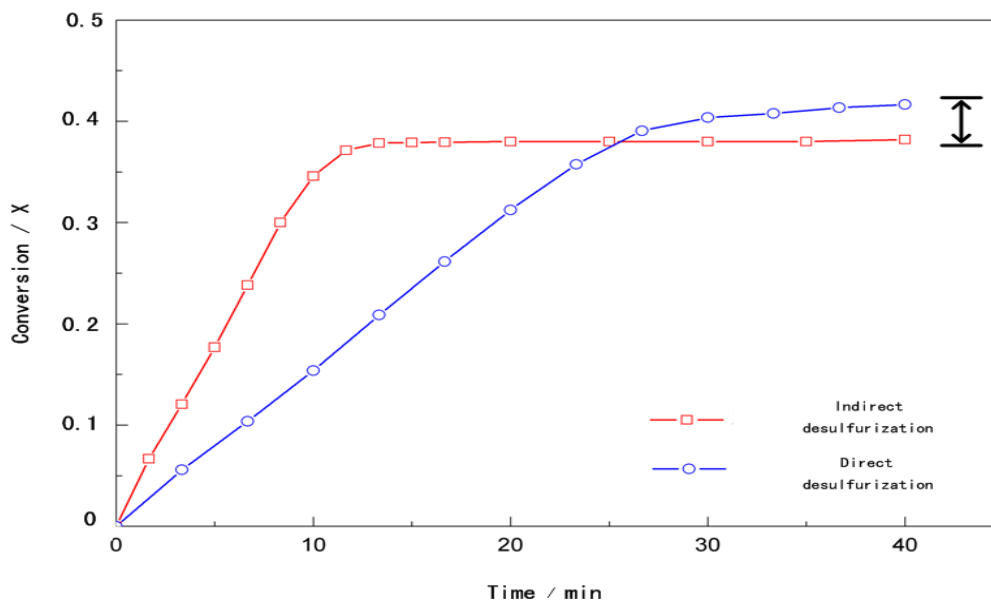


Figure 7. SO₂ removal Conversion of indirect/direct desulfurization.

calcium sulfate, at the same time CO molecule is precipitated and combined with free O₂ into stable CO₂ molecule at high temperatures. The precipitation of CO is continuous and is synchronized to the desulfurization reaction, so some channels will occur for CO emissions.

The type of chemical mechanism leads to its type of microscopic structure and this supports Equation (3) from a new perspective which considers that the gas is CO. This reaction pattern is highly efficient because those micro-porous passages can guarantee continuous reactive substance transmission, and it will result in high calcium utilization.

Indirect desulfurization rate is calculated as:

$$X = \frac{M_{CaO}}{M_{CaSO_4} - M_{CaO}} \times \frac{\Delta m}{m_0} \quad (5)$$

Direct desulfurization rate is calculated as:

$$X = \frac{M_{CaCO_3}}{M_{CaSO_4} - M_{CaCO_3}} \times \frac{\Delta m}{m_0} \quad (6)$$

Where X is conversion rate, M is molecular weight, m_0 means inlet gas quality, Δm means quality change. To observe the TGA curve as shown in Figure 7, we can find that the final conversion of direct desulfurization is really higher than that of indirect desulfurization; this is just a proof of the above discussion. However, these micro-pores are about one magnitude smaller than those in indirect desulfurization, so in the internal of sulfide product layer, it is easy to form many closed micro-cavities. Theoretically, for the outward growth solid-state Ca²⁺, whether each closed cavity in the internal maybe play an impediment role or play a short-circuit role, which has not been reported anywhere, will also be that we are very interested in.

Conclusions

In summary, for the limestone particle in coal-fired flue gas, its microstructure is closely related to its desulfurization reaction mechanism. The sizes of internal pore within sorbent particles differ by an order of

magnitude in two kind reaction atmospheres, one is about 200 nm for indirect desulfurization, and the other is about 20 nm for direct desulfurization. For the indirect desulfurization reaction, the sulfide products are chaotic derivatives like numerous cluster mountains, and the blocking phenomenon occurs seriously. For the direct desulfurization reaction, the product layer belongs to honeycombed micro structure without blockage, and a lot of smaller micro-porous passages can guarantee continuous reactive substance transmission, which may be a meaningful enlightenment to further improve the efficiency of SO₂ removal in industry.

ACKNOWLEDGMENTS

This work was supported by the National Key Technology R&D Program of China (2012BAC24B01), the National Natural Science Foundation of China (51276064), the Beijing Nature Science Foundation (3132028), and the Beijing Postdoctoral Research Foundation (2012ZZ-19).

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