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THE ROLE OF MICRO-ORGANISMS IN THE FORMATION OF ACID MINE DRAINAGE IN THE NORTH EASTERN COAL FIELD OF INDIA

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ABSTRACT

The paper deals with the nature of mine drainage in the North Eastern Coalfield, Margarita, Assam (India). The drainages from the Margerita group of mines are found to be acidic with high sulphate ranging up to 1500 ppm and iron content rising up to 40 ppm. The total sulphur in coals is up to 7% out of which 50-80% is non-reactive organically found sulphur. The acidity mainly arises from the oxidation of pyrites of coal. Microscopic studies reveal that both the reactive (size 0-5 micron) as well as stable (50 micron) pyrites are present in coal samples studied. Leaching studies indicate that oxidation of reactive pyrites followed by dissolution of sulphate sulphur is sufficient to produce the observed acidity and organic sulphur does not seem to play any significant role in acid production in mine drainages. The presence and chemical activity of iron oxidising; sulphur oxidising; and iron sulphur oxidising bacteria in mine water was ascertained by the chemical oxidation of ferrous iron to ferric iron; decrease in pH and production of acid. Iron and sulphur oxidising bacteria which are having maximum activity were examined under electronmicroscope for morphological study. The rod shaped bacteria with rounded ends, size varying from 1.20 - 3.20 micron in length and 0.51 - 1.25 micron in breadth are identified as *Thiobacillus ferrooxidans.* This bacteria is found to accelerate the sulphur leaching rate from coal and is indigenous to mine drainages.

INTRODUCTION

One of the major problems encountered by the coal mining industry is of removing the water that percolates into the mines. The mine drainages in Margerita group of coal mines of North Eastern Coalfield (NEC), India, are found to be acidic and highly corrosive[1]. The problems arising out of these acidic drainages are extremely complex and variable in the region. The well known adverse effects due to these acidic mine drainages are potable water supplies, loss of recreational values, corrosion of the mining machinery and environmental degradation.

Considerable amount of research has already been done pertaining to general aspects of acidic mine drainages elsewhere but no such work has so far been reported about NEC mines. However, studies on the distribution of different forms of sulphur in the high organic sulphur tertiary coals of NEC were reported recently[2]. This study has been undertaken to understand the mechanism and to study the various factors responsible for the acid formation in NEC, Assam.

EXPERIMENTAL PROCEDURE

Collection and Analysis of Water and Coal Samples :

Original coal samples as well as fresh mine water samples were obtained from Ledo and Baragoloi Collieries. Standard methods were employed for estimations of various constituents in water samples[3]. The pH value was measured with a Philips pH meter. Coal samples were analysed for total sulphur, pyritic sulphur and sulphate sulphur according to standard procedures[4]. The amount of organic sulphur was obtained by deducting the amount of pyritic and sulphate sulphur from toal sulphur. Iron was estimated spectrophotometrically by using VSU2-P spectrophotometer.

Growth of Bacteria :

The culture growth preparation of iron-oxidising, sulphur oxidising, iron and sulphur oxidising bacteria were done as described[5]. The media were analysed for Fe^{2+}, Fe^{3+} iron and development of acid measured by titrating 1 ml of the growing culture against N/100 NaOH solution.

Microscopic Study :

The bacteria were observed under ordinary microscope at x1000. For electronmicroscopic study, cells of iron and sulphur oxidising bacteria were harvested by centrifuging in refrigeration at 15,000 rpm for half an hour. The harvested cells were negatively stained with 1% phosphotungstic acid and viewed in Hitachi Electron microscope at x9600. Size of the bacteria were measured from electronphotomicrographs.

Pyrites of the coal samples were mounted on a polished section and viewed with reflected light through an oil immersion lens attached to microscope at x500. Size of the particles were measured from the photomicrographs.

Leaching Studies :

Coal samples were crushed to pass a 4 mm sieve retained by a 2 mm sieve. 5 gm of powdered coal sample was taken in 1 litre Erlenmeyer flask and to this 500 ml of H_2SO_4 acid leach solution was added. In the microbiological experiments, in addition to the above 10 ml of active culture of iron and sulphur oxidising bacteria containing 10^7 cells/ml was added in each set of experiments.

RESULTS AND DISCUSSION

The chemical analysis of minewater samples (Table 1) shows that they contain high sulphate, hardness and acidity content, coupled with low pH. This indicates that the water flowed through coal seams and strata which contain sufficient amount of sulphates and reactive pyrites[6]. The high hardness values coupled with high acidity and low pH infers that the primary cation contributing to it is soluble iron. The pH of the ground water when passed over mined coal considerably decreased from 6.9 to 2.7 and 4.1 indicating the variation and differences of reactivity of pyrites in the two mines[6,7].

Table 1

Chemical Analysis of Mine Water Samples

Mine water sample	Physical appearance (with suspension)	pH	Acidity	SO_4^{2-}	Hardness ppm	Fe^{2+} ppm	Fe^{3+} ppm
Ledo (Tirap) L	Yellow	2.9	596	1946	850	2.0	12.6
-do- L	Yellow	3.1	198	1412	330	1.86	17.4
-do- L	Clear	6.5	20	526	676	0.75	4.0
-do- L	Yellow	2.59	530	1800	490	1.52	30.8
-do- Main sump	Yellow	3.0	322	1488	910	1.06	36.0
Baragoloi 8L	Orange - Reddish	2.97	386	1825	900	1.24	20.0
-do- 5L	Clear	8.40	-	512	306	0.75	6.08
-do- 6L	Light Yellow	3.58	194	1510	670	1.00	18.45
-do- Main sump	Clear	4.1	257	1235	980	0.82	14.0

The distribution of total sulphur and its form in two coal samples show that the organic sulphur is predominant and this organically bound component is generally not chemically reactive[8] This is further supported by the chemical analyses of mine waters. The difference of acidity produced in two mines is mainly because of the associated pyritic sulphur content and independent of the amount of total sulphur present in coal.

Microscopic observation of coal samples reveals that both contain various types of pyrites. The pyrites occur as spheroids of the clusters of the size of 0.5 µm and these again occur as spheroids of different sizes, i.e. from 0-5 µm, 5-50 µm and >50 µm. Among these reactive pyrites, the framboidal type (particle size 0-5 µm) is extremely reactive and decomposes rapidly to produce severe acid mine drainages[8]. The other pyrites averaging 50 µm are relatively stable. The acidity they produce can be readily neutralised by the alkalinity available in rock strata and in ground water. The variation in physicochemical characteristics of water in various levels of collieries are explained by above facts.

The presence of iron-oxidising, sulphur-oxidising and of iron and sulphur-oxidising bacteria in mine water is ascertained by chemical oxidation

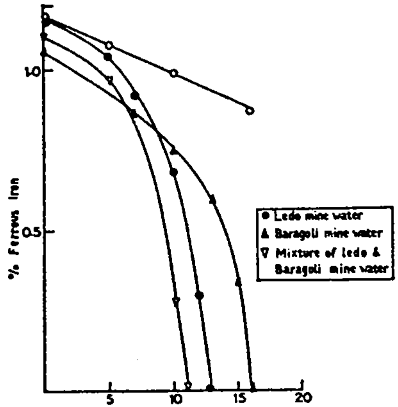

Fig. 1 Decrease in Ferrous Iron conc. in media by growing culture of a) Iron & sulphur oxidising bacteria ▽ b) Iron oxidising bacteria ● ▲

of $FeSO_4$ to Fe_2SO_3, decrease in pH and oxidation of sulphur to H_2SO_4 acid, as represented in Fig.1, 2 and 3 respectively. The oxidation of Fe^{2+} iron to Fe^{3+} iron (completed in 10 to 16 days) decrease in Ph (from 3.5 to 1.4) and production of acid (4.2 to 7.5 ml of N/100 NaOH consumed by 1 ml of growing culture in 25 days), is more in the experiments with mine waters as inoculas compared to the control. With mine water all the Fe^{2+} iron is oxidised to Fe^{3+} iron whereas in control only 25% oxidation took place during the same period (Fig.1). This confirms the role of the bacteria as biocatalyst in AMD production[9]. The above results also indicate that sulphur oxidising bacteria alone do not influence the acid formation reaction rate but iron and sulphur oxidising bacteria exhibit a faster effect in accelerating the oxidation of Fe^{2+} to Fe^{3+} and thus contribute a large part of acidity associated with acid mine drainages[10,11].

Iron and sulphur oxidising bacteria used as inocula in microbiological leaching experiments was observed under microscope as rods. Fresh culture when observed under microscope exhibits that the bacteria are motile occurring mostly single. Electronphotomicrographs show the morphology of bacteria. The bacteria are rod shaped with rounded ends and contain single polar glagellum. The size of bacteria is 1.20 - 3.20 µm by 0.52 - 1.25 µm which is identified as thiobacillus-ferroxidans as confirmed by various reports[9,12]. This bacteria is harmless as being gram negative.

Colliery/ Coal sample	Total Sulphur	Distribution percentage of total sulphur		
		Pyritic	Sulphate	Organic
Ledo (Tirap)	4.42	11.0	18.5	70.5
Baragoloi	6.05	2.3	17.5	80.2

Table 2

Total sulphur percentage and distribution of different forms in sulphur in coal samples

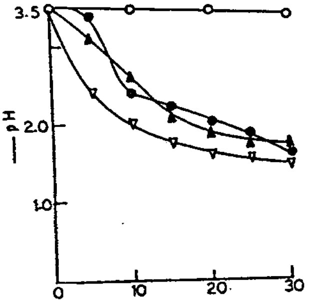

Fig. 2 Decrase in pH in media by a) iron & sulfhur oxidising bacteria∇ b) sulphur oxidising bacteria ● Δ

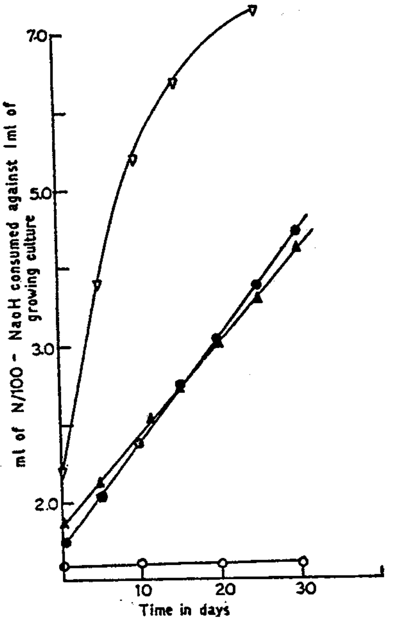

Fig.3 Production of acid in media by a) iron & sulphur oxidising bactria ∇ b) sulphur oxidising bacteria ● Δ

Leaching experiments (Table 3 and 4) show that in microbiological sets, the amount of sulphur leached is greater as compared to those in absence of bacteria. Sulphur leached in both the coal samples is mainly pyritic and sulphate sulphur. The organic sulphur remain more or less unaffected. The bacteria accelerates the sulphur leaching rate considerably after getting active and hence explains the slow rate in the initial stage. Sulphur leaching results after 20-25 days in microbiological experiments indicate some inhibition of activity of bacteria. At this stage, along with sulphur leaching some iron also started getting leached out which is further oxidised to ferric state by atmospheric oxygen and bacteria, followed by the precipitation as basic iron sulphates on the coal surface in the form of jarosites (A $Fe_2/SO_4/_2/OH/_6$), where A stands for Na, K and NH_4 ions[13]. This suggests that fresh culture of bacteria is required after 20-25 days to continue the leaching of sulphur. The leaching results are based on the fact that sulphur content greater than 1.5% is expected to produce acidic leachetes in mine drainages[7]. The generally accepted chemical reactions explaining the oxidation of pyrites (FeS_2) and the production of acidity (H^+) are given by the following equations :

Table 3

Total sulphur leached at different time intervals

Time (days)	pH = 3.0 Coal sample/colliery				pH = 4.0 Coal sample/colliery			
	Ledo		Baragoloi		Ledo		Baragoloi	
	WB	WOB	WB	WOB	WB	WOB	WB	WOB
5	1.75	1.20	1.54	1.29	0.95	0.8	0.95	0.68
10	6.5	6.0	4.46	4.4	4.2	4.3	3.9	4.0
15	14.4	11.1	11.2	10.0	12.0	6.5	10.0	8.8
20	21.1	14.6	16.6	12.3	15.6	9.7	12.4	10.3
25	23.6	17.2	18.3	14.6	17.1	10.3	16.2	11.7
30	25.1	20.7	19.0	16.9	19.0	15.0	17.7	12.1

WB = Sulphur leached with bacteria
WOB = Sulphur leached without bacteria

Table 4

	pH = 3.0 Coal sample/colliery				pH = 4.0 Coal sample/colliery			
	Ledo		Baragoloi		Ledo		Baragoloi	
	WB	WOB	WB	WOB	WB	WOB	WB	WOB
Pyritic sulphur	.38	.33	.12	.12	.30	.30	.12	.11
Sulphate sulphur	.58	.55	.89	.84	.48	.36	.82	.60
Organic sulphur	.15	.04.	.14	.05	.06	.003	.12	.02
Total sulphur	1.11	.92	1.15	1.01	.84	.663	1.06	.73

WB = Sulphur leached with bacteria
WOB = Sulphur leached without bacteria

$$2FeS_2(S) + 7\ O_2 + 2\ H_2O = 2Fe^{2+} + 4\ SO_4^{2-} + 4\ H^+ \qquad (1)$$

$$Fe^{2+} + 2\ O_2 + 2\ H^+ = Fe^{3+} + H_2O \qquad (2)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3(S) + 3\ H^+ \qquad (3)$$

The stoichiometry of equation (1) shows that 1 mole of FeS_2 will produce 2 moles of H^+ (acidity). In turn, the Fe^{2+} generated by equation (1) can readily oxidise into Fe^{3+} and produce an additional 3 moles of H^+ (equation (3)). The iron oxidation is the rate limiting step of the reaction in equation (2) and proceeds slowly under sterile conditions[14]. However, bacteria greatly accelerates this oxidation contributing a major part of acidity formed in acid mine drainage[10, 11]. Results obtained in this investigation are also in accordance with the chemical reactions described above.

In actual practice, the rate of acid production is much higher than the results obtained in the laboratory. The problem of AMD in NEC commences with the very high rainfall, about 400 cm annually, in the area and its seepage from the hill to the opencast mine and finally from quarry into the underground mines. Field investigation shows that average humidity in these mines is above 90%, average temperature inside is about 25-32°C and there is a good percentage of CH_4, CO_2 and O_2 in mine atmosphere which further aid in easy pyrite oxidation and also help in easy growth of autotropic aerobic bacteria and ultimately lead to rapid rate of acid production. Moreover the trickling of mine water drops from the roof of the galleries and worked out seams makes the pyrites and other substances to get rapidly oxidised by atmospheric air. This aspect is clearly shown by the formation of 2-3 m long tubular structures of hydroxides and clayey material.

CONCLUSIONS

The oxidation and decomposition of reactive pyrites in coal and associated strata followed by sulphate dissolution is mainly responsible for acid formation in NEC mines. The organic sulphur component is found to be chemically inert. *Thiobacillus ferrooxidans* (the iron and sulphur oxidising bacteria) accelerate the acid formation step to a greater extent as compared to sulphur oxidising bacteria.

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