

MICROBIAL DESULFURIZATION OF BITUMINOUS COALS

Charanjit Rai

Department of Chemical & Natural Gas Engineering
Texas A&I University
Kingsville, Texas 78363

INTRODUCTION

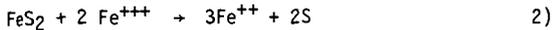
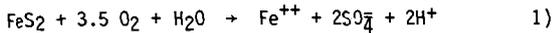
Our environment has constantly been polluted by the combustion of conventional fuels like petroleum, coal and natural gas. It is estimated that about 88 million tons of sulfur dioxide gas (SO_2) is discharged to the environment due to the combustion of fossil fuels. The Clean Air Act Amendment of 1977 set an emission limit of 1.2 lb SO_2 per million Btu of fuel combusted. Most bituminous coals contain 3 to 6 percent sulfur as inorganic or organic sulfur. The inorganic sulfur compounds are primarily metallic sulfides, pyrite or marcasite and sulfates formed by the air oxidation of metallic sulfides (1,2). The organic sulfur in coal is believed to be in the form of monosulfide, disulfide or condensed thiophenes, benzothiophenes, dibenzothiophenes and thioxanthenes having varying reactivities. Physical and chemical processes have been developed for coal desulfurization, some of them operate at high temperatures and are energy intensive. Removal of organic sulfur by these processes is difficult. Microbial desulfurization offers an effective means of precombustion sulfur removal (3,4,5).

Colmer and Hinkle (6) identified *T. ferrooxidans* in acidic mine waters. Subsequent studies by Silverman *et al.* (7,8) confirmed that *T. ferrooxidans* could be utilized to oxidize FeS_2 in coal in 3 to 4 days and the rate of oxidative dissolution was a function of the particle size and rank of the coal. Dugan and Apel (4) showed that a mixed culture of *T. ferrooxidans* and *T. thiooxidans* was most effective at a pH of 2 to 2.5 when the nutrient was enriched with NH_4^+ . They reported 97% removal of pyritic sulfur from a coal sample with 3.1 weight percent sulfur. Norris and Kelly (9) reported that another acidophilic bacteria, *Leptospirillum ferrooxidans* in mixed cultures with *T. thiooxidans* was effective for FeS_2 removal.

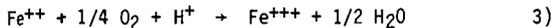
Hoffmann *et al.* (10) conducted a parametric study to determine the effect of bacterial strain, N/P molar ratio, the partial pressure of CO_2 , the coal source and the total reactive surface area on the rate and extent of oxidative dissolution of iron pyrite at a fixed oxygen pressure. The bacterial desulfurization of high pyritic sulfur coal could be achieved in 8 to 12 days for pulp densities of $\leq 20\%$, and particle size $\leq 74 \mu m$. The most effective strains of *T. ferrooxidans* were isolated from the natural systems and the most effective nutrient medium contained low phosphate levels, with an optimal N/P molar ratio of 90:1.

MECHANISM OF MICROBIAL DESULFURIZATION

The mechanism of microbial dissolution of pyritic sulfur in coal by acidophilic bacteria has been thoroughly investigated (10,11,12). The pyrite is readily oxidized by oxygen or the ferric ion resulting in the ferrous state as follows:



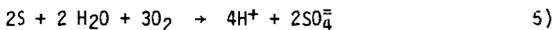
Thiobacillus ferrooxidans derives energy by catalyzing the oxidation of the ferrous ions back to the ferric state (12):



Ferric sulfate, a reaction product, reacts with FeS_2 to form more ferrous sulfate which is again catalyzed by *T. ferrooxidans* to the ferric state.



Elemental sulfur, likewise, is oxidized by *T. thiooxidans* forming sulfuric acid.



The oxidation reactions are dependent on the microbial reactions with the end result of accelerating the transformation of FeS_2 to ferrous sulfate and thus equation (1) precisely represents the overall reaction stoichiometry for kinetic purpose. Other reactions provide the possible mechanistic pathways for the microbial pyritic dissolution.

Most microbial desulfurization studies have been conducted in the laboratory shake-flask type experiments and the major drawback cited against such a process has been that the rates of pyritic sulfur removal were not high enough to reduce the reactor size to a reasonable capacity (2,5). In this study an attempt has been made to determine the effectiveness of *Thiobacillus ferrooxidans* under simulated pipeline conditions for pyritic sulfur removal. Since the microbial desulfurization process is conducted under acidic environment, an attempt has been made to determine the corrosion rates under dynamic conditions using Illinois #6 and Indiana #3 bituminous coals and to investigate the effectiveness of a commercial corrosion inhibitor for controlling the corrosivity.

EXPERIMENTAL

Coal Samples:

The samples of Illinois #6 and Indiana #3 were obtained from the Amax Coal Company's Delta and Midwest mines and Ziegler Coal Company's mine in the Randolph County of Illinois. The pyritic sulfur content data on the coal samples is shown in Table 1. The samples were ground in a ball mill and then sieved to obtain the desired particle size distribution.

TABLE 1

Bituminous Coal Samples and Their Pyritic Sulfur Content

<u>Coal Sample</u>	<u>FeS₂ (wt%)</u>
1. Illinois #6, Delta Mine (CS-1280-004) Amax Coal Company	2.02

- | | |
|---------------------------------------------------------------------------------------------------|------|
| 2. Indiana #3, Ayrshire Mine
(CS-1180-007)
Amax Coal Company | 2.60 |
| 3. Illinois #6, Randolph
County, Ziegler Coal
Company | 4.20 |
| 4. Illinois #6 (C22024)
Herrin Coal, Northern
Illinois, Illinois State
Geological Survey | 4.90 |

The shake-flask and two-inch pipeline experiments were initially conducted with various particle sizes; such as: As Received, 417 to 1651 μm , 208 to 417 μm , 147 to 208 μm , and 43 to 147 μm . However, for detailed study a sample size, 74 to 147 μm , was selected.

Microbial Procedures:

A pure culture of *Thiobacillus ferrooxidans* obtained from the American Type Culture Collection (ATCC) was used in this study for the shake-flask experiments and the 2-inch slurry pipeline experiments. A mineral salts medium having the following composition was used in these experiments: $\text{Fe}(\text{SO}_4) \cdot 7 \text{H}_2\text{O}$ 20 g/l; $(\text{NH}_4)_2 \text{SO}_4$ 0.8 g/l; $\text{KH}_2 \text{PO}_4$ 0.4 g/l; $\text{Mg}(\text{SO}_4) \cdot 7 \text{H}_2\text{O}$ 0.16 g/l. The mineral salts were dissolved in distilled water and the pH was adjusted to 2.8 by addition of 1N H_2SO_4 . The medium was autoclaved at 20 psia for one hour. The growth medium consisted of slurried coal samples consisting of Illinois #6 or Indiana #3 as desired.

Analytical Procedures:

The samples of bituminous coals were analyzed for pyritic sulfur, sulfate sulfur and total sulfur using conventional wet chemical procedures adapted from the American Society of Testing Materials (13,14). The Eschka method was used for the total sulfur, and D-2494-79 was used for sulfate and pyritic sulfur analysis.

The treated samples were filtered through a Whatman #2 filter paper to separate the coal particles from the liquid medium. The filtered sample was washed with 0.1 N HCl followed by distilled water to remove traces of absorbed sulfate and iron.

The total sulfur content of the coal samples was determined by the Eschka method. The sulfate sulfur content of the test samples was determined by extraction of a one gram sample with dilute hydrochloric acid followed by turbidimetric determination of sulfate (13). The pyritic sulfur content was determined by extraction of the weighed coal samples with 2N nitric acid followed by titrimetric or atomic absorption determination of iron in the extract (14).

Laboratory Corrosion Test:

The laboratory test procedure for the determination of corrosion rates of coal slurry used in this study was adapted from the method developed by Bomberger (15). The corrosion rates were determined by using ASTM Standard Corrosion Test,

also known as Total Immersion Method (16). The Bomberger technique consists of keeping coal slurry in suspension in a two-liter reaction vessel at a constant temperature. The corrosion rates are determined either by actual weight loss of steel coupons suspended in the reaction vessel or by the use of corrosometer probe over a 24 to 72 hour period. The weight loss of steel coupons is a measure of the corrosion rates expressed as Inch Per Year (IPY). In the case of corrosometer probe, it is initially calibrated by means of a weight loss measurement.

The ASTM Corrosion Test procedure by Total Immersion Method requires that all specimen in a test series should have the same dimensions when comparisons are to be made. In these experiments, carbon steel was used representing the pipeline material. The coupons were cleaned, polished and weighed. Coal-water slurry, 10 to 40 weight percent was used in the corrosion tests. Specimens were immersed in the reaction vessel maintained at a constant temperature of 86°F for 72 hours or the specified time. The coupons were removed, washed with deionized water, dried and weighed. The loss in weight of the specimen, before and after the test was attributed to corrosion. From the weight loss data, the corrosion rates were calculated as Inch Per Year (IPY) and also as gram per square centimeter per year. ($\text{g}/\text{cm}^2 \cdot \text{year}$).

RESULTS AND DISCUSSION

1. Shake-Flask Experiments with *Thiobacillus Ferrooxidans*.

A limited number of experiments were conducted using *Thiobacillus ferrooxidans* to determine the influence of process variables on the rate and extent of pyritic sulfur release from the coal samples in shake-flask experiments using a mechanical shaker. No attempt was made to optimize the mineral salts medium composition since the influence of NH_4^+ , N/P molar ratio and the nitrogen requirements for the growth of *T. ferrooxidans* have been thoroughly investigated by other workers (4,7,8,10). A mineral salts medium with the composition described earlier in the Microbial Procedures section was used in all the experiments with *T. ferrooxidans*.

A number of samples of pulverized coals were used having the following particle sizes: As Received, 417 to 1651 μm , 147 to 208 μm , < 147 μm . Coal/water slurries (10 wt%) made from the sterilized coal samples in mineral salts medium were inoculated with a strain of *T. ferrooxidans* and were subjected to mechanical shaking from three to twelve days. At the end of the desired test period, 3, 6, 9 or 12 days, the coal samples were filtered, thoroughly washed with deionized water and analyzed for pyritic sulfur content. The data was plotted as mg/liter of pyritic sulfur released as a function of time as shown in Figure 1 for a coal sample of Illinois #6 from the Zeigler Coal mine. The data shows a maximum reduction in pyritic sulfur content was achieved with < 147 μm (-100 mesh) particle size, the average rate being 377.4 mg/liter x day during the nine day oxidation period versus 199.0 mg/liter x day for the 417 to 1651 μm (-10 to +35 mesh) particles. Indiana #3 coal from the Ayrshire mine exhibited similar trends, the average pyritic oxidation rate being 291.1 mg/liter x day for a 147 to 417 μm particles over an eight day period with *T. ferrooxidans*.

2. Two-Inch Slurry Pipeline Experiments: (a) Slurry Pipeline System.

A two-inch PVC pipeline loop, 60 feet in length, was installed on a laboratory wall and a 2 horsepower positive displacement type Gould pump, Model 3196 was

incorporated in the flow system. The flow rate through the pipeline could be varied from a low of 2 ft/sec to 15 ft/sec. The system was designed to recirculate coal/water slurry through an open drum where air was bubbled in the line. A copper cooling coil was immersed below the slurry level in the drum for recirculating cold water through the medium in order to remove heat from the system. The flow rate in the pipeline was monitored by the use of a Polysonics flow meter, model UFM-P. The equipment was capable of continuous operation. The critical velocity for flow of slurries in the pipeline was calculated using a correlation developed by Oroskar and Turian (17). The critical velocity, defined as the minimum velocity needed to keep the coal particles suspended in the liquid medium, was calculated to be 5.5 ft/sec for a 50 wt% coal/water slurry for the two inch laboratory pipeline.

(b) Particle Size Distribution

A 6.6 wt% slurry consisting of Indiana #3 bituminous coal with 60.5% of 417 to 165 μm and 39.5% of 147 to 417 μm particles was recirculated through the pipeline loop for 6 hours at 5.6 to 5.8 ft/sec at 85-95°F using deionized water for preparation of the slurry. At the conclusion of the experiment, the coal particles were filtered, dried and sieved to determine the particle size distribution. The data for final size distribution of the slurried coal is shown in Table II.

TABLE II
Slurry Recirculation in Laboratory Pipeline

Indiana #3 (Ayrshire) (6.6% wt% slurry in deionized water)	417 to 1651 μm , 60.5% 147 to 417 μm , 39.5%
Flow Rate:	5.6 to 5.8 ft/sec
Temperature:	85-95°F
Run, Hours:	6

Final Particle Size Distribution

Particle Size	Percent
+1651 μm	0.62
-1651 to +417 μm	4.69
-417 to +147 μm	40.45
-147 to +74 μm	39.40
-74 μm	14.79

(c) Microbial Desulfurization Experiments in the Two-Inch Pipeline.

Illinois #6 (Delta Mine) and Indiana #3 (Ayrshire Mine) bituminous coals were used in the slurry pipe desulfurization experiments using *T. ferrooxidans* for inoculating the coal/water slurry used in these experiments. A 10 wt% coal/water slurry was prepared using deionized water and the mineral salts medium described earlier, the coal particle size range was from 147 μm to 1981 μm . The slurry flow rate was kept at 6 to 6.2 ft/sec, and the temperature in the system was controlled by recirculating cold water through the copper cooling coils in the slurry drum. Duplicate samples of coal slurry were taken once a day for the determination of pyritic sulfur content in the slurry. The experiment was continued for seven days with recirculation of the slurry through the pipeline system for 8 hours/day. The experimental data with Illinois #6 (Delta) is shown in Table 3, and the rate of pyrite desulfurization is shown in Figure 2. The desulfurization rates in the slurry pipeline experiments and the

Laboratory shake-flask experiments are in good agreement.

Another slurry pipeline desulfurization experiment was conducted using Indiana #3 (Ayrshire) coal in deionized water as a 25 wt% slurry. The other process variables were carefully controlled: flow rates 6-6.5 ft/sec, temperature, 70-90°F, and pH, 2.5-2.8. The experiment was continued for 14 days and the slurry samples for pyritic sulfur determination were taken daily. The desulfurization rates with Indiana #3 coal in the pipeline experiment are shown in Figure 4 and are in good agreement with the laboratory data and the results with Illinois #6 coal. As observed in the laboratory experiments, the rate of desulfurization of bituminous coals is directly proportional to the pyritic sulfur content and the particle size of the coal sample.

3. Corrosion Test Results:

The corrosion rates were determined using a 10 wt% to 40 wt% coal water slurry with 147 to 417 μm coal particles. The corrosion rates ranged from 1.223×10^{-3} IPY for Illinois #6 to 1.272×10^{-2} IPY for Indiana #3 coal slurry consisting of 40 weight percent each coal.

The addition of *T. ferrooxidans* in salt medium at the desired concentration to the coal/water slurry increased the corrosion rates for both the coals tested. The corrosion rates for 72-hour and 500-hour experiments in the presence of *T. ferrooxidans* in salt medium with 10 weight percent slurry of Illinois #6 ranged from 4.2×10^{-3} IPY to 1.41×10^{-2} IPY respectively. However, the introduction of upto 10 ppm of a commercial corrosion inhibitor, Calgon T G-10, inhibited the corrosion rates with Illinois #6 and Indiana #3 coals to very low levels approaching those obtained with the deionized water. Black Mesa pipeline has used this corrosion inhibitor on a regular basis with very satisfactory results.

CONCLUSIONS

About 80 to 85% pyritic sulfur removal has been achieved by microbial desulfurization of Illinois #6 and Indiana #3 coals using *Thiobacillus ferrooxidans* in laboratory shake-flask experiments and in a two-inch pipeline loop. The 10 to 25 wt% coal/water slurry was recirculated at 6-7 ft/sec for 5 to 12 days at 70-90°F. Results also show that the rates of bacterial desulfurization are higher in the pipeline loop under turbulent flow conditions for particle sizes, 43 to 200 μm as compared to the shake-flask experiments. It is visualized that the proposed coal slurry pipelines could be used as biological plug flow reactors under aerobic conditions. The laboratory corrosion studies show that use of a corrosion inhibitor will limit the pipeline corrosion rates to acceptable levels.

ACKNOWLEDGEMENTS

This study was supported by research grants from Texas Energy Corporation, Amax Foundation and Atlantic-Richfield Foundation. Their support is gratefully acknowledged. The graduate students Theresa Chang, Rasik Patel and Edward Eke conducted the experimental work described in this paper. Their contributions are much appreciated.

TABLE 3
 SLURRY PIPELINE DESULFURIZATION
 COAL/WATER SLURRY (10 WT%)
 ILLINOIS #6 BITUMINOUS COAL (DELTA MINE)
 (*Thiobacillus ferrooxidans*)

<u>DAYS</u>	<u>PYRITIC SULFUR, WT%</u>	<u>PYRITIC SULFUR REDUCTION, %</u>	<u>RATE OF DESULFUR- IZATION MG/LITER X DAY</u>
0	1.70	0.00	0.00
1	1.45	14.7	257.35
2	1.13	33.5	293.26
3	0.80	52.9	308.82
4	0.60	64.7	283.08
5	0.48	72.0	251.17
7	0.41	76.0	189.70

SLURRY FLOW RATE: 6 to 6.2 FT/SEC
 SLURRY TEMPERATURE: 70-90°F
 COAL PARTICLE SIZE: 147 μm to 1981 μm
 pH OF SLURRY: 2.5 to 2.8

TABLE 4
 SLURRY PIPELINE DESULFURIZATION
 COAL/WATER SLURRY (25 WT%)
 INDIANA #3 BITUMINOUS COAL (AYRSHIRE MINE)
 (*Thiobacillus ferrooxidans*)

<u>DAYS</u>	<u>PYRITIC SULFUR, WT%</u>	<u>PYRITIC SULFUR REDUCTION, %</u>	<u>RATE OF DESULFUR- IZATION MG/LITER X DAY</u>
0	2.58	0	0.00
4	1.75	32	558.57
5	1.55	40	554.53
7	1.82	30	292.26
9	1.03	60	463.60
11	0.645	75	473.53
12	0.516	80	463.01
13	0.52	80	426.56

SLURRY FLOW RATE: 6 FT/SEC
 SLURRY TEMPERATURE: 70-90°F
 COAL PARTICLE SIZE: 147 μm to 1981 μm
 pH OF SLURRY: 2.5 to 3.0

EFFECT OF PARTICLE SIZE ON PYRITIC DESULFURIZATION

(*Thiobacillus ferrooxidans*)

Illinois #6: Ziegler Coal
 Temp. 75-85°F
 pH 2.5-2.8

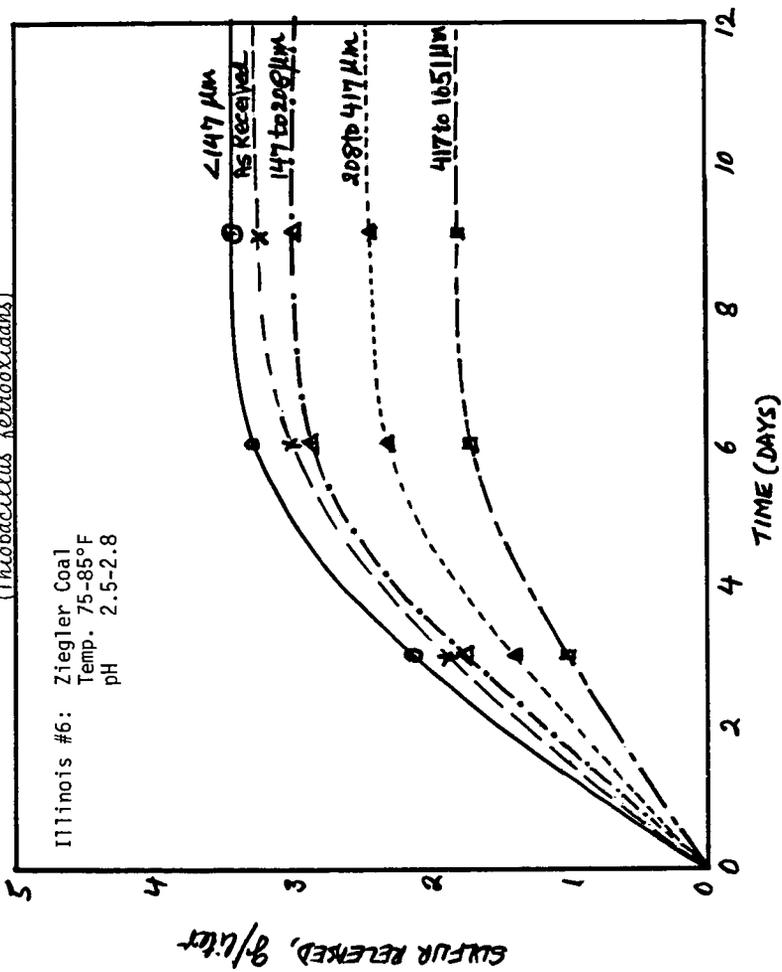


FIGURE 1.

SLURRY PIPELINE DESULFURIZATION

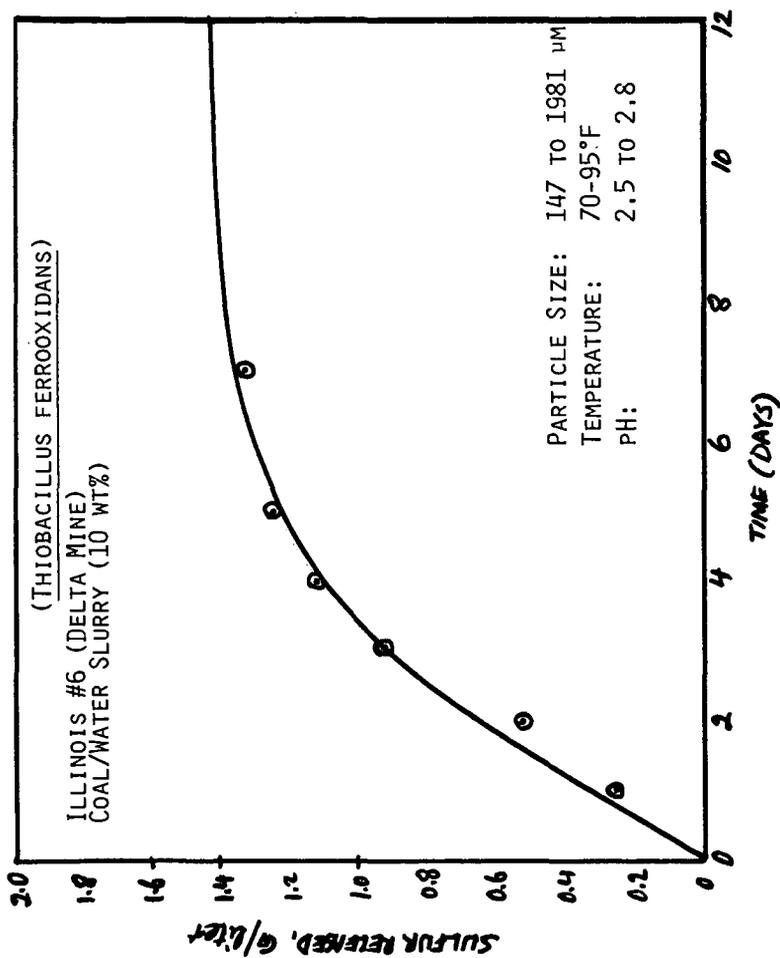


FIGURE 2

REFERENCES

1. Wheelock, T.D., Editor, 1977, "Coal Desulfurization Chemical and Physical Methods." ACS Symposium Series 64, Washington, D.C., p. IX-XI, 101-120.
2. Rofmann, H.K., Proc. Inst. Environ. Sci. 1979, pp. 266-270.
3. Robert C. Eliot, "Coal Desulfurization Prior to Combustion," Noyes Data Corporation, New Jersey, 1978, pp. V-VI, 33-42, 141-153.
4. Dugan, P.R. and W.A. Apel, 1978. "Microbial Desulfurization of Coal." In Metallurgical Application of Bacterial Leaching and Related Microbial Phenomenon." Editors, L.E. Murr, A.E. Torma and J.A. Brierley. Academic Press, N.Y. pp. 223-250.
5. Kargi, F. 1982, Microbial Coal Desulfurization, Microbial Enzyme Technol. 4(1): 13-20.
6. Colmer, A.R. and M.E. Hinkle, 1947. The Role of Microorganisms in Acid Mine Drainage, Science 106: 253-256.
7. Silverman, M.P. and D.G. Lundrger, 1959. Studies on Chemosynthetic Iron Bacterium *Ferrobacillus ferrooxidans*. J. Bacteriol. 78: 326-331.
8. Silverman, M.P., M.H. Rogoff and I. Wender. 1963. Removal of Pyritic Sulfur from Coal by Bacterial Action. Fuel 42, 113-124.
9. Norris, P.R. and D.P. Kelly. 1978. Toxic Metals in Leaching Systems. p. 83-102. In L.E. Murr, A.E. Torma and J.A. Brierly (ed) Metallurgical Applications of Bacterial Leaching and Related Phenomena. Academic 85, Inc. New York.
10. Hoffmann, M.R., B.C. Faust, F.A. Panda, H.H. Koo and H.M. Tsuchiya. 1981. Kinetics of the Removal of Iron Pyrite from Coal by Microbial Catalysis. Applied & Environ. Microbiology. 42: 259-271.
11. Andrews, G.F. and J. Maczuga, 1984. Bacterial Removal of Pyrite From Coal, Fuel 63, 297-301.
12. Singer, P.C. and W. Stumm, 1970. Acidic Mine Drainage: The Rate Determining Step. Science 167: 1121-1123.
13. Karr, C. 1978. "Analytical Methods for Coal and Coal Products." Academic Press, N.Y., Vol. I, pp. 224, 280-321.
14. American Society of Testing Materials. Annual Book of ASTM Standards, Part 26, Methods D2492-79 and D3177-75, American Society of Testing Materials, (1979) Philadelphia, PA.
15. Bomberger, D.R., "Hexavalent Chromium Reduces Corrosion in Coal-Water Slurry Pipeline." Materials Protection, Vol. 4, p. 43-49 (January 1965).
16. American Society of Testing Materials. Annual Book of ASTM Standards, Part 10, p. 913-943 (1979).
17. Oroskar, A.R. and R.M. Turian. 1980, "The Critical Velocity in Pipeline Flow of Slurries", AIChE J. 26, 550-558.