A SURVEY OF CORROSIVITY OF UNDERGROUND MINE WATERS FROM INDIAN COAL MINES

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ABSTRACT

The coal mining industry is facing serious corrosion problems. Millions of litres of water is disposed off from some underground coal mines every day. In this survey, mine water samples from various underground coal mines were collected and analysed in an attempt to correlate the various physico-chemical characteristics with their corrosivity. The analyses include determination of the values of pH, alkalinity, acidity, specific conductivity, hardness, total solids, sulphate, chloride, cupric, ferrous and ferric ions. Corrosion rates of steel in minewaters were also measured by weight-loss trial method.

The present survey shows that mine waters are nearly neutral, alkaline, mildly acidic and highly acidic in nature. The corrosivity of these vary from mildly to extremely corrosive. An evaluation of minewaters corrosivity using Langelier Saturation Index has also been made but no definite relationship has been found between the corrosion rate and Langelier Saturation Index. A classification on the basis of corrosivity of these mine waters is also made.

Causes of aggressiveness of Fe^{3+}, Cu^{2+}, SO_4^{2-}, Cl^- in acid mine waters have also been discussed which conclude that corrosion rates were significantly increased by Fe^{3+} and Cu^{2+} due to their reduction to Fe^{2+} and metallic Cu, respectively. Occurrence of these ions in acid mine waters has also been discussed.

INTRODUCTION

Water is corrosive by reason of its ability to dissolve the material with which it comes into contact and corrode the metals because of the thermodynamic instability. As in all other industries corrosion is a pressing problem in mining. The more so because, in addition to the monetary loss, it is of vital concern in relation to safety measures in mines. With increasing mechanisation in mines the problem of corrosion is increasing in intensity.

Mine waters occupy a unique place in corrosion study in view of their highly complex nature and widely varying composition from mine to mine. Coal mine industry has to pump out millions of litres of water every day. The problems of mines water corrosion are widespread in underground coal mines. The main bulk of underground water from major Indian coalfields is neutral to alkaline in nature, and as such does not normally give rise to any serious corrosion problems. Acute corrosion problems are, however, encountered when mine waters are acidic. Rawat et al (1976, 1981, 1983) have analysed some mine waters from Indian coalfields and have studied their corrosivity. Earlier Hoey et al (1971, 1975) have reported the similar work on Canadian mine waters.

This paper presents a survey carried out in various underground coal mines of Indian coalfields to ascertain the corrosivity of mine waters. An evaluation of the corrosivity of the waters is also assessed to determine whether the Langelier Saturation Index (SI), as widely used in the drinking water industry, is a reliable indicator of a water's corrosive potential. A classification of mine waters from Indian coalfields is also made.

EXPERIMENTAL METHODS

Chemical Analysis of Mine Water Samples

Mine water samples collected from underground mines of Indian coalfields were analysed by employing standard methods (Amer. Public Health Assoc., 1971). The pH and conductivity values were measured using Philips pH-meter and Systronics conductivity bridge, respectively. Total iron and ferrous ions were estimated spectrophotometrically using VS U2 spectrophotometer.

Corrosion Rates Determination

Corrosion rates were calculated on the basis of weight loss of the metal specimen (2.5 x 4.0 cm) immersed in stagnant mine water sample for 15 days. However, in the case of acidic mine waters, 24 hours weight-loss measurement were carried out.

Mild steel specimens used in this study had the following composition: C - 0.06%, Mn - 0.51%, P - 0.045%, S - 0.41%, W - 0.02% and Al 0.011%, as given by Quantovac, R&D Lab., Bokaro Steel Plant. The surface of the specimens was prepared by degressing in boiling acetone and pickling in 10% HCl for one minute.

RESULTS AND DISCUSSION

Physico-chemical characteristics of mine waters from Jharia coalfield (Dhanbad) and Eastern coalfield of Raniganj, are given in Tables 1 and 2 respectively - which show that these underground mine waters are neutral to slightly alkaline in nature. Corrosion rates of mild steel specimens in these mine waters indicate that under normal conditions they should not pose any serious corrosion problem. These mine waters are quite hard with varying amounts of dissolved solids i.e. from 300-1500 ppmconcentration range. The effect of the total dissolved solids is primarily that of increasing the electrical conductivity of the water, thus reducing the resistance of electrolytic path of the corrosion cell, through some salts (chlorides and sulphates) have a specific effect on the corrosion reactions (Ahmadi, 1981). Corrosivity of these mine waters is mainly due to the presence of SO_4^{2-} when coupled with high concentration of total dissolved solids. Generally, Cl^- in the concentration present in these mine waters does not effect overall rate of corrosion.

Corrosivity of these neutral to slightly alkaline mine waters by hydrogen evolution reaction can account for only a very small metal dissolution. Only cathodic reaction that can occur at any significant rate of corrosion is oxygen

Table-1. Chemical Analyses of Mine Waters from Jharia Coalfield

pH	Total hardness (as ppm $CaCO_3$)	Calcium (ppm)	Magnesium (ppm)	Total Alkalinity (as ppm of $CaCO_3$)	Dissolved (ppm)	Sulphate (ppm)	Chloride (ppm)	Iron (ppm)	Corrosion rate for mild steel (mg/dm^2/day)
7.9	1000	102.20	180.91	271.20	1429.33	704.48	14.97	15.70	17.40
8.1	830	120.24	128.64	304.80	1112.00	457.31	37.43	12.50	17.72
8.0	820	124.24	123.78	222.00	1212.00	549.48	19.65	15.00	18.96
8.0	685	110.22	99.49	206.40	1040.00	420.00	30.88	8.70	19.59
8.1	570	80.16	89.81	294.00	914.66	236.74	31.81	9.20	20.71
8.2	558	101.80	73.84	176.80	781.30	325.63	31.35	4.00	32.95
7.9	505	74.14	77.67	177.60	926.66	316.30	24.33	17.00	21.94
7.4	500	74.14	76.45	158.40	817.33	330.57	38.37	18.50	21.65
8.3	450	126.20	32.68	90.84	1374.00	73.65	52.82	10.50	18.77
8.2	434	74.96	60.00	304.30	563.90	118.10	33.37	9.20	18.62
8.0	405	62.12	60.67	276.00	549.33	129.21	28.07	6.40	21.56
7.3	326	59.08	43.38	188.70	790.60	84.49	85.51	24.00	23.90
8.2	238	49.68	27.69	329.80	734.60	80.10	29.45	14.20	24.05
7.8	90	16.27	12.00	93.50	194.60	45.26	20.90	21.30	18.55
7.8	75	12.82	10.43	510.00	798.66	14.81	38.37	7.00	12.87

Table-2 Chemical Aalyses of Mine Waters from Raniganj Coalfield

Sample No.	pH	Total hardness (as ppm $CaCO_3$)	Calcium (ppm)	Magnesium (ppm)	Total Alkalinity (as ppm of $CaCO_3$)	Dissolved solids (ppm)	Sulphate (ppm)	Chloride (ppm)	Iron (ppm)	Corrosion rate for mild steel ($mg/dm^2/day$)
1	8.1	382	68	53	420	570	75	35	1	11.82
2	7.04	780	162	98	410	990	376	29	16	22.00
3	7.82	665	118	90	335	880	368	150	15	19.65
4	8.01	380	84	39	85	756	270	41	10	17.40
5	8.0	753	156	101	353	949	436	176	19	23.00
6.	7.4	1248	216	180	448	1622	789	22	28	22.16
7.	7.42	897	162	125	390	1210	500	18	22	21.50
8.	8.0	50	16	5	400	576	15	48	15	14.16
9	8.2	132	26	17	395	408	30	78	1	13.68
10.	7.3	92	19	11	130	286	28	26	5	13.89

depolarisation. Hard waters with low dissolved solids content, however restrict the oxygen diffusion due to the deposition of $CaCO_3$ film on the steel surface.

Dissolved CO_2 gas increases the H^+ concentration (low pH) in water by forming carbonic acid which dissociates to form H^+ and CO_3^{-2} ions and cause hydrogen evolution type corrosion. This effect of CO_2, however, is counter acted by the presence of alkaline salts so that for practical purposes pH will depend upon the ratio between the two.

When metal is corroding in these mine waters, alkali is formed by the reduction of dissolved oxygen according to following equations :

$$O_2 + 2H_2O + 4e^- = 4OH \qquad (1)$$

$$2H_2 + 2e^- = 2OH^- + H_2 \qquad (2)$$

This increases the pH at cathode and thus enables the precipitation of $CaCO_3$ on the metal surface as many waters are supersaturated in calcium carbonate and bicarbonate. Actually a layer of alkali saturated solution of hydrous ferrous oxide (pH 9.5), always remains on iron and steel surface when it is immersed in nearly neutral and alkaline water (Uhlig, 1964). Gurdeep (1985) observed that corrosion rate of steel specimens is independent on pH within the pH range of 4-10. Since pH on the iron surface under these conditions remains 9.5 which keeps the hydrated ferrous oxide layer unaffected.

Mine Water Corrosivity and Langelier Saturation Index

The Langelier Saturation Index (SI) is based upon the analysis of water for pH, Ca hardness, alkalinity, and total dissolved solids. SI is simply the difference between actual pH of water and the calculated pH of calcium carbonate saturation, that is :

$$SI = pH\ (measured) - pHs\ (computed) \qquad (3)$$

If there is no difference, that is, SI is zero, the water is believed to stable. If SI is positive ($pH > pHs$) the water is expected to be protective and, thus, noncorrosive. A negative SI ($pH < pHs$) is interpreted to indicate that the water is aggresive and, therefore, corrosive.

The plots of rates of corrosion of mild steel in mine waters against SI are demonstrated in Fig.1. The pHs were obtained from the chart of Powell et al (1945). This shows that it is not easy to establish a direct relationship between the two values.

The positive saturation indices are likely to be obtained as long as hardness values are sufficiently high but it, of course, will depend upon the relative calcium ion and alkalinity values. It is, however, interesting to note that waters having values of SI as +0.76 and -0.68, have the same corrosion rate for steel. Further corrosion rates of steel in these mine waters depend upon the concentration of chloride and sulphate ions and is irrespective of the sign and value of SI.

This study indicates that regardless of the algebraic value of saturation indices, waters with dissolved electrolytes are all corrosive. Hence, the Lengelier Saturation Index needs to be thoroughly examined along with other parameters, when it is to be applied to aqueous systems, in contact with a corroding metal.

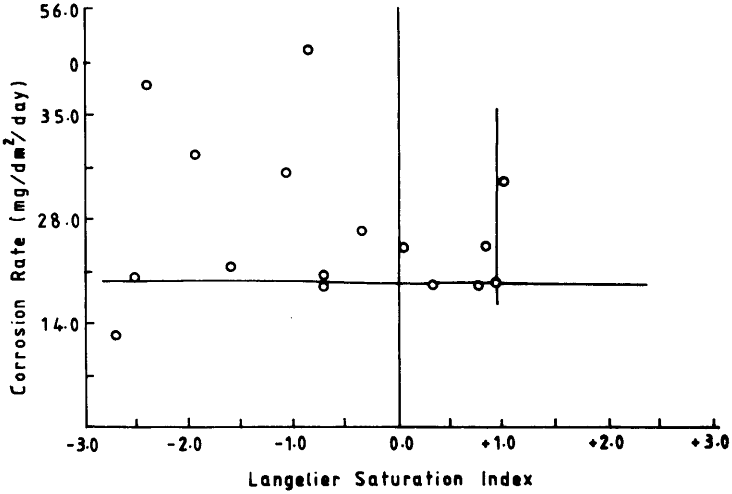

Figure.1 Graph between corrosion rate and langelier saturation index.

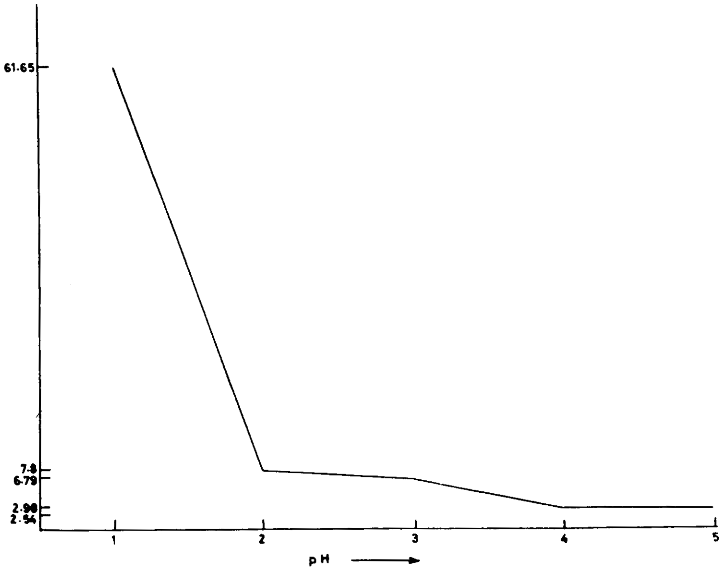

Figure.2 Effect of pH on the corrosion of Mild Steel.

Corrosivity of Acid Mine Waters

Chemical analyses of mine water samples from Northeastern Coalfield of India (Assam) is given in Table 3. These mine waters are, in general, highly acidic and contain high sulphate and iron content coupled with low pH. The high hardness values coupled with high acidity and low pH indicate that primary cation contributing to it is soluble iron apart from Ca^{2+} and Mg^{2+}. These mine waters inspite of having high hardness show a very high degree of corrosivity as hard crusty deposit on the metal surface tend to dissolve in acidic media. Surface oxide film of hydrous ferrous oxide is dissolved at pH below 4 and directly comes into contact with the acidic environment. Increased rate of corrosion is the result of both hydrogen evolution and oxygen depolarisation. Fe^{3+} and Cu^{2+} ions in acid mine waters further make them more aggressive by giving rise to additional reduction reactions on the metal surface. However, presence of Cu^{2+} is not detected in these mine waters.

Acidity in mine waters results by oxidation of pyritic materials associated with coal deposits during mining operations. Gurdeep and Rawat (1982, 1983) studied the nature and occurrence of acid mine drainage in Northeastern Coalfield of India. The rate of pyrite oxidation is greatly accelerated by certain iron and sulphur-oxidising chemoautotrophic acidophilic bacteria particularly Thiobacillus ferrooxidans. This explains the existence of sulphuric acid, iron sulphates and other ions in acid mine waters.

Effect of pH on the corrosion rate of mild steel is shown in Fig.2 indicates that corrosion rate dropped considerably from 61.65 mpy at pH 1.0 to 2.54 mpy at pH 5.0. This is due to the fact that corrosion effects of dissolved oxygen are much increased in addition to hydrogen evolution in acid water at low pH. However, corrosion rates of mild steel in sulphuric acid solutions in the pH range of 2-3 is only between 6-8 mpy. Hence, sulphuric acid alone can not account for the high corrosion rates of mild steel when compared in the original acid mine water under similar pH conditions.

Effect of Aggressive Ions :

Various aggressive ions such as SO_4^{2-}, Cl^- and Fe^{3+} are present in acid mine waters at significant concentration levels as shown in Table 3. SO_4^{2-} and Cl^- ions occur due to the breakdown and subsequent dissolution of pyrite and other materials due to mining. Fe^{2+} iron as resulted by pyrite oxidation undergoes oxidation in sulphuric acid medium by Thiobacillus ferrooxidans at a considrable rate and thus explains the existence of Fe^{3+} ions in acid mine waters.

The effect of these aggressive ions on corrosion rate of mild steel in sulphuric acid solution of pH 2.5, is demonstrated in Fig.3 which shows that an increase in the concentration of these ions causes an increase in the corrosion rate. The corrosive aggressiveness of these ions at the same concentration level is found in the following order :

$$Fe^{3+} > Cl^- > SO_4^{2-} \qquad (4)$$

Table-3 Chemical Analyses of Mine Waters from Northeastern Coalfield (Assam)

pH	Acidity (ppm)	Total hardness (as ppm $CaCO_3$)	Calcium (ppm)	Sulphate (ppm)	Chloride (ppm)	Fe^{3+} (ppm)	Fe^{2+} (ppm)	Corrosion rate for mild steel (mpy)
2.7	2040	2300	104	3050	28	200	150	36.00
2.7	2100	1800	98	2500	17	168	218	29.18
5.3	95	990	125	1662	50	65	40	3.90
2.5	980	1130	116	3210	34	46	92	20.80
2.9	1090	2900	65	2420	42	210	335	28.00
3.1	1230	3300	245	2880	18	245	405	32.10
2.8	1185	3170	60	3100	40	300	460	33.25
2.45	2350	2120	52	3110	50	88	200	20.16
2.9	1090	2900	65	2420	18	210	335	38.40
2.5	2110	1930	58	2956	35	76	312	30.51
2.3	2480	1490	50	3030	21	101	91	34.27
3.98	190	900	250	984	18	38	22	4.95
4.1	160	595	288	529	42	30	26	4.70
4.1	100	890	440	984	19	21	24	5.25

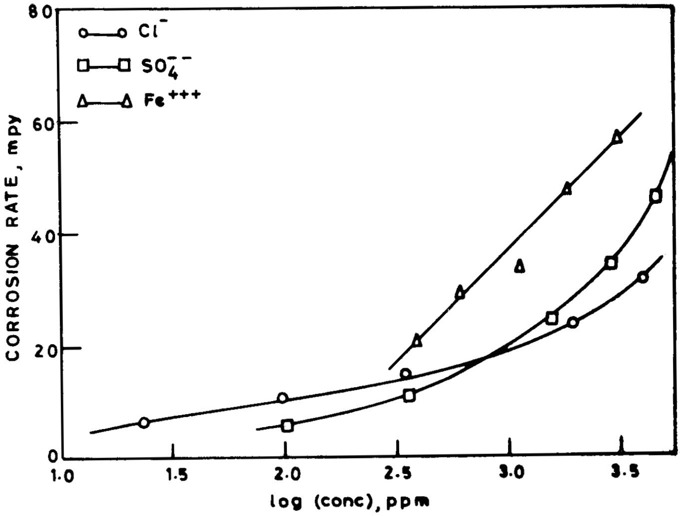

Fig. 3 Effect of concentration of ions on corrosion rates

However, the order of aggressiveness is changed as per their available concentrations in acid mine water as :

$$Fe^{3+} > SO_4^{2-} > Cl^- \tag{5}$$

The aggressiveness of Fe^{3+} ions is due to its rapid reduction on the metal surface. This reduction increases the rate of corrosion as the concentration of Fe^{3+} ions in solution goes on increasing. The other reduction reactions occurring in acid solutions are oxygen depolarisation and gaseous hydrogen evolution reactions. The partial reduction and oxidation processes contributing to the overall corrosion of mild steel in these acid mine water are :

Reduction Reactions

$$Fe^{3+} + e = Fe^{2+} \tag{6}$$

$$2H^+ + 2e = H_2 \tag{7}$$

$$O_2 + 4H^+ + 4e = 2H_2O \tag{8}$$

Oxidation Reaction

$$Fe = Fe^{2+} + 2e \tag{9}$$

The comparative increase in corrosion rates at higher sulphate concentrations is usually attributed to the higher conductivity of the solutions in the presence of these ions and formation of basic ferric sulphate which causes intense pitting on the metal surface. Cl^- ions in acid solutions form soluble FeOCl complex and thus carries away Fe^{2+} from the surface of the metal. Synergistic effect of these ions result in aggressive attack on the metal surface.

Classification of Mine Waters :

From the results of this survey, mine waters can be classified into following types as follows :

Type 1	A highly acid water, pH 2.0 to 4.5
Type 2	A soft, slightly acid water, pH 5.0 to 7.0
Type 3	A soft, alkaline water, pH 7.5 to 9.0
Type 4	A hard, neutral to alkaline water, pH 7.0 to 8.5
Type 5	A soft, acid water, pH 3.5 to 8.5
Type 6	A highly saline water, pH 6.0 to 8.0

The above classification is convenient one to adopt to describe the nature and degree of corrosivity of mine waters. Type 6 is uncommon in these mine waters. Experience of laboratory corrosion testing with simulated waters of the six types and experience of corrosion problems encountered underground has shown that waters of Type 1 are particularly troublesome ones.

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