Depyritization of US Coal Using Iron-Oxidizing Bacteria: Batch Stirred Reactor Study

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

Abstract-Microbial depyritization of coal using chemoautotrophic bacteria is gaining acceptance as an efficient and eco-friendly technique. The process uses the metabolic activity of chemoautotrophic bacteria in removing sulfur and pyrite from the coal. The aim of the present study was to investigate the potential of Acidithiobacillus ferrooxidans in removing the pyritic sulfur and iron from high iron and sulfur containing US coal. The experiment was undertaken in 8L bench scale stirred tank reactor having 1% (w/v) pulp density of coal. The reactor was operated at 35°C and aerobic conditions were maintained by sparging the air into the reactor. It was found that at the end of bio-depyritization process, about 90% of pyrite and 67% of pyritic sulfur was removed from the coal. The results indicate that the bio-depyritization process is an efficient process in treating the high pyrite and sulfur containing coal.

Keywords—*At. ferrooxidans*, Batch reactor, Coal desulfurization, Pyrite.

I. INTRODUCTION

THE combustion of coal for power generation is known to L cause environmental damage in the form of acid rain and emission of sulfur dioxide [1]. The sulfur dioxide caused formation of sulfate aerosol, lead to respiratory illnesses, whereas acid rains cause serious damages to the building material, biota and natural ecosystems. The emission of sulfurdioxide and acid rain is due to the combustion of sulfur present in the coal. Sulfur present in variety of coals largely in three forms: pyritic, organic and sulfate sulfur. The sulfur associated with organic matter is the integral part of the coal matrix, whereas pyritic sulfur present in coal as mineral matter. The pyritic sulfur is generally present in highest concentration in most of the coals. The heterogenous nature and varied mineralogical composition makes it difficult to demineralize the coal prior to its combustion. The removal of pyritic sulfur prior to combustion is an effective way to ensure environmental clean combustion of coal. Various physical and chemical methods have been tested to remove the sulfur from coal by floatation, oxidation and reduction with chemicals [2].

However, the physical methods suffer problems such as loss of a major portion of coal and inadequate removal of mineral matter embedded in the matrix. On the other hand, the chemical methods employed were found efficient in removing sulfur from coal but they produce secondary waste products and also affect structural integrity of the coal [3], [4]. Therefore, research interest has been shifted to biological depyritzation processes which offer a clean and economical alternative to remove sulfur from coals. In biodepyritization process, microbes catalyze the biochemical reactions resulting in oxidation and conversion of insoluble pyrite sulfur into soluble sulfate [5]. The chief microorganisms used in biodepyritization process are chemoautotrophic mesophilic bacteria such as Acidithiobacillus ferrooxidans (At. and Acidithiobacillus thiooxidans *ferrooxidans*) (At. thiooxidans) [6], [7]. The process has also been conducted using thermophilic microorganisms. However, thermophilic process is not preferred due to the high energy cost associated with it.

In recent years, researchers have attempted to utilize the efficiency of chemoautotrophic microorganisms [8]-[10] in depyritization of coal. These studies have reported the effect of solids concentration, particle size, type of microbes etc. on the efficiency of biodepyritization process. Though, the process has been fairly investigated, most of these studies were conducted in shake flasks and results varied due to the different experimental conditions and types of coal employed. Therefore, for development of an efficient and economical biodepyritization process more in-depth studies are required. The aim of the present study is to remove pyrite and pyritic sulfur from coal having high sulfur and iron content. The study was undertaken in 8 L working batch stirred reactor by employing *At. ferrooxidans* and using US coal.

II. MATERIAL AND METHODS

A. Coal Sample

The coal sample was procured from Eagle river coal LLC, Harrisburg, Illinois, US. The coal was first crushed into small pieces by Jaw crusher followed by grinding into small particles by pulverizer. The pulverized coal particles were subjected to vibrating cup mill for grinding to obtain the desire particle size (100-200 μ m). The physical and chemical properties of the coal used in the present investigation are presented in Table I.

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TABLE I CHEMICAL PROPERTIES OF THE COAL

SI. No	Parameter	Value	Unit
i.	Total moisture content	1.77	Wt. (%)
ii.	Total ash content	17.40	Wt. (%)
iii.	Volatile matter content	33.97	Wt. (%)
iv.	Fixed carbon	46.86	Wt. (%)
v.	Pyritic sulfur content	6.34	Wt. (%)
vi.	Total iron content	4.08	Wt. (%)
vii.	Gross calorific value	6,810	Kcal/kg

B. Microorganisms and Growth Conditions

At. ferrooxidans was the main microorganism responsible for biodepyritization in the present study. At. ferrooxidans is mesophilic acidophilic bacteria which utilize reduced ferrous and sulfur compound for its growth. At. ferrooxidans were grown in 9K medium. The 9K medium was composed of the following chemicals: (NH₄)₂SO₄ (3.00g), KCl (0.1g), K₂HPO₄ (0.50g), Ca(NO₃)₂ (0.01g), MgSO₄ 7H₂O (0.50g) and dissolved in 1L of distilled water and adjusted to pH 1.5 using concentrated H₂SO₄. The 9K medium was supplemented with 4.5g/L of ferrous iron and 2mM of potassium tetrathionate at pH 1.5. The bacteria were grown at 35°C and 220rpm in a batch reactor. During the growth of At. ferrooxidans all of the Fe^{2+} was oxidized to Fe^{3+} . After growth completion, the bacterial culture was filtered to separate the cells and the harvested cells were added to a fresh nutrient medium for repetitive subculture.

C. Analytical Techniques

The pH was monitored by using a pH meter, whereas a platinum electrode fitted with an Ag/AgCl reference electrode was used for the measurement of redox potential. The sulfate concentration in the liquid was measured by barium chloride method, whereas the total iron content was measured using the inductively coupled plasma atomic omission spectrometry (ICP-OES). The feed coal was also subjected to X-ray diffractogram (XRD) study for examines the detailed mineral phases in the coal. The XRD analysis was performed using Rigaku RTC 300 by continuous scanning method at 30 mV and 40 mA. The minerals phases present in the coal are presented in the Table II. It can be seen that significant concentration of pyrite was present in the coal. Besides pyrite, other common minerals in coal were quartz, clay mineral (especially albite, kaolinite) and carbonates such as calcite.

D. Coal Biodepyritization Experiment

The biodepyritization experiment was conducted in a batch stirred tank reactor having 8L working volume. Before starting the experiment, the bacterial culture was grown in a bioreactor having a pH 1.5.

The experiment was conducted using 1% (w/v) pulp density of coal in an iron free 9K medium (pH 1.5) inoculated with *At. ferrooxidans* (10% v/v). The batch reactor was operated under mesophilic conditions at 35°C and 220rpm. The mixing in the reactor was achieved by a propeller.

TABLE II MINERALOGICAL CHARACTERISTIC OF THE COAL Mineral Weight (%) 61.23 Coal Quartz 3.49 23.71 Pyrite Illite 10.4 0.05 Albite Cordierite 0.17 Zircon 0.02 Enstatite 0.1 0.26 TiO₂ 0.04 Monazite Sanidine 0.2 0.2 Apatite 0.02 Gorceixite 0.09 Calcite Arsenopyrite 0.02

The air was provided in the reactor at a rate of 1 LPM. The reactor was monitored daily and the samples were analyzed for changes in pH, redox potential, iron, and sulfate concentration. The daily loss in water due to evaporation was compensated by adding the fresh de-ionized water to the reactor. After completion of the experiment, the reactor pulp was harvested and filtered to separate the solid and liquid. The solids coal was washed with acidified deionized water to avoid precipitation of iron in the coal. The coal was oven dried and grounded using mortar and pestle. The elemental analysis of the feed coal and treated residue was used for the calculation of the leaching yield accounting the weight of the feed and treated coal.

100

Total

The recovery of iron and pyritic sulfur was calculated as per formulae given below:

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

where M(r) is the Fe and pyritic S content in the treated coal residue and M(f) is the Fe and pyritic S content in the feed coal. The yield was also calculated from elemental content of feed and leach liquor.

III. RESULTS AND DISCUSSION

Fig. 1 shows the changes in pH as a result of bio-oxidation of pyrite in the coal. During the reactor operation, *At. ferrooxidans* oxidized the Fe^{2+} ion into ferric ion by the following equation:

$$Fe^{2^+} + 1/4O_2 + H^+ \longrightarrow Fe^{3^+} + 1/2H_2O$$

During the bio-oxidation reaction, $S_2O_3^{2-}$ is also produced which is oxidized by the Fe³⁺ ions and bacteria to produce SO_4^{2-} ion.

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Bacteria

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

Therefore, the overall reaction can be written as:

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

It can be seen that during the reactor run, pH in the reactor decreased slightly from an initial value of 1.5 to 1.3. This shows luxuriant growth of the microorganisms and subsequent oxidation of pyrite resulting into generation of acid. The ferric rich inoculum along with bacteria caused liberation of pyrite from the coal. The liberated pyrite was efficiently oxidized by *At. ferrooxidans* leading to the generation of acid and subsequent decrease in pH. Generally, the low pH observed in the reactor is conducive for the bacterial growth and subsequent oxidation of pyrite. The depyritization of US coal by *At. ferrooxidans* resulted in production of low sulfur clean coal.

Fig. 1 also shows the changes in redox potential during the biological depyritization process. During the process *At. ferrooxidans* oxidized the ferrous iron into the ferric which maintained the redox potential of the reactor. It is to be noted that redox potential is a measure of the ratio between ferrous and ferric in the solution. The biodepyritization experiment was started with a redox potential of 495 mV. Initially, a slight decrease in the redox potential was observed during the process which may have been due to the reduction of ferric into ferrous. However, after 1 week of experiment, redox potential was found to increase till the end of experiment. The increase in redox potential during depyrtization process was due to bio-oxidation of ferrous iron into ferric. At the end of process, redox potential increased to 646 mV from an initial value of 495 mV.



Fig. 1 The changes in pH and redox potential with time

The removal of pyrite and pyritic sulfur content during the reactor experiment are shown in Fig. 2.



Fig. 2 Removal of pyrite and pyritic sulfur with time

The results indicate that during reactor operation, removal of pyrite increased gradually and most of the pyrite was removed from the coal at the end of experiment. In fact, in first 9 days more than 50% of the pyrite was removed which increased gradually till the end. At the end of experiment, about 90% of pyrite was removed from the coal. The bio-oxidation of pyrite also led to the removal of pyritic sulfur from the coal. The removal of pyrite sulfur also followed the similar profile and about 67% of the pyritic sulfur was removed from the coal at the end of experiment.



Fig. 3 Removal of pyrite and pyritic sulfur

This suggested that biochemical action of bacteria led to the release of iron and sulfur from the coal into the liquid.

The extent of pyrite and pyritic sulfur removal was based on the element content in the feed and in the liquor. For cross check, the elemental content remaining in treated residue was also calculated and a good mass balance was obtained. It can be concluded from the Fig. 3 that after 18 days of the reactor experiment, about 90% of pyrite and 67% of pyritic sulfur was removed from the coal.

IV. CONCLUSION

The results of the present investigation suggested that application of *At. ferrooxidans* in biodepyritization of coal led to the oxidation of pyrite. This resulted into the solubilization of iron and pyritic sulfur into the solution. After 18 days of experiment, about 90% of iron and 67% of pyritic sulfur were removed from the coal. The results confirmed that microbial depyritization process using *At. ferrooxidans* is an effective method for treatment of high sulfur containing coal. Moreover, due to the less energy demand, process can be applied for a large scale application.

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REFERENCES

- Acharya, C., Sukla, L.B., Misra, V.N. Biodepyritisation of coal. Journal of Chemical Technology and Biotechnology 79 (1) 1–12 (2004).
- [2] Li, Z.L., Sun, T.H., Jia, J.P. An extremely rapid, convenient and mild coal desulfurization new process: sodium borohydride reduction. Fuel Processing Technology 91 (9) 1162–1167 (2010).
- [3] Cara, J., Vargas, M., Morán, A., Gomez, E., Martínez, O., García, F.J. Biodesulfurization of a coal by packed-column leaching. Simultaneous thermogravimetric and mass spectrometric analyses. Fuel 85: 1756–1762 (2006).
- [4] Cardona, I.C., Marquez, M.A. Biodesulfurization of two Colombian coals with native microorganisms. Fuel Processing Technology 90: 1099–1106 (2009).
- [5] Ivanov, I.P. Main trends in the biotechnological processing of coals: a review. Solid Fuel Chemistry 1: 3–10 (2007).
- [6] Acharya, C., Kar, R., Sukla, L. Bacterial removal of sulfur from three different coals. Fuel 80: 2207–2216 (2001).
- [7] Kargi, F., Robinson, J.M. Biological removal of pyritic sulphur from coal by the thermophile organisms *Sulfolobus acidocaldarius*. Biotechnology and bioengineering 27:41-49 (1985).
- [8] Larsson, R.T. Licentiate thesis. University of Lund, Lund, Sweden (1982).
- [9] Clark, T.R., Baldi, F., Olson, G.J. Coal depyritization by thermophilic archaeon metallosphaera sedula. Applied and Environmental Microbiology 59 (8): 2375-2379 (1193).
- [10] Hu, J., Zheng, B., Finkleman, R.B., Wang, B., Wang, M., Li, S., Wu, D. Concentration and distribution of sixty-one elements in coals from DPR Korea. Fuel 85:679-686 (2006).