Effect of Pulp Density on Biodesulfurization of Mongolian Lignite Coal

Ashish Pathak, Dong-Jin Kim, Byoung-Gon Kim

Abstract**—**Biological processes based on oxidation of sulfur compounds by chemolithotrophic microorganisms are emerging as an efficient and eco-friendly technique for removal of sulfur from the coal. In the present article, study was carried out to investigate the potential of biodesulfurization process in removing the sulfur from lignite coal sample collected from a Mongolian coal mine. The batch biodesulfurization experiments were conducted in 2.5 L borosilicate baffle type reactors at 35 ºC using *Acidithiobacillus ferrooxidans*. The effect of pulp density on efficiency of biodesulfurization was investigated at different solids concentration (1-10%) of coal. The results of the present study suggested that the rate of desulfurization was retarded at higher coal pulp density. The optimum pulp density found 5% at which about 48% of the total sulfur was removed from the coal.

Keywords**—**Biodesulfurization, bioreactor, coal, pyrite.

I. Introduction

THE direct combustion of coal containing sulfur results in several environmental problems, viz. emission of oxides of sulfur and acid rain [1].The sulfur dioxide has deleterious effects on human health and lead to respiratory illness. Acid rain causes erosion of building materials and corrosion of steel structures. Therefore, the best possible way to prevent environment damages from sulfur dioxide and acid rain is to reduce the amount of sulfur in coal before combustion. The sulfur in the coal tends to found mostly in the inorganic form, whereas a small amount of sulfur is also present as organically bound. Therefore, removal of inorganic sulfur (pyrite) is a major thrust area for obtaining the clean coal. In the past, many physicochemical methods have been tested to remove the sulfur from coal. These methods include floatation, oxidation and reduction with chemicals [2]. However, physical techniques results in incomplete removal of the coal pyrite embedded in the matrix. On the other hand, the chemical methods are energy intensive and also generate secondary waste products [3], [4].

Dr. Ashish Pathak is a Post-Doctoral Research Fellow at Mineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources, Gwahang-no 124, Yuseong-gu, Daejeon, 305-350, South Korea (e-mail: ashishpathak05@gmail.com).

Dr. Dong Jin Kim is a Principal Researcher at Mineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources, Gwahang-no 124, Yuseong-gu, Daejeon, 305-350, South Korea (Corresponding author-Tel: +82-42-8683592; Fax: +82-42-8683415; e-mail: djkim@kigam.re.kr).

Dr. Byoung-Gon Kim is the Principal Researcher at Mineral Resource Research Division, Korea Institute of Geoscience and Mineral Resources, Gwahang-no 124, Yuseong-gu, Daejeon, 305-350, South Korea (e-mail: bgkim@kigam.re.kr).

In the light of above, the use of microorganisms capable of oxidizing the sulfur compounds present in coal represents a clean and economical alternative. In biodesulfurization process microorganisms promote the oxidative conversion of the reduced sulfur compounds to soluble, easily washed-out compounds. Moreover, these microorganisms can grow and thrive at ambient temperature and pressure, making them convenient for use [5]. The dominant microorganisms used in biodesulfurization process belong to the genus of *Acidithiobacillus*. The main species belong to this genus are chemoautotrophic bacteria, namely *Acidithiobacillus ferrooxidans* (*At. ferrooxidans)* and *Acidithiobacillus thiooxidans* (*At. thiooxidans)* [6], [7]. These species oxidize the pyrite present in the coal and subsequently liberate the sulfur as soluble sulfate.

In recent years, many studies were conducted in different types of reactor system for utilizing the efficiency of these microorganisms in removing the sulfur from coal [8]-[10]. It has also been reported that many operating parameters such as pulp density, particle size, type of microbes, etc. can affect the efficiency of the overall biodesulfurization process. Among these, pulp density of coal is one of the most important parameter which affects the rate of sulfur removal and also influences greatly the operating cost of biodesulfurization process. The high quantity of coal decreases the volume of slurry to be processed. Therefore, the aim of the present study was to investigate the effect of an important parameter on biodesulfurization i.e. pulp density. The study was undertaken in 2.5 L stirred baffled type batch bioreactors by employing *At. ferrooxidans*.

II. Materials and Methods

A. Sample

The lignite coal sample was procured from a coal mine located in Mongolia. The coal sample was first crushed by Jaw crusher followed by grinding by pulverizer. The pulverized coal was subjected to vibrating cup mill and then sieved to obtain the desire particle size (106-212 μm).The physicochemical parameters of the coal sample used in the present study are provided in Table I.

B. Microorganisms

Pure culture of *At. ferrooxidans* was used for the desulfurization activity in the present study. *At. ferrooxidans* was procured from culture collection centre of Korea Research Institute of Bioscience and Biotechnology, South Korea. *At. ferrooxidans* were grown in 4.5 K medium. The 4.5 K medium was consist of the following chemicals: $(NH_4)_2SO_4$(3.00 g), KCl (0.1 g), K_2HPO_4 (0.50 g), $Ca(NO_3)_2$(0.01g), $MgSO_4 \cdot 7H_2O$ (0.50 g) and dissolved in 1.00 L of distilled water. This medium was supplemented with 4.5 g/L of ferrous iron and 2mM of potassium tetrathionate at pH 1.68.*At.ferrooxidans* was grown at 35 ºC and 220 RPM. During the growth of *At. ferrooxidans,* the Fe^{2+} was completely oxidized to Fe^{3+}which turn the color of medium as red. After complete bio-oxidation of ferrous to ferric, the bacterial culture was filtered through a membrane filter (0.45 μ) and the harvested cells were transferred to a fresh nutrient medium for further subculture under similar conditions.

TABLE I
PHYSICO-CHEMICAL ANALYSIS OF THE FEED COAL

SI. No	Parameter	Value	Unit
1	Total moisture content	26.15	Wt.(%)
2	Total ash content	19.01	Wt.(%)
3	Volatile matter content	29.62	Wt.(%)
4	Fixed carbon	25.22	Wt.(%)
5	Total sulfur	3.99	Wt.(%)
6	Pyritic sulfur	1.87	Wt.(%)
7	Gross calorific value	4140	Kcal/kg

C. Analytical and Instrumentation Techniques

The analytical techniques used in the present study were followed by the estimation of pH, redox potential, planktonic cell count and sulfate concentration. The pH was monitored by using a pH meter and three point calibration of pH meter was carried out once every day using standard buffers of pH 1.68, 4.0 and 7.0. The changes in microbial concentration were studied by cell count of the viable planktonic cells using an improved Neubauer Haemocytometer under Olympus made phase-contrast microscope (model No BX51TF). A platinum electrode combined with an Ag/AgCl reference electrode was used for the measurement of redox potential. The sulfate concentrations were analyzed by barium chloride method. The total sulfur in the feed coal and treated residues was measured using the inductively coupled plasma atomic omission spectrometry (ICP-OES).The mineralogical analysis of the coal was performed using X-ray diffractogram (XRD) study. XRD analysis was performed using Rigaku RTC 300 by continuous scanning method at 30 mV and 40 mA. The XRD analysis confirmed the presence of pyrite in the coal sample (Fig. 1). The chemical composition of the feed coal was analyzed by LECO analyzer, and is shown in Table I.

D. Biodesulfurization Experiment

Batch biodesulfurization experiments were performed in 2.5 L borosilicate baffled stirred tank reactors at a working volume of 1L.The experiments were conducted in separate reactors at different pulp densities of 1, 5 and 10%(w/v) in an iron free 4.5 K medium (initial pH 1.5). The bioreactor medium consisted of 100 mL of previously grown culture of *At. ferrooxidans* and 900 mL of iron free 4.5 K medium. The batch reactors were operated under mesophilic conditions at 35 ºC and 220RPM. The pulp in the reactors was mixed through a propeller, whereas aerobic conditions were maintained by providing the air at a rate of 1 LPM.

Experiments were followed by the daily measurements of pH, redox potential, sulfate concentration and planktonic cell count in the reactor. Water lost due to evaporation was compensated by adding the fresh deionized water to the reactor. The reactor run was continued until stable redox potential and pH was achieved. After completion of the experiment, the reactor content was harvested and filtered. The filtered solids were washed with acidified deionized water. The washed coal was oven dried and subjected to chemical analysis.

The desulfurization yield was calculated based on the amount of sulfur present in the feed coal as well as in leachate. The leaching yield of sulfur was calculated as per formulae given below:

$$\text{Yield (\%)} = \left[\frac{M(r)}{M(f)}\right] X\ 100 \tag{1}$$

where M(r) is the S content in the leachate and M(f) is the S content in the feed coal.

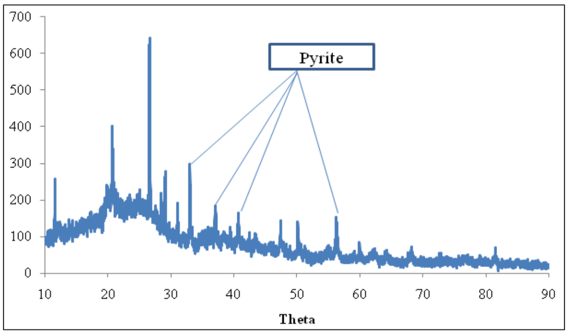

Fig.1 XRD spectrum of the feed coal

III. RESULTS AND DISCUSSION

Biodesulfurization experiments conducted at different pulp densities of Mongolian coal exhibited slight variation in changes in pH (Fig. 2). It is to be noted that about 10% (v/v) of the inoculum (microbial culture) was added to each reactor at the start of the experiment. The inoculum was rich in ferric iron, which caused the initial attack on the pyrite present in the coal. The ferric attack on the pyrite is known to produce $S_2O_3^{2-}$ and Fe^{2+} ion as intermediate products:

$$FeS_2 + 6Fe^{3+} + 3H_2O \longrightarrow 7Fe^{2+} + S_2O_3^{2-} + 6H^+ \tag{2}$$

The released Fe^{2+} ions from FeS_2 oxidation oxidized to Fe^{3+} ion by the *At. ferrooxidans* (3).

$$Fe^{2+} + 1/4O_2 + H^+ \xrightarrow{\text{Bacteria}} Fe^{3+} + 1/2H_2O \tag{3}$$

On the other hand, produced $S_2O_3^{2-}$ is further oxidized by the Fe^{3+} ions and bacteria to produce SO_4^{2-} ions (4).

$$S_2O_3^{2-} + 8Fe^{3+} + 5H_2O \longrightarrow 2SO_4^{2-} + 8Fe^{2+} + 10H^+ \tag{4}$$

The overall reaction can be written as (5):

$$FeS_2 + 7/2O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{5}$$

As seen from the reaction 5, the overall bio-oxidation of coal pyrite is an acid generating reaction. The generated acid during biodesulfurization helps in maintaining the desired acidic pH for the growth of *At. ferrooxidans*. It was observed that during the reactors run, pH in all reactors (except for 1% pulp density) increased slightly within first 3 days from an initial value of 1.5 (Fig. 2). However, after an initial increase, there was not much change in the pH of the reactors and pH remained constant throughout the course of the experiment. Overall, it was observed that the pulp density has a slight impact on the changes in pH and maximum pH (1.86) was observed in the reactor operated at 10% slurry density. The pH in all three reactors varied between 1.39-1.86. This suggested that microorganisms in the reactors efficiently oxidized the coal pyrite which results in generation of acid, thus maintaining the acidic conditions within the reactors.

Fig. 2 represents the changes in redox potential during biodesulfurization process at different pulp densities. The redox potential in all reactors was measured on a regular basis to follow the growth of the microorganism and oxidation of ferrous to ferric iron. During the initial days of the experiment, ferric ion present in the inoculum was consumed in FeS_2 oxidation. The oxidation of FeS_2 released Fe^{2+} ion in solution resulting in an increase of Fe^{2+} ions in the solution and decrease in the redox potential, which can be clearly seen from Fig. 2. All the reactors were started with a redox potential of 598 mV. A rapid decrease in the redox potential was observed in all reactors and redox potential decreased to 432, 374, and 345 mV in the first 3 days. After initial decrease, there was a gradual increase in the redox potential in all reactors till the end of the experiment. The maximum final redox potentail (601 mV) was achieved for the reactor operating at 5% pulp density, whereas lower final redox potential (535 mV) was observed for the reactor having a highest pulp density (10%). The low redox potential in the reactor operating with 10% pulp density may have been due to the incomplete oxidation of ferrous to ferric iron at higher pulp density.

It was also observed that due to the oxidation of pyrite, a significant decrease in sulfur content was observed in all the reactors, though with different rates. Due to the microbial oxidation of pyritic sulfur, the amount of sulfate also increased in the liquid medium (Fig. 3). The results also suggested that the removal of sulfur increased gradually till the end of the experiment (Fig. 4).

During biodesulfruization, the pulp density of the coal was found to have a pronounced effect on the efficiency of sulfur removal. At a pulp density of 1 and 5%, not much difference in the removal of total sulfur was observed. At 1% pulp density, about 52% of the total sulfur was removed from the coal. By increasing the pulp density from 1 to 5%, a slight decrease in the removal of sulfur was observed and about 48% of the total sulfur was removed from the coal. Nevertheless, a substantial decrease in removal efficiency was observed when pulp density increased from 5 to 10%. At 10% pulp density only 39% of the total sulfur could be removed from the coal.

The lower sulfur removal at a higher pulp density can be explained on the basis that at higher pulp densities, the transfer capacity of O_2 and CO_2 decreases. Further, improper mixing of the pulp inhibits reaction of coal particles with lixiviant. These cause the reduction in overall biodesulfurization efficiency at higher pulp density. The decrease in microbial desulfurization efficiency due to the high solids concentration of coal has been reported previously in a study carried out using Indian coal [11]. The results of the present investigation suggested that 5% is an optimum pulp density for conducting the coal biodesulfurization using Mongolian lignite coal.

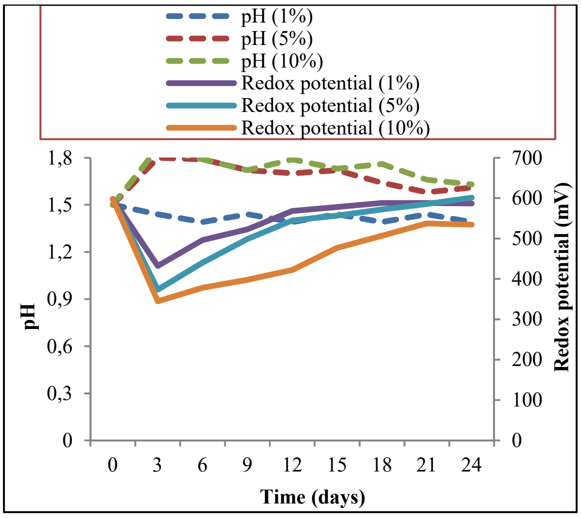

Fig. 2 The changes in pH and redox potential with time

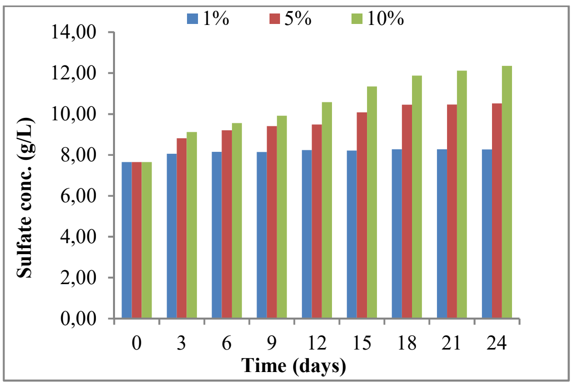

Fig. 3 The changes in sulfate concentration with time

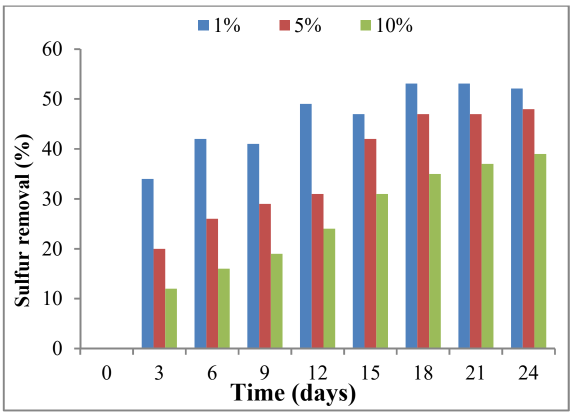

Fig. 4 Removal of total sulfur with time at different pulp densities

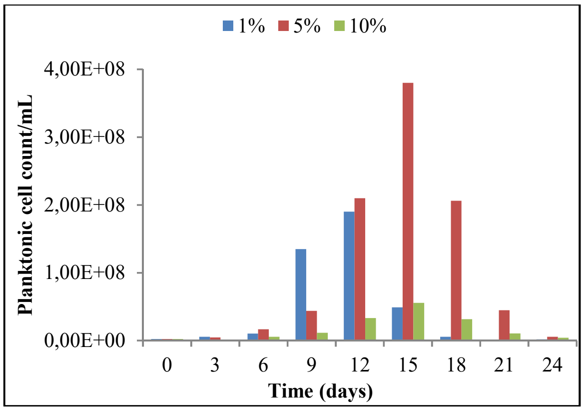

Fig. 5 Change in planktonic cell count with time

During biodesulfurization, there were differences in the planktonic cell dynamics in different pulp densities. The number of viable planktonic cells at the start of the experiment was 2.4×10^{6}cells/mL. The planktonic cell count decrease drastically within the first 3 days in all reactors. This initial decrease was due to the sudden decrease in the redox potential. Moreover, most of the cell initially presents in the medium also got attached to the coal particles which lead to the initial decrease in planktonic cell count. After initial decrease, cell count tends to increases in all the reactors owning to oxidation of pyrite present in the coal. The maximum cell count was observed in the reactor operated with 5% pulp density. The maximum cell count was found to be at $3.8\times 10^{\wedge 8}$ on the 15th day of experiment after which cell count starts to decline till the end of the experiment. At 10% pulp density, the cell count was significant less compared to the reactor having 5% pulp density. The decrease in cell count at a higher pulp density was due to the suppress growth of microorganisms as a result of poor mixing and decreased mass transfer of gases.

IV. Conclusion

The results of the study conducted with *At. ferrooxidans* confirmed the effectiveness of biodesulfurization process in removal of sulfur from coal. The study also suggested that pulp density has an important effect on the efficiency of the process. At a higher pulp density, the efficiency of biodesulfurization process was found to decrease. Overall, 5% was found to be the optimum pulp density for efficient and economical biodesulfurization. At 5% pulp density about 48% of the total sulfur was removed from the coal.

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