REMOVAL OF TRACE ELEMENTS FROM ACID MINE DRAINAGE

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ABSTRACT

The mine drainages in some coal mines of North Eastern India, are found
to be highly acidic and contain trace elements which are highly undesir-
able for drinking purposes. This water requires neutralization together
with trace metal removal prior to its supply to the public.

This paper describes the results of a study conducted to determine the
ability of lime neutralization to remove inorganic trace elements from
acid mine drainage under different operating conditions. The specified
trace elements were arsenic, cadmium, chromium, copper, mercury, lead,
zinc, manganese, aluminium, iron and nickel etc. Results of this study
indicate that treatment by lime neutralization was very effective in
removing these trace metals from acid mine drainage.

INTRODUCTION

One of the most troublesome mine drainage problems in some of the North
Eastern Coal Mines of India is caused by acidity. The occurrence of
acidic drainages associated with these mines has been well studied [1-5].
Acid mine drainage offers favourable medium for existence of trace metals
such as Fe, Ca, Mg, Al, Mn, Cu, Zn, Pb etc., which are acid soluble and
are leached from coal and associated strata during mining operations.
Water of this type supports only limited water-flora, such as acid
tolerant molds and algae; it will not support fish life, destroy mining
equipment, increases the cost of water treatment for various water
supplies and leaves the water unacceptable for drinking and recreational
purposes.

Environmental degradation caused by these acidic, iron rich effluent
drainages has required assiduous efforts to find cost-effective abatement
and treatment methods. The most commonly used method for treating acid-
mine drainage and removing trace (heavy) metals is neutralization. A
typical system would include adding an alkaline reagent mixing, aerating
and removing the precipitate. Alkaline reagents that may be used are
NH_3, Na_2CO_3, NaOH, lime and limestone. In most cases lime is used because
of its lower cost and higher reactivity in conjunction with the effective
removal of trace metals from acid mine drainages [6].

The purpose of this investigation is to determine the effectiveness of lime neutralization of acid mine drainage in removing trace metals.

EXPERIMENTAL PROGRAM

Collection and Chemical Analysis of Mine Water Samples

Acid mine water samples from various sumps were collected from Ledo (Tirap) and Jeypore collieries where severe conditions exist.

The pH of mine water was measured with a Philips pH meter. Standard methods were employed for estimation of various constituents in mine water samples [7]. The quantitative analysis of trace elements were done by using Atomic Absorption Spectrophotometer SP 1900 Pye Unicam. For each element a calibration curve is drawn by taking standard solution for comparison with the unknown samples. Dilution has been done wherever necessary in case of samples.

Lime Neutralization Studies

Samples of acid mine water were neutralized with lime and agitated for 10 minutes. Then the samples were allowed to set undisturbed and the supernatant pHs were periodically recorded.
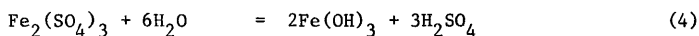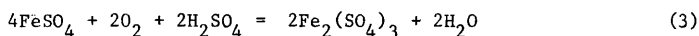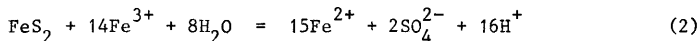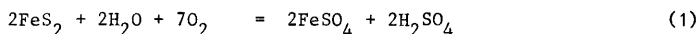
After completion of the reaction, the standard procedure of analyzing samples as described above, was adopted after 24 hours, in the filtered neutralized samples.

RESULTS AND DISCUSSION

Background of Problem

It is generally recognized that the oxidation of iron-disulphides occurring either as pyrite or marcasite in coal and associated strata, to hydrous ferrous sulphates and the subsequent hydrolysis of these compounds is the cause of acidity found in acid mine drainages in most coal mining areas. Under the influence of bacterial activity (iron and sulphur bacteria) in acid mine drainages, the ferrous (Fe^{++} is oxidised to ferric (Fe^{3+}) state, which complexes further to form ferric and ferrous oxyhydroxides indicating the characteristic yellow and red colour of acid drainages [8].

The general chemical reactions explaining the oxidation of pyrite and the production of acidity are given by the following equations :

$$2FeS_2 + 2H_2O + 7O_2 = 2FeSO_4 + 2H_2SO_4 \tag{1}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{2}$$

$$4FeSO_4 + 2O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O \tag{3}$$

$$Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4 \tag{4}$$

The stoichiometry of equations show that for each mole of iron sulphide oxidised, four moles of acid are produced. This results in lowering of the pH of water draining from the material. At the lower pH levels, the
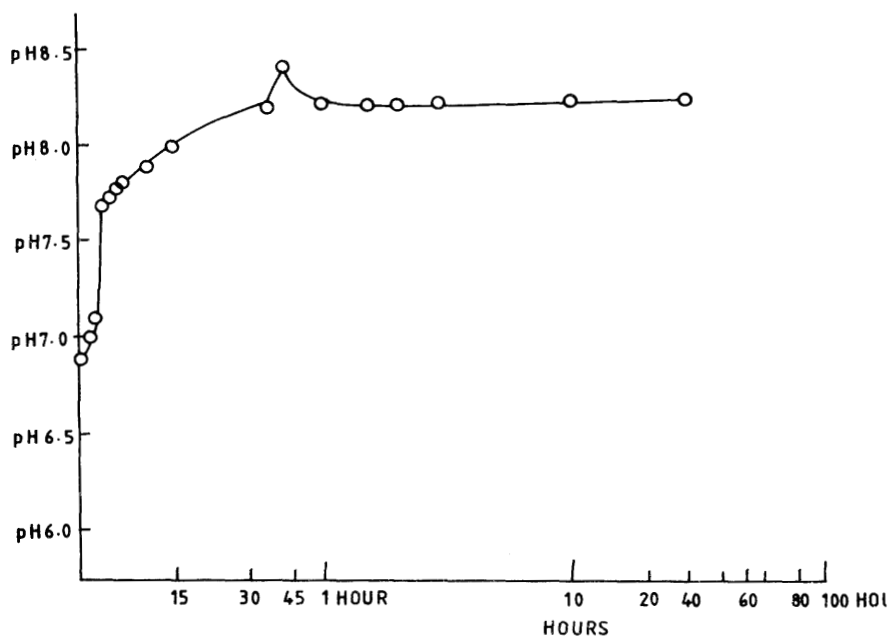
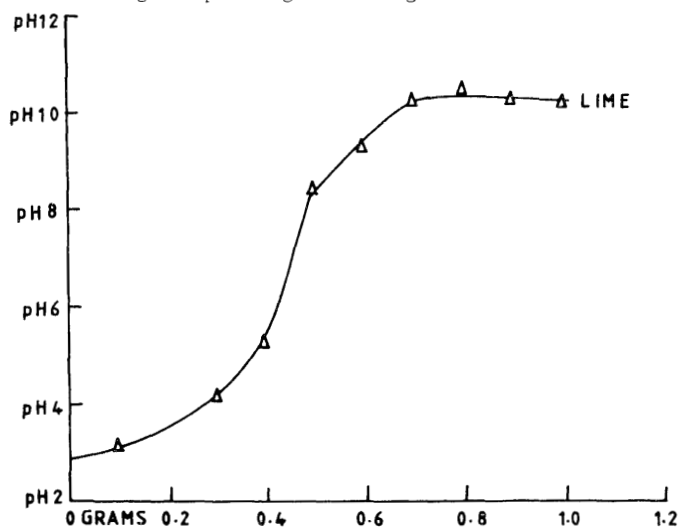Fig.1. pH change following lime neutralization

Fig.2. Lime (grams) added to one liter of run water

heavy (trace) metals are more soluble and enter into solution as a result of secondary reactions between iron sulphates, sulphuric acid and the compounds in nearby clays, limestones, sandstones, sulphides, and various organic substances present in mines or streams and explain the existence of Ca, Mg, Na, K, Fe, Al, Mn, silicates etc. in mine drainage.

Chemistry of Lime Neutralization

In the treatment of high ferric iron acid mine drainages only neutralizations is involved since the system has already attained equilibrium with respect to iron and further hardly any significant amount of acid will be generated during treatment. For the influent water containing ferric iron and sulphuric acid, the overall lime $Ca(OH)_2$ neutralization reaction is as follows :

$$4Ca(OH)_2 + Fe_2(SO_4)_3 + H_2SO_4 = 4CaSO_4 + 2Fe(OH)_3 + 2H_2O \qquad (5)$$
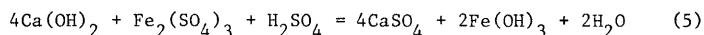
Most trace (heavy) elements tend to precipitate as the pH is raised. In Table 1 typical pH ranges at which various metals will precipitate are presented. Metals such as Cu, Zn, Fe, Al, Mn and Co can be reduced to low levels, less than half mg/l with pH adjustment, precipitation and solids separation [9].

Table 1 Precipitation of Trace Elements by pH Control

Ion	pH Range	Ion	pH Range
Fe (III)	3.5-4.5	Na (I)	7.0-8.0
Al (III)	4.5-6.0*	Cd (II)	7.0-8.0
Cr (III)	5.5-6.5	Hg (II)	7.5-8.5
Pb (II)	6.0-7.0	Fe (II)	7.5-9.0
Cu (II)	6.5-7.5	Zn (II)	8.0-9.5
		Mn (II)	8.5-9.5

* Al will become soluble again at pH greater than 7.5

GENERAL DISCUSSIONS

Since pH was found to vary with time following neutralization and as solubility of metal salts in the water is dependent upon pH, it was critical to establish a standard time of analysis following neutralization with lime. Fig.1 shows the study of pH change following neutralization which was obtained by neutralized acid mine water after 10 minutes. This indicates that the reaction was rapid and the pH was stabilized after a half hour, thus the reaction had gone to completion.

The reactivity of lime was measured by addition of measured amounts of lime to separate samples of acid mine water (tests were run allowing 5 minutes reaction time between incremental addition of the neutralizing agent), as depicted in Fig.2. In this reaction, the steep slope between 4.0 and pH 8.0 is indicative of the quantitative sensitivity of the lime

Table 2   Example of Acid Mine Drainages

Parameter (mg/1)	Ledo (Tirap)				Jeypore				
	1	2	3	4	1	2	3	4	5
pH	2.7	2.7	2.5	3.1	2.9	2.8	2.45	2.3	2.5
Acidity	20.40	2100	980	1230	1090	1185	2350	2480	2110
Sulphate	3050	2500	3210	2880	2420	3100	3110	3030	2956
Hardness	2300	1800	1130	3300	2900	3170	2120	1490	1930
As	1.6	0.4	–	–	0.4	0.4	–	1.0	0.6
Cd	1.2	–	0.9	4.8	–	–	0.3	4.0	1.6
Cr	6.6	0.8	10.0	6.5	11	2.0	0.8	4.6	8.5
Cu	0.4	0.7	0.7	–	–	0–6	0.9	–	0.3
Hg	0.3	–	–	–	0.5	–	–	0.2	–
Pb	1.1	0.7	1.6	0.9	0.5	1.2	1.0	0.9	0.9
Zn	2.5	1.0	2.4	3.0	1.2	4.6	0.8	1.5	0.8
Mn	2.4	17.0	12.0	8.2	8.2	8.2	1.6	1.2	3.4
Al	2.0	1.9	49	3.6	10.5	44	29	56	13
Fe	350	358	136	670	545	760	388	192	385
Fe(11)	5	15.0	5.6	6.5	6	60	21.5	11	4.8
Ni	3.0	3.6	3.1	3.5	3.1	4.0	N.D.	4.5	6.0

Table 3   Maximum Contaminants in Drinking Water Allowed by Various Authorities (mg 1 litre). In parentheses = (desirable maximum) [Refs.10]

Parameter	EPA (1976)	WHO (1971)	USPHS (1962)
pH	6.0 – 8.5	6.0 – 8.5	6.0 – 8.5
Sulphate	250	400 (200)	250
Hardness (as $CaCO_3$)	–	500 (100)	–
Total dissolved solids	500	1500 (500)	500
As	0.05	0.05	0.05 (0.01)
Cd	0.01	0.01	0.01
Cr	0.05	–	–
Cu	1.0	1.5 (0.05)	0.2 (0.01)
Hg	0.002	0.001	–
Pb	0.05	0.1	0.05
Zn	5.0	15 (5)	5.0
Mn	0.05	0.5 (0.05)	0.05
Al	–	–	–
Fe(III)	0.3	1.0 (0.1)	0.3
Fe(II)	0.3	1.0 (0.1)	0.3

reaction in this portion of curve. It is obvious that a very small change in the amount of lime added at pH 6.0 can easily shift the pH one to two full points, hence accuracy of feed is of vital importance. This was also noted that pH can be raised to any desired level with the addition of requisite-amount of lime.

Example of typical acid mine drainages occurring in two mines from North Eastern Coal Mines of India has been given in Table 2. The various physico-chemical characteristics and especially traced elements contained in these exceed the drinking water standards as laid down by various international organisations [10] (Table 3). The effectiveness of removal of trace elements by lime neutralization process at various pH's for sample 1 of Table 2, is shown in Table 4. The lime neutral-ization process investigated trace element removal effectiveness as a function of pH. Significant removals were observed for all elements except manganese at pH 8 and below, and a large portion of sulphate content was remained ineffective in the resulted water. Coprecipitation and absorption of trace elements with sludge (mainly ferric hydroxide) may be possibility as the mechanism of removal at the higher pH's.

Table 4 Lime Neutralization Water Quality Analysis

Parameter	Typical influent Sample 1 (Ledo)	Nominal pH of effluent					
		7	8	9	10	11	12
pH	2.7	7.0	7.9	8.7	10.0	10.9	12.3
As	1.6	0.1	0.05	0.04	0.02	0.03	0.02
Cd	1.2	0.24	0.1	0.08	0.01	0.01	0.01
Cr	6.6	0.08	0.08	0.07	0.06	0.05	0.04
Cu	0.40	0.3	0.16	0.11	0.05	0.05	0.07
Hg	0.03	0.06	0.02	0.01	0.01	0.01	0.01
Pb	1.1	0.02	0.04	0.02	0.02	0.02	0.01
Zn	2.5	0.9	0.23	0.11	0.07	0.08	0.08
Mn	2.4	2.0	1.8	0.21	0.06	0.06	0.05
Al	20	0.5	0.33	0.31	0.40	0.40	0.23
Fe(III)	350	1.2	0.65	0.30	0.35	0.30	0.00
Fe(II)	5	0.25	–	–	–	–	–
Acidity	2040	16	–	–	–	–	–
Alkalinity	–	35	36	44	50	90	1220
Sulphate	3050	3000	2710	2760	2740	2410	2340

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