DESULFURIZATION OF COAL

Yasuo Ohtsuka

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan

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Contents

Summary

Sulfur in coal exists in inorganic and organic forms, the former being mostly pyritic sulfur. Total sulfur contents in major coalfields are in the range of roughly 0.5–10 wt%. In coal combustion, to generate electric power and process heat, the sulfur is emitted as SO_2, which is seen as one of the main causes of acid rain. This effect has led to an interest in the three main methods of removing coal sulfur: coal cleaning, in-bed desulfurization, and flue gas desulfurization. Coal cleaning includes physical, chemical, and biological processes. Since physical cleaning is generally based on the differences in either specific gravity or surface properties between the organic matter in coal and the associated minerals, it can remove the inorganic sulfur alone. This method is the commercially proven technology. Chemical or biological cleaning can offer the potential to remove organic sulfur, but these methods have not yet been used commercially. Development work is currently directed towards establishing effective, low-cost techniques. In-bed desulfurization involves the use of Ca-based sorbent, which captures *in situ* the SO_2 emitted during fluidized bed combustion. Although this high

temperature desulfurization process is well proven, the reduction of sorbent consumption is required to minimize the costs for sorbent and residue management. Flue gas desulfurization (FGD) removes the SO_2 from the flue gas of coal-fired plants. This post-combustion method is the most widely used technology for controlling SO_2 emissions. Among commercial FGD processes, wet scrubbers account for more than 80% of the total capacity and achieve SO_2 removal efficiencies of more than 90%. The majority of them uses the limestone (or wet lime)/gypsum system. Spray dry scrubbers and sorbent injection processes have been used for relatively small to medium capacity boilers and for retrofitting on existing coal-fired plants.

1. Introduction

Coal is one of the main sources of world energy. Economic growth and industrialization in developing countries are leading to a rapid increase in the demand for energy; in other words, an increased demand in the use of coal, which is inexpensive and readily available, for electric power and process heat. When coal is burned, generally 90% or more of the sulfur present in it is emitted into the atmosphere as sulfur oxides (mainly SO_2), if no desulfurization methods are used before, during, and after combustion. It is well-known that SO_2 emissions are considered one of the main causes of acid rain, which leads to the acidification of soils, forests, and surface waters. The growth in coal-fired capacity has therefore led to increasing concern about environmental issues, such as increased emissions of SO_2, nitrogen oxides (NO_x), trace elements, and particulates, although most effort has been directed towards the control of SO_2 emissions. This article focuses on the reduction of SO_2 emissions in the use of coal, in particular from coal combustion, and addresses the following options for this purpose:

- The use of low-sulfur coal
- Pretreatment of coal for sulfur removal.
- *In situ* sulfur capture during combustion.
- Post-combustion treatment of flue gas

2. Sulfur in Coal

2.1 Sulfur Content

The total sulfur content of coal can vary within a single deposit as well as between deposits. As summarized in Table 1, the content for selected coalfields of major coal producing countries ranges between below 0.5 wt% and roughly 10 wt%. Since coals on the international market have stricter specifications regarding sulfur and ash content, however, the former is generally in the range of 0.6–1 wt%. Global sources of such low-sulfur coals are diverse, with the largest deposits in China, South Africa, Australia, USA, and Russia. With increasingly stringent environment legislation, coal sulfur content has become one of the most important factors for fuel choice, and the supply of low-sulfur coal on the international coal market has increased considerably in recent years. Nevertheless, major users such as power stations have often been tied to local supplies of high-sulfur coal because of quality, cost, or policy. In the USA and Indonesia, for example, many low-sulfur coals are of low rank with decreased calorific value and increased moisture content, compared with high-sulfur coals. With limited

supplies of high quality low-sulfur coal, blending with high-sulfur coals may help utilities meet SO_2 emission standards.

Country	Coalfields and Region	Total sulfur content, wt%
Australia	Queensland basin	0.2-1.3 (air dried)
Canada	Western	0.2-1.2
China	Shanxi	0.4-6.0
Columbia	Cerrejon	0.4-0.9 (air dried)
Germany	Ruhr	0.7-0.8
India	Raniganj and Jharia	0.5-0.8 (air dried)
Indonesia	Kalimantan	0.1-0.9
Poland	Upper Silesian basin	0.8-1.8
Russia	Kuznetsk basin	0.3-0.8
South Africa	Witbank and Highveld	0.3-2.4 (air dried)
UK	East Pennine	0.8-4.0
USA	Illinois basin	0.2-7.7

Table 1. Total sulfur contents for selected coalfields of major coal producing countries
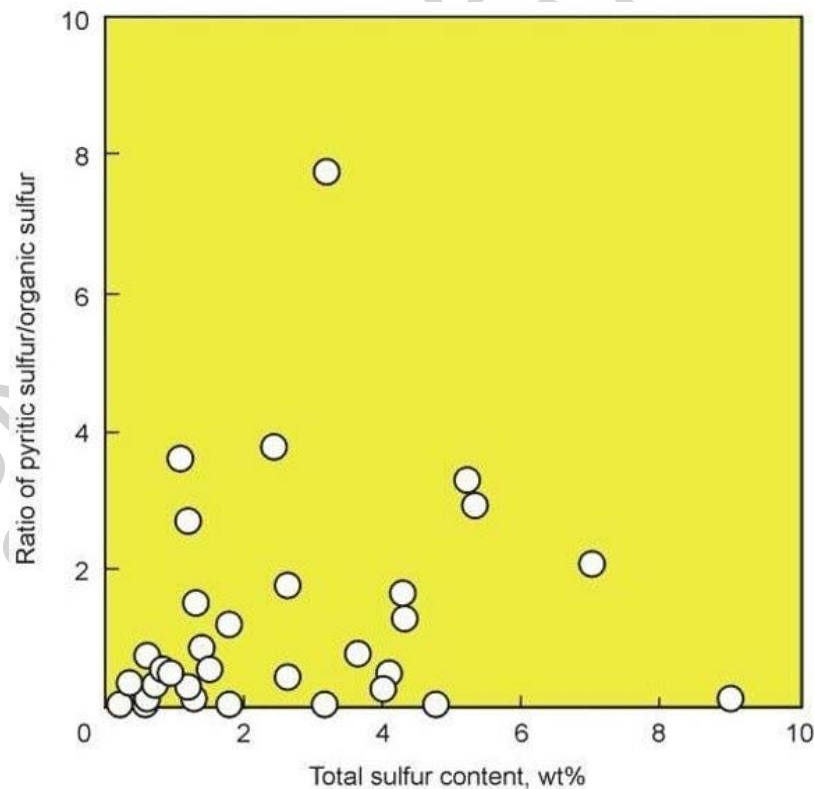
2.2 Sulfur Form

Figure 1. Ratio of pyritic sulfur/organic sulfur as a function of total sulfur content

Sulfur present in coal exists as both inorganic and organic forms. The inorganic form is mostly pyritic sulfur (FeS_2), which occurs in two crystalline habits, pyrite (cubic) and

marcasite (orthorhombic), the former being more common. Although sulfate and elemental sulfur are also observed, their contents are low. The sulfatic form is mainly gypsum and iron sulfate, the latter usually resulting from oxidation of pyritic sulfur during storage.

Pyritic and organic sulfur together account for the large majority of sulfur in coal. The ratio of the two forms as a function of total sulfur content is shown in Figure 1, where 35 coal samples from major coal producing countries are used. Although there is no distinct relationship, the ratio is less than two in most samples. Since pyritic sulfur can be removed by physical cleaning, as mentioned below (see 2.1), it is usually easy to reduce the total sulfur in the coal with a high ratio of pyritic sulfur/organic sulfur.

The ASTM standard test method (D 2492) applies to the determination of pyritic and sulfatic sulfur. In this method, briefly, coal particles are first extracted with hot dilute HCl to remove sulfatic sulfur, and the residue is then extracted with dilute HNO_3 to measure the iron content, which makes it possible to calculate the content of pyritic sulfur from the 1:2 stoichiometry of FeS_2. Organic sulfur is determined by difference; that is, by subtracting the sum of pyritic and sulfatic forms from total sulfur content, and is thus subject to the accumulated errors in these measurements. To remove such uncertainty, some analytical techniques for the direct determination of organic sulfur, such as chemical and instrumental methods, have recently been proposed.

The forms of organic sulfur are less well established. Organic sulfur compounds have been identified in extracts and soluble reaction products from coal, and thiophenic sulfur forms in coal have been evidenced substantially. Chemical methods, such as flash pyrolysis, temperature-programmed reduction and oxidation, have been used to quantify organic sulfur forms.

Furthermore, new instrumental quantification techniques, which involve X-ray photoelectron spectroscopy and X-ray absorption near edge structure spectroscopy, have recently been developed. Since all of these quantitative analyses rely on models to de-convolute the data, however, there are difficulties in data interpretation. In summary, the majority of the organic sulfur in high rank coal is in thiophenic forms, and the proportion of non-thiophenic groups including sulfide forms is higher in low rank coal, but the presence of thiol forms in coal is unclear. A better understanding of organic sulfur forms and quantities is essentially needed for chemical and biological coal cleaning (see 3.2 and 3.3).

3. Coal Cleaning for Sulfur Removal

The coal cleaning process has traditionally focused on reducing ash-reforming minerals and not necessarily aimed at removing sulfur in coal until recently. However, increasingly stringent regulations for SO_x emissions during coal combustion have encouraged technical development of coal cleaning for sulfur removal. Physical cleaning techniques to remove inorganic sulfur forms, mainly pyritic sulfur, are well established and widely used. On the other hand, chemical and biological cleaning can offer the potential to remove organic sulfur, but these methods have not yet been applied commercially.

3.1 Physical Cleaning

Physical cleaning of coal is essentially based on the differences in either specific gravity or surface properties between the organic matter and the associated minerals, although a few separations that are conducted on the basis of their magnetic and electrostatic properties have been proposed. All of these methods are generally carried out within three distinct size ranges, that is, coarse (10–150 mm), intermediate (0.5–10 mm), and fine (< 500 µm). Coarse and intermediate sizes are separated by gravity-based methods, which become increasingly inefficient for smaller particles. Methods based on surface property differences are then used. Since conventional techniques are not readily applicable to ultra-fine particles (generally below 100 µm), advanced technologies focus mainly on cleaning ultra-fines.

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Biographical Sketch

Yasuo Ohtsuka is an associate professor at the Research Center for Sustainable Materials Engineering, the Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, and he is leading the Laboratory of Catalytic Conversion Chemistry. His research interest includes fossil fuels conversion, heterogeneous catalysis, environmental protection, and porous materials. After receiving a Ph.D. in applied chemistry at Tohoku University, he joined the Chemical Research Institute of Non-Aqueous Solutions (the former name of IMRAM). He was a visiting fellow at CSIRO Division of Coal and Energy Technology, Sydney, in 1988, and at Energy Research Laboratories, CANMET, Ottawa, in 1993. The Fuel Society of Japan (currently the Japan Institute of Energy) awarded him the prize for advancements in fuel science in 1989. His group's paper presented in the Division of Fuel Science Symposium at the ACS National Meeting held in 2000 was also awarded the Richard A. Glenn Award. He is one of the authors in a Japanese textbook entitled "Organic Resources Chemistry" to be published in 2002.