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ORIGINAL PAPER

Acid drainage potential from coal mine wastes: environmental assessment through static and kinetic tests

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Abstract The present study involved the assessment of potential generation of acid drainage from a coal mining area in India. Laboratory-based static and kinetic tests on overburden samples were conducted. Results of the static tests using acid base accounting indicate that all samples may be acid generators, and their generation capacity varied between likely, possible and low. To verify the acid generation potentiality of those samples showing a high acid drainage production in the static test, the kinetic test, using humidity cell, was conducted for a period of 15 weeks. The samples were leached with simulated rain water to mimic the chemical weathering under controlled laboratory conditions and imitate actual mine site leaching. Data obtained from chemical analysis of collected leachate were used to estimate production and reaction rates of acid generation and neutralizing capacity. Based on the kinetic test, it can be concluded that presently the neutralizing capacity of the samples is better than the oxidation capacity (acid generation). But due to the high weathering rate of carbonates, as reflected by the simulated leaching test, the neutralizing materials (carbonates) will eventually be exhausted earlier (since they showed dissolution rate) than the acid generation species (sulfates). Thus, acid drainage production is predicted from that point of time, when the neutralizing capacity has been exhausted for these mine sites.

Keywords Acid base accounting · Humidity cell · Leaching kinetic · Oxidation–neutralization · Weathering rate

Introduction

Acid mine drainage and metal leaching from mine waste dumps are naturally occurring process which is accelerated by intensification of mining operations. Such activities have profound impact on the local environment and ecology (Kimmel 1983; Johnson et al. 1987; Kaeser and Sharpe 2001). The impact depends on the magnitude of the acid drainage and the sensitivity of the receiving environment along with other factors like the degree of neutralization, dilution and/or attenuation. The main sources of acid drainage from mining areas include drainage from underground workings, surface runoff from open pit mine faces and pit workings, seepage and runoff from waste rock dumps and spoil piles, tailings and process residue storages, ore stockpiles and spent ore piles from heap-leach operations (ELAW 2010). Factors which enhance metal leaching include swiftly weathering metal-containing minerals, drainage conditions that increase solubility and high flow rates through contaminated materials. Acid rock drainage (ARD) is generated at mine sites when metal sulfide minerals present in the host rock associated with most types of metal mining activity, get oxidized. During pre-mining stage, oxidation of these minerals and the formation of sulfuric acid is a function of natural weathering processes. The oxidation of unbroken ore bodies followed by release of acid and mobilization of metals is slow, but extraction and beneficiation operations associated with mining activity increase the rate of these same chemical reactions by exposing large volumes of sulfide rock

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material with increased surface area to air and water. The chemistry of oxidation of pyrites, the production of ferrous ions and subsequently ferric ions, is very complex, and this complexity has considerably inhibited the design of effective treatment options. Although a host of chemical processes contribute to acid mine drainage, pyrite oxidation is by far the greatest contributor. The net process is given as Eqs. (1) and (2) below.

$$2\mathrm{FeS}_2(\mathrm{s}) + 7\mathrm{O}_2(\mathrm{g}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l}) = 2\mathrm{Fe}^{2+}(\mathrm{aq}) + 4\mathrm{SO}_4^{2-}(\mathrm{aq}) + 4\mathrm{H}^+(\mathrm{aq}) \quad (1)$$

$$4\mathrm{Fe}^{2+}(\mathrm{aq}) + \mathrm{O}_2(\mathrm{g}) + 4\mathrm{H}^+(\mathrm{aq}) = 4\mathrm{Fe}^{3+}(\mathrm{aq}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l}) \quad (2)$$

Equation (1) shows the oxidation of sulfide to sulfate taking place and consequently the solubilization of the ferrous ions (Fe^{2+}) and generation of H^+ ions. In the Eq. (2), this ferrous ion is oxidized to ferric ion (Fe^{3+}). The Fe^{3+} produced oxidizes additional pyrite and converts them into ferrous ions. Either these reactions can occur spontaneously or they can be catalyzed by microorganisms that derive energy from the oxidation reaction. The net effect of these reactions is the release of H^+ ions, which lowers the pH of the system and facilitates the solubility of the ferric ion and other heavy metals. The dissolution of pyrite by ferric iron in conjunction with the oxidation of the ferrous ion constitutes a cycle of dissolution of pyrite. $\mathrm{Fe(OH)}_3$ precipitates and is identifiable as the deposit of amorphous, yellow, orange or red deposit on stream bottoms termed as 'yellow boy.'

Predictive testing is used to determine whether a discrete volume of mining waste will generate acid and also to forecast the quality of the drainage based on the rate of acid formation measured, thus providing a effective way of acid mine drainage management (Brady et al. 1988; BC-AMD 1989; Brady et al. 1994; Geidel et al. 2000; Gautama and Hartaji 2004). Analytical methods to predict acid generation are mainly of two types—static test and kinetic test. The static test quantifies both the total acid generating and total acid neutralizing potential of a sample, whereas acid drainage is predicted as either the difference of the values or a ratio of the values. The static test can only predict the potential to produce acid drainage, whereas the rate of acid generation can be estimated using the kinetic test. Kinetic tests simulate the reactions occurring at the mining sites, usually at an enhanced rate. Results from this exercise are used to evaluate materials according to their acid generating potential. The framing of standard methods to evaluate the propensity of mine site materials to produce acid drainage has been the theme of research for many years with notable contributions from Sobek et al. (1978), Sullivan and Sobek (1982), Noll et al. (1988), Bradham and Caruccio (1990), Lapakko (1993), Morin and Hutt (1997), Hornberger and Brady (1998), and Chotpantarat (2011).

The acid base accounting (ABA), a form of static test, predicts mine drainage quality by comparing the sample material's maximum potential acidity (MPA) with its neutralization potential (NP) (Skousen et al. 2002). Sobek et al. (1978) formally presented a detailed laboratory methodology for conducting the ABA on mine overburden material and is frequently cited as a pioneer protocol, whereas Noll et al. (1988) provided an exhaustive account of considerations fitting to planning an overburden analysis and collection of samples. Skousen et al. (1997) described a protocol for a quantitative method of rating overburden samples based on the percent insoluble residue. Kinetic tests are different from static tests in that they attempt to simulate the natural oxidation reactions of the mine site (Bradham and Caruccio 1990; Lapakko 1993). The humidity cell is a method of kinetic testing of mine samples to predict drainage quality from mine site samples (Hanna and Brant 1962; Sobek et al. 1978; Hornberger et al. 2003). The application of results from static and kinetic tests is used to classify mine wastes and predict acid drainage on the basis of their potential to generate acid (Geidel et al. 2000). These tests are extremely useful for management of acid mine drainage in various types of mines include coal. Recent relevant studies include those by Méndez-Ortiz et al. (2007), where the processes and products involved in the generation of acid rock drainage—metal leaching from mine waste material (tailings) derived from the exploitation of an ore type Pb–Zn–Ag were characterized. Laboratory tests (static and kinetic) of historic and recent tailings were conducted. Studies conducted by Benzaazoua et al. (2001) used kinetic test data to predict acid drainage from sulfide tailings and mine wastes. Gautama and Hartaji (2004) studied the accuracy of geochemical rock modeling based on the static test of coal mine samples in East Kalimantan. Kinetic testing was conducted to analyze the long-term behavior of rock samples being classified as potential acid forming by the static test. Some others studies include those by Jennings and Dollhopf (1995), Benzaazoua et al. (2001), Banerjee and Niyogi (2005), Bouzahzah et al. (2009) and Banerjee (2011). Studies in the Indian context related to static and kinetic tests to predict acid drainage from mines are limited based on lack of publications.

The main objective of the present study was to assess the acid drainage potentiality of coal mining waste related to the Raniganj Coalfield (RCF) area of West Bengal, India through static (ABA) and kinetic (humidity cell) leaching tests. The kinetic test would mimic chemical weathering under controlled laboratory conditions to simulate actual mine site leaching, and data would be used to estimate reaction rates along with oxidation–neutralization analysis

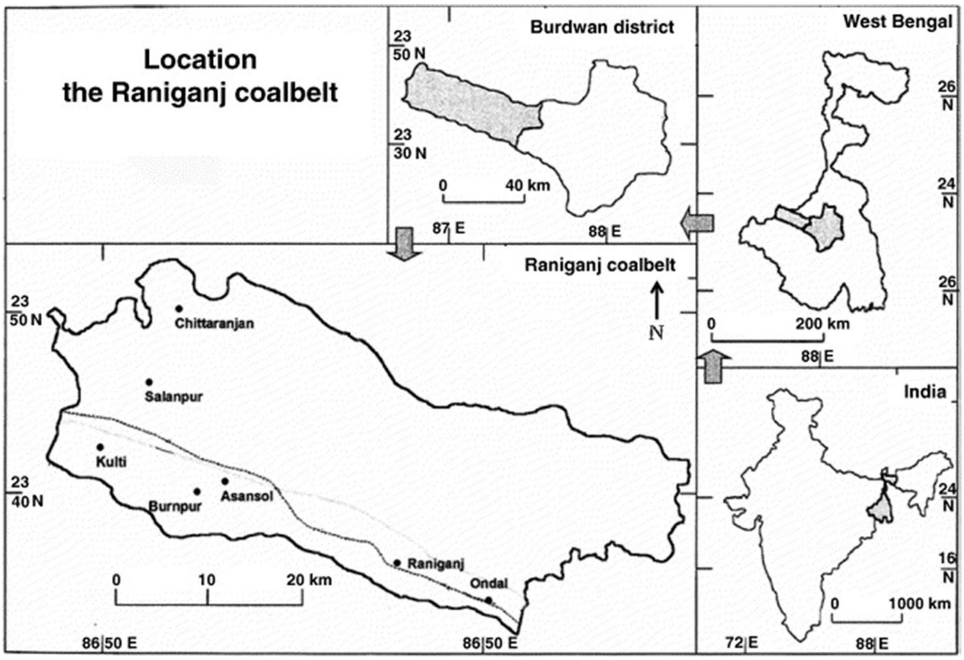

Fig. 1 Map showing location of study area (Source: Gangopadhyay et al. 2006)

Table 1 Volume and normality of hydrochloric acid used for each fizz rating

Fizz rating	HCl (mL)	HCl (molarity)	Typical end pH	pH range
None	20	0.1	2.0–2.5	1.6–5.2
Slight	40	0.1	1.5	0.76–2.1
Moderate	40	0.5	1.0	0.77–1.83
High	80	0.5	0.8	0.35–1.07

to predict whether the samples may produce acid drainage. The present research will add to the pool of data in this theme of research and would be important in the context of the regional and global mining environmental degradation management. Results from this study can be extrapolated to other mining areas in India and worldwide, on a large scale with classification of the mine areas with potential to produce acid drainage, and the predictive modeling may provide tools for estimating the potential extent of acid generation and weathering rates prior to its occurrence

The study area of Raniganj Coalfield (RCF) is 1,530 km^2 spreading over Burdwan, Birbhum, Bankura and Purulia districts in West Bengal and Dhanbad district in Jharkhand state, located in the western part of India. Geographically this coalfield lies between latitudes 23°25′N and 23°50′N and longitudes 86°38′E and 87°20′E falling in 8 Survey of India toposheets (Scale 1:50,000) Nos. 73–1/9, 73–1/10, 1/13, 1/14, M/I, M/2, M/5 and M/6. The map of the study area is given as Fig. 1. Physiographically, the RCF overlies the granite plateau fringe with a general elevation of about 100 m. Permo carboniferous rock formations are exposed in many planes with small isolated occurrences of upper Gondwanas near the southern boundary fault. The lower Gondwanas of the RCF consist of the general stratigraphy sequence of Talchir, Damuda and Panchet rocks of which Damuda series is the most important. The important rock types are sandstones, shales, traps and coal seams (Murthy et al. 2010). Representative sampling of overburden material from four locations in the RCF area was conducted on a seasonal basis for the period of March 2008 to February 2010. Three samples were taken from each site and mixed to obtain a composite sample at each location. A total of 12 mine site overburden samples were used for the study, where 9 samples represented operational mine areas and 3 from abandoned (historic) site (tailings at a depth of 4 m). Approximately 5 kg of each sample was collected in plastic bags for further analysis (Sobek et al. 1978)

Materials and methods

At present, the Eastern Coalfields Limited, a subsidiary of Coal India Limited, India, operates in this area with 107 mines (89 are underground and 18 opencast mines) having total coal reserve of up to 600 m depth of 23 billion ton (t). Out of this, proven extractable reserve is 6 billion tons. The coalfield contains the best type of non-coking coal reserves in India. All the heat intensive industries in and around the area exclusively depend on the Raniganj coal. The entire export of coal from the country is being done from this coalfield. The RCF also contains large reserves of iron ore occurring chiefly as nodules along with good quality fire clay in the Barakar stage of RCF (Sikdari et al. 2004). The high

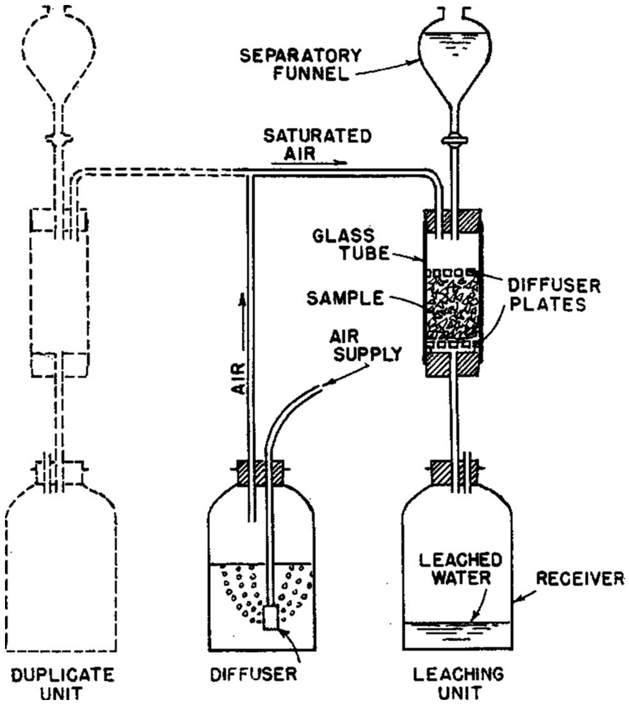

Fig. 2 Design of humidity cell used for the kinetic test study (Source: Hanna and Brant 1962)

demand for coal from this area has ensued in intensive mining activities and expansion of the lease hold areas, along with the piling up of vast areas of overburden material and tailings, thus resulted in significant long-term environment hazards in the form of acid mine drainage and contamination of local water resources with toxic trace metals (Singh and Singh 2010; Banerjee 2011; Singh et al. 2012).

Static test (acid base accounting)

The ABA study was performed as per the methods of Sobek et al. (1978) and Skousen et al. (1997). The ABA test is the most common static test to assess the balance between the acid generating and acid neutralizing minerals, and thus, determine whether acid drainage would be produced. The maximum potential acidity (MPA) was stoichiometrically calculated by multiplying the sulfur content with 31.25, where sulfur was estimated by gravimetric method with precipitation by 10 % barium chloride, after fusing in a mixture of 2:1 magnesium oxide and sodium carbonate. The neutralization potential (NP) of the samples was estimated using the peroxide siderite correction method of Skousen et al (1997), since overburden material in this region contains siderite (Mishra et al. 1990). For NP estimation, 2 g of sample was taken in each of three beakers with a fourth beaker having no sample. Next an amount and strength of HCl was added to each beaker based on the sample fizz rating as indicated in Table 1, and the volume was adjusted to 100 mL using deionized distilled water. The mixtures were covered with watch glass and boiled gently for 5 min and then allowed to cool. Further, all solutions were filtered by Whatman No. 40 (0.45 μm) filter. The next step included the addition of 5 mL of 30 % H_2O_2 to the filtrate and boiling for further 5 min and then cooled. Finally, the solutions were hand titrated with 0.5 M NaOH to pH 7 using an electrometric pH meter until a constant reading of pH 7.0 remained for at least 30 s. Acid consumed in the digestion of the neutralizing species was used to calculate the NP according to:

$$\begin{aligned} t\ \mathrm{CaCO_3eqv}/1000\,t \text{ of material} \\ = (\text{mL of acid consumed}) \times (25.0) \\ \times (\text{molarity of HCl used}) \end{aligned} \tag{3}$$

where mL acid consumed was estimated by the difference of mL acid added and mL alkali added multiplied by ‘constant’ (constant = (mL acid in blank)/(mL alkali in blank)). t represents tons of the material. Eq. (3) represents tons of $CaCO_3$ per 1,000 ton of overburden. The net neutralization potential (NNP) criterion to evaluate the capacity of the materials to generate acid drainage was calculated by subtracting the MPA from the NP. The NP/MPA ratio, known as the neutralization potential ratio (NPR), was also used as an evaluation criteria (Price and Errington 1998). An NNP of 0 is equivalent NP/MPA ratio of 1. From this criterion, the samples showing a high potential for acid drainage generation were subjected to subsequent kinetic test.

Table 2 Analytical method for chemical analysis of leachate

S. no.	Analyte	Reference method	Method	Detection limits	Units of reporting
1	pH	APHA 4500–H^+–B	Electrometric	1–14	pH scale
2	Acidity	APHA 2310 B	Titrimetric	–	mg/l
3	Fe	APHA 3500–Fe–B	Spectrophotometric	0.05–20	mg/l
4	Ca^{2+}	APHA 3500–Ca–B	Flame photometric	5–2,000	mg/l
5	Mg^{2+}	APHA 3500–Mg–B	Calculation		mg/l
6	SO_4^{2-}	APHA 4500–SO_4^{2-}E	Spectrophotometric	0–40	mg/l

Table 3 Acid base accounting (Static test) analysis for prediction of acid drainage

Sample ID	Acid base account				Acid mine drainage potential screening criterion
	MPA	NP	NNP	NPR	Morin and Hutt; Price and Errington (1998)
Samples before leaching					
OB-M1S1-N01	11.88	21.67	9.8	1.82	Possibly
OB-M2S1-N02	12.81	18.98	6.17	1.48	Possibly
OB-M3S1-N03	18.44	24.98	6.54	1.35	Possibly
OB-M4S1-N04	14.38	21.87	7.5	1.52	Possibly
OB-M1S2-N05	17.81	18.19	0.38	1.02	Possibly
OB-M2S2-N06	24.69	28.61	3.92	1.16	Possibly
OB-M3S2-N07	19.06	23.67	4.61	1.24	Possibly
OB-M4S2-N08	13.13	27.87	14.75	2.12	Low
OB-M1S3-N09	9.69	23.56	13.87	2.43	Low
OB-M2S3-N10	25.31	26.12	0.81	1.03	Possibly
OB-M3S3-N11	20.63	26.98	6.36	1.31	Possibly
OB-M4S3-N12	15.31	20.74	5.43	1.35	Possibly
Samples after 15 weeks leaching in humidity cells					
OB-M3S1-N03	17.81	22.16	4.35	1.24	Possibly
OB-M1S2-N05	16.25	15.88	−0.37	0.98	Likely
OB-M2S3-N10	24.38	22.98	−1.40	0.94	Likely
OB-M4S3-N12	15.00	18.34	3.34	1.22	Possibly

A total of 4 samples from the post-leaching ABA were selected for kinetic test, based on the acid producing potentiality. Units of MAP, NP, NNP in tons $CaCO_3$ eqv./1,000 tons of overburden; Acid mine drainage potentiality: NPR <1—likely; NPR = 1– <2—possibly; NPR = 2– <4—low and NPR ≤4—none

MPA maximum acid potential, *NP* neutralization potential, *NPR* neutralization potential ratio (NP/AP), *NNP* net neutralization potential

Kinetic test (humidity cell)

The use of humidity cells as a method of kinetic testing was conducted on mine site materials showing potentially high acid generation capacity based on the static test. Kinetic tests were carried out using a 7 day test cycle that alternated between humid and dry air conditions followed by chemical analyses of collected leachate over a period of 15 weeks (Morin and Hutt 1997; Méndez-Ortiz et al. 2007). The humidity cell (Hanna and Brant 1962) apparatus used for the study is given in Fig. 2. The humidity cell leaching system consisted of cylindrical cells (200 mm in diameter) containing 0.5 kg of mineral sample. Humidified air was generated in a separate glass tank half-filled with deionized water. The sample was leached once a week for 15 weeks with 500 mL of simulated rainwater (distilled water with pH adjusted to 5.5). The leaching procedure consisted of three and half days of exposure to humidity conditions and three and half days of dry air. Before starting the leaching cycle (0 days), the sample was flushed with 750 mL of simulated rainwater, soaked for 2 h and the leachate collected. At the end of the cycle (7th day), again humidity cell residue was flushed with deionized water. The leachate (representing the water that flowed through the mine tailings material) was collected in glass beakers, filtered, preserved and stored until analysis. Chemical analysis of leachate collected was conducted as per standard methods (APHA 1998). The details of analytical methodology used for the study are given in Table 2. The concentrations of cations, namely Ca^{2+} and Mg^{2+} were estimated by titrimetric method; Acidity was also estimated by titrimetric method. Fe was estimated using spectrophotometric method. SO_4^{2-} was estimated by spectrophotometric method. pH values were determined with digital pH meter. All instruments/systems were properly standardized and calibrated ahead of every estimation.

Leachate kinetics and production rates

Based on the results of the kinetic test, the reaction rates of the analyte were plotted as a function of time for predicting the quantity of acidity or alkalinity produced. Carbonate dissolution and pyrite oxidation rate in samples is an important estimate because this shows which suite of species is weathering faster, the acid producers (sulfides) or the neutralizers (carbonates). The carbonate and sulfur dissolution rate was determined by cumulative addition of the carbonate and sulfur mass in the leachates collected from the 15 weeks (EPA 2009). Here the steps included the

Table 4 Analyses of leachates from the kinetic tests using humidity cell for a period of 15 weeks of four coal mine waste samples

Week		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	X	σ
Sample ID	OB-M3SI-03																	
pH		7.04	6.95	6.81	5.12	6.19	6.48	5.89	6.91	7.15	7.35	7.83	7.16	6.73	7.76	7.12	6.83	0.70
Acidity	mg/l	110.6	101.7	96.6	87.3	85.7	81.1	72.6	65.4	61.6	52.1	38.9	29.5	21.2	27.7	19.9	63.46	30.58
Fe	mg/l	2.4	2	1.2	1.8	3.2	3.8	1.6	2	10	4.2	2.8	0.8	1.8	2.6	1.4	2.77	2.21
SO_4	mg/l	55.8	67.8	70.1	77.3	69.4	43.7	64.8	59.8	28.7	33.7	22.7	41.6	61.7	81.5	74.6	56.88	18.50
Ca	mg/l	370.6	498.7	398.9	459.6	416.9	398.6	466.7	467.8	410.6	378.7	345.9	279.6	259.8	300.8	333.6	385.79	71.89
Mg	mg/l	68.7	88.5	46.7	85.6	35.6	65.6	54.5	14.5	75.6	35.6	45.6	25.6	31	21	18.9	47.53	24.49
Sample ID	OB-MIS2-N05																	
pH		6.98	7.12	5.56	5.8	6.39	5.1	6.78	6.14	6.19	6.17	5.88	6.19	7.17	7.29	7.27	6.40	0.67
Acidity	mg/l	126.6	98.7	87.9	77.8	71.7	64.7	57.8	49.8	42.5	40.8	31.6	27.8	22.7	17.3	18.7	55.76	32.14
Fe	mg/l	3.6	3	2.2	1.4	1.8	2.6	3.8	5.6	6.2	4.8	2.8	4.4	2	1.6	2.2	3.20	1.49
SO_4	mg/l	67.7	28.7	78.4	61.7	48.3	68.9	55.8	60.5	52	62.7	70.1	57.8	38.7	31.5	22.8	53.71	16.58
Ca	mg/l	377.7	567.8	569.2	525.6	539.8	467.8	489.3	324.5	510.6	435.8	412.7	475.6	345.7	312.6	345.7	446.69	89.08
Mg	mg/l	89.6	64.5	21.7	75.6	56.6	42.3	32.5	126.7	113.4	78.9	24.5	83.4	46.7	34.5	26.6	61.17	32.81
Sample ID	OB-M2S3-N10																	
pH		6.44	6.13	7.18	4.78	5.67	6.78	7.12	7.45	7.23	6.45	5.67	5.12	6.23	7.1	6.97	6.42	0.82
Acidity	mg/l	141.7	131.7	120.9	103.8	91.7	85.6	79.6	71.4	62.8	55.8	47.8	42.7	38.7	27.5	23.7	75.03	37.35
Fe	mg/l	2.8	1	3	5.8	3.6	1.8	3	1.4	1.6	3.4	2.6	3.8	1.6	0.8	1.4	2.51	1.33
SO_4	mg/l	50.7	66.9	38.7	90.8	67.8	53.9	32.8	23.5	28.8	43.8	55.8	64.7	60.3	39.2	42.8	50.70	17.76
Ca	mg/l	289.9	466.9	435.9	422.9	416.8	389.9	277.8	328.9	428.9	344.8	322.4	387.4	317.8	298.7	288.5	361.17	63.06
Mg	mg/l	41.6	16.7	22.4	28.9	31	28.8	18.7	21.1	77.8	54.5	29.4	17.7	25.8	21.3	57.8	32.90	17.64
Sample ID	OB-M4S3-12																	
pH		6.95	6.77	5.45	4.22	6.22	6.9	7.13	7.29	7.11	6.44	6.78	7.2	7.89	7.06	7.03	6.70	0.88
Acidity	mg/l	76.9	58.7	61.6	55.3	48.7	41.5	34.8	29.6	23.8	17.9	14.5	10.7	13.8	9.5	9.3	33.77	22.14
Fe	mg/l	4.6	1.6	3.6	3	6.4	5.4	1.6	1.8	3.2	3.8	6.4	5.6	5	4	1.8	3.85	1.69
SO_4	mg/l	19.8	23.8	60.7	89.5	57.3	41.8	36.4	25.5	30.7	47.6	56.2	23.7	18.7	28.9	36.1	39.78	19.53
Ca	mg/l	422.9	523.8	643.9	450.8	423.9	510.9	544.7	432.8	499.4	512.8	433.9	556.9	455.9	329.8	422.9	477.69	75.22
Mg	mg/l	68.6	48.9	79.8	89.1	65	68.9	74.4	18.7	27.8	68.7	36.7	39.8	26.7	35.8	48.7	53.17	21.78

Results are from those samples that showed acid drainage potential in the static test

X = mean, σ = standard deviation

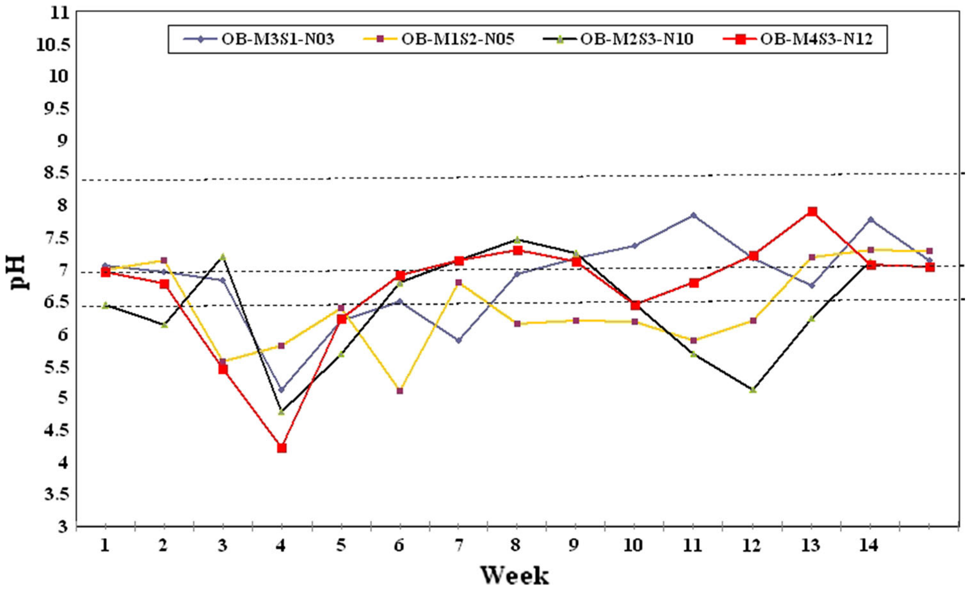

Fig. 3 Evaluation of pH for kinetic test leaching period

estimation of the calcium and magnesium carbonate equivalent in the humidity cell samples, followed by the determination of the amount of calcium carbonate weathered each week using the 'cation approach,' and the addition of the two was done. The sulfur oxidation rate was determined by estimating the amount of sulfur in the sample leached, followed by the determination of the sulfur oxidation rate and the percentage of sulfur available that was weathered. For analysis of acid generation potentials, the oxidation–neutralization and production rate curves were plotted.

Results and discussion

Acid base accounting analysis

The results of the ABA analyses of the samples before and after the kinetic test are given in Table 3. Samples having NPR <1 were complemented with kinetic tests. After the completion of the kinetic tests, the solid residue was subjected to the static test again to observe changes in ABA pre-and post-leaching condition. For the raw samples, the MPA ranged between 9.69 and 25.31 with a mean of 16.93 t $CaCO_3$/1,000 t overburden. NP ranged between 18.19 and 28.61 with a mean of 23.60 t $CaCO_3$/1,000 t overburden. The NPP (NP-MPA) is seen to range between 0.38 and 14.75 with an average of 6.68, while the NPR (NP/MPA) ranged between 1.02 and 2.43 t $CaCO_3$/1000 t overburden with an average value of 1.49 t $CaCO_3$/1,000 t overburden. Where t is tons of material. Based on the criteria of Price and Errington (1998) which assumes any NPR value of <1 as 'likely' and 1–<2 as 'possibly' acid generating, ten samples were identified to be probable acid generators. Two were found to be 'low' (2– <4) in terms of potential acid mine drainage. Among the ten possible acid drainage producers, four samples with lowest value of NPR, suggesting that these materials could potentially generate acidity, were subjected to the kinetic test using humidity cell to complement the ABA (Méndez-Ortiz et al. 2007). After the kinetic test using weekly soaking in simulated rainwater, all samples showed decrease in the NPR values with 50 % samples having NPR <1, which indicate a 'likely' chance of materials to produce acid drainage. It may be said that after the weathering of the mine site samples, their acid drainage generation potential increased, signifying that similar activity takes place during and after the rainy season. It was observed that post-leaching both the MPA and the NP of all the four samples was reduced considerably. This provides evidence that they are potential acid generators, and also the fact that the rate of removal of the neutralizing species (NP) is occurring at a faster rate than those of the acid producing species (MPA), based on the laboratory scale rain water leaching simulation.

Humidity cell analysis

Humidity cell tests were conducted on four of the identified mine samples based on their performance in the static test and potential to generate acid drainage. Prior to humidity cell leaching, the samples had NP values of 18.1 to 26.12 t $CaCO_3$/1,000 t, MPA values of 15.31 to 25.31 t $CaCO_3$/1,000 t and NPR values of 1.02 to 1.35 (Table 3). The parameter wise results of the leaching for the period of 15 weeks are given in Table 4.

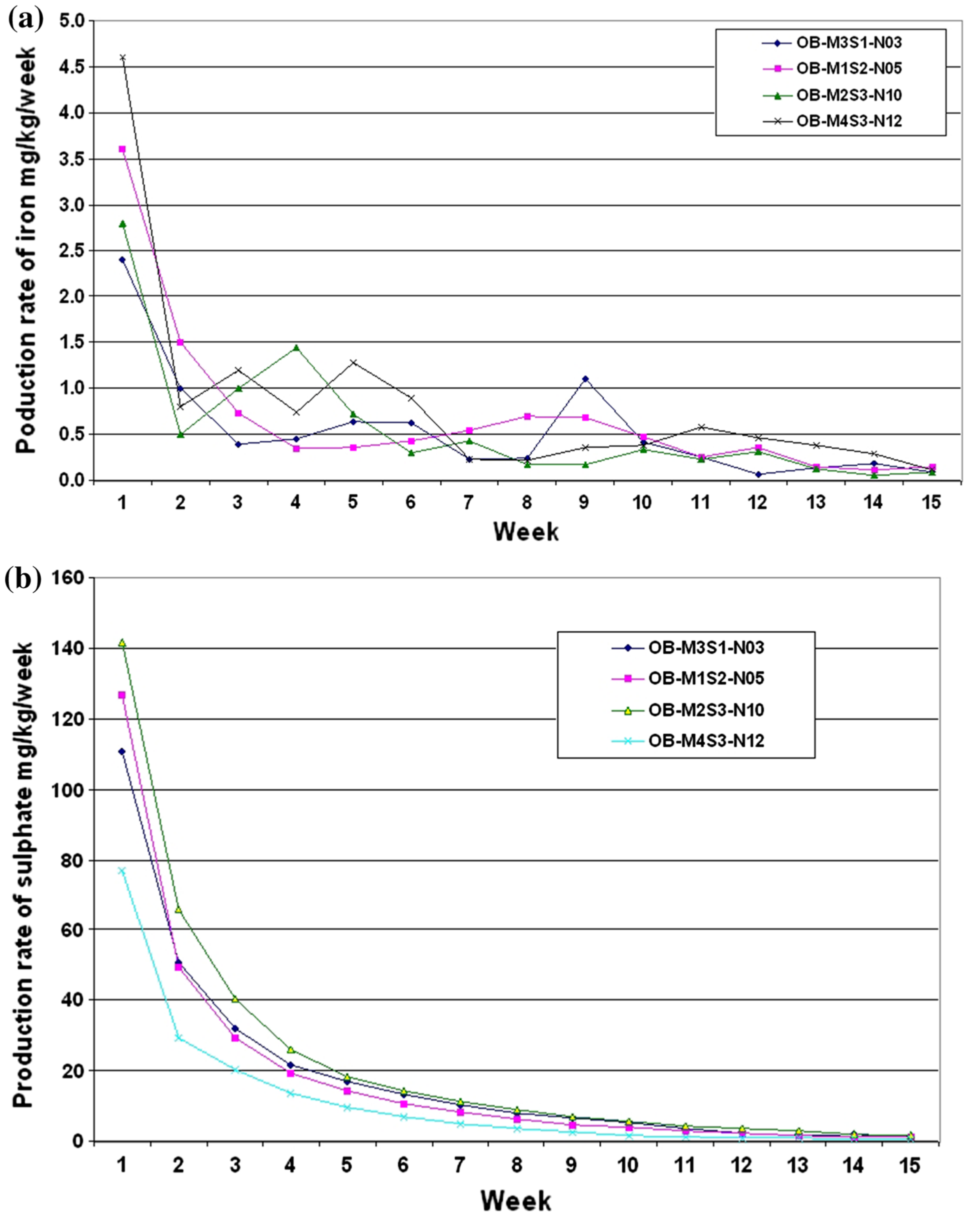

Fig. 4 **a** Production rate of iron during the humidity cell leaching. **b** Production rate of sulfate during the humidity leaching period. **c** Production rate of calcium during the humidity cell leaching period. **d** Production rate of magnesium during the humidity cell le

The pH evaluation from the leachate generated by the humidity cell over the course of the kinetic test is shown in Fig. 3. The graph represents data from 60 analysis of pH (4 samples for 15 weeks) and can be broadly divided into two categories. A total of 26 % of the pH values were in the near neutral to alkaline region (>7 up to 8) and 74 % pH values under 7 and much lower (<7 up to 3). The results show that majority of data predict acid generation during this leaching period with the lowest level being 4.22. The most alkaline leachate recorded a value of 7.89 pH. Lower acidity in the range of 2–3 was not recorded. This may not be indicative of acid mine drainage, but probably acid generation was suppressed by the high amount of neutralizing species like carbonate (Méndez-Ortiz et al. 2007). On the other hand, the presence of heavy metal (represented by Fe) indicates that acid generation has taken place, but neutralized by the presence of neutralizing species in the sample. The final pH values at the end of the humidity cell test ranged between 7.03 and 7.27.

Analysis of the first sample, OB-M3S1-N03, reveals that the sulfate content ranged between 19.9 and 110.6 with a mean value of 63.46 mg/l during the test period. The accumulative mean per week was 634.11 mg/l. The sulfate content in leachate gradually slowed down until the 11th week, with sharp decline in its production thereafter. Total sulfate accumulated for the 15 week period was 951.9 mg/l. In contrast, the acidity values fluctuated from 22.7 to 81.5 mg/l with an initial increase till the 5th week, declined

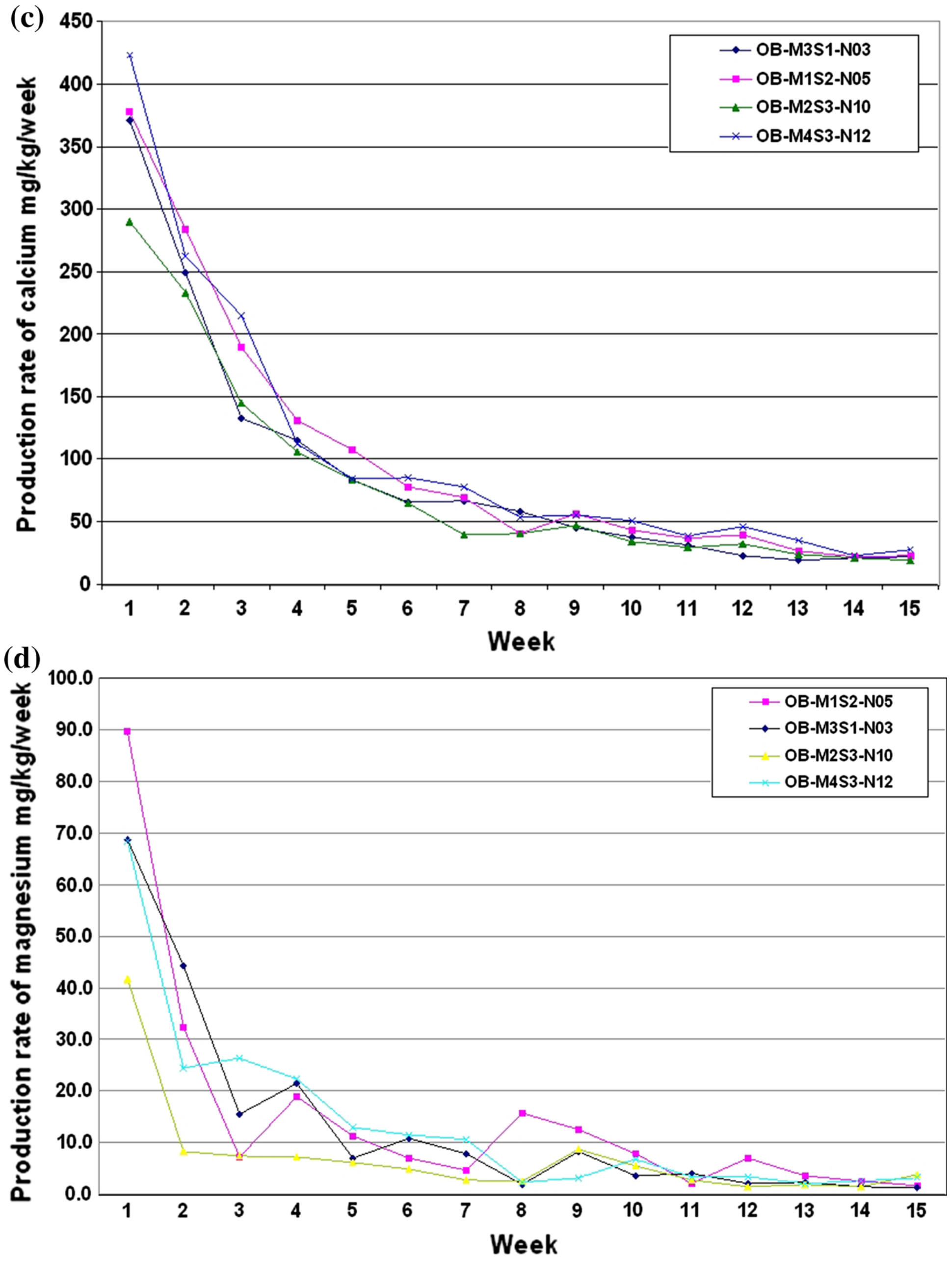

Fig. 4 continued

thereafter until the 11th week and increased modestly. The mean acidity generation was 56.88 mg/l. The total iron content, an indicator of possible acidic system, varied between 0.8 and 3.8 mg/l with a mean value of 2.77 mg/l generation per week. The average per week accumulation of the metal was 21.95 mg/l, while the total leached during the study period was 41.6 mg/l. This accumulated mass in the leached matrix is significant in terms of the standard safe limit and health perspective. This also indicates that metal mobility and availability is taking place and which is also facilitating the release of other toxic elements in the system. The calcium contest ranged between 259.8 and 498.7 mg/l, while the total accumulation for the test period was 5786.8 mg/l. The average weekly accumulation was 3297.68 mg/l. The high calcium concentration in the leached matrix provides evidence of high weathering rate and indicates that although this will provide a strong neutralizing potential presently, but will be exhausted very quickly in the near future. The magnesium concentration varied between 1.45 and 10.68 with a decline amount

Table 5 Summarized (15 week) average weekly weathering rates of samples in humidity cell

Sample ID		Average weekly weathering rate of neutralizing species (carbonate)							Average weekly weathering rate of acid producing species (sulfur)			
		$CaCO_3$ in Sample gm	Ca mg	Ca as $CaCO_3$ mg	Mg mg	Mg as $CaCO_3$ mg	Cumulative Ca +Mg as $CaCO_3$ mg	$CaCO_3$ weathered %	Sulfur content in sample gm	Rate of sulfur oxidation m	Available sulfur weathering %	Cumulative sulfur weathering %
OB-M3S1-N03	X	12.49	125.02	312.55	15.38	63.04	3358.58	2.69	2.95	6.76	0.23	2.32
	σ		28.21	70.51	8.01	32.86	1886.16	1.51		3.51	0.12	1.17
OB-M1S2-N05	X	9.10	149.53	373.84	58.59	82.11	4030.85	4.43	2.85	6.06	0.21	2.22
	σ		33.48	83.69	33.34	45.35	2285.90	2.51		3.70	0.22	1.05
OB-M2S3-N10	X	13.06	120.15	300.37	10.84	44.45	2935.27	2.25	4.05	8.14	0.20	2.04
	σ		24.90	62.25	6.17	25.28	1719.43	1.32		4.28	0.11	1.01
OB-M4S3-N12	X	10.37	156.68	391.71	17.83	73.08	4015.16	3.87	2.45	3.70	0.15	1.64
	σ		33.78	84.46	7.29	29.89	2307.23	2.22		2.50	0.10	0.75

X = mean, σ = standard deviation

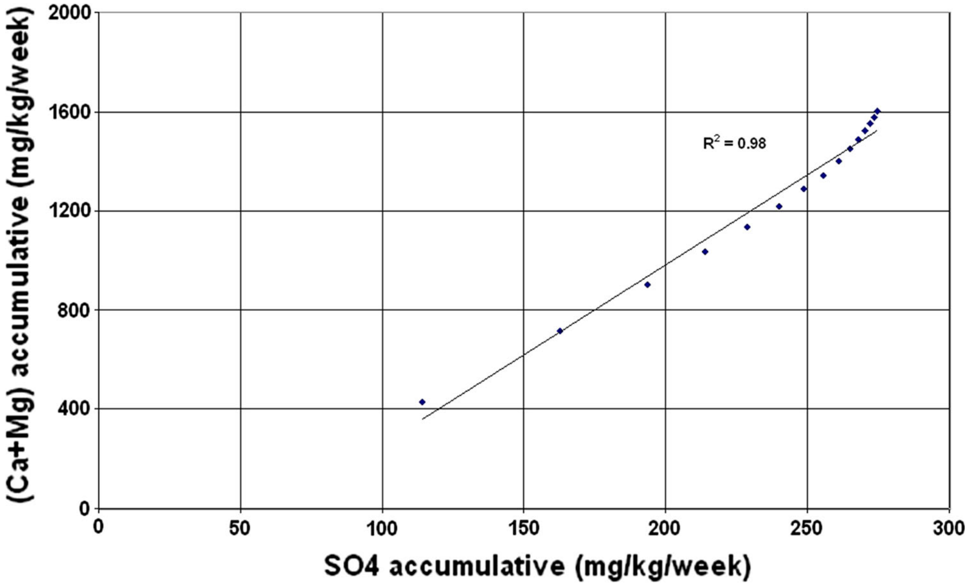

Fig. 5 Oxidative-neutralizing curve for leachate obtained from humidity cell treatment

gradually. The total accumulation was 76.04 with a weekly rate of 49.91 mg/l. For the second sample, OB-M1S2-05, pH of the generated leachate ranged between 5.1 and 7.29 and a mean of 6.40 for the study period. The pH level drops initially and then returns to the neutral drainage by the end of the kinetic test. The sulfate content ranged between 17.3 and 126.6 with a mean concentration of 55.76 mg/l. Sulfate accumulated at an average rate of 576.29 with a total accumulation of 836.4 mg/l. Acidity in the generated leachate ranged between 22.8 and 78.4 mg/l with mean acidity of 53.71 mg/l. The total iron content ranged between 1.40 and 6.2 mg/l with a mean of 3.20 mg/l. The average accumulation rate each week was 25.43 mg/l, while the total iron leached from the sample was 48.0 mg/l. The calcium contest ranged between 312.6 and 569.2 mg/l, while the total accumulation for the leaching period was 6700.4 mg/l. The accumulation rate was 3806.66 mg/l/week. The magnesium concentration varied between 2.66 and 12.67 mg/l with a total accumulation of 104.29 mg/l and an accumulation rate of 64.19 mg/l per week. In the third sample, OB-M2S3-N10, pH of leachate ranged between 4.78 and 7.45 with average of 6.42. The low level of pH of the leachate indicates acid drainage and facilitation of metal mobility and leaching out. Sulfate

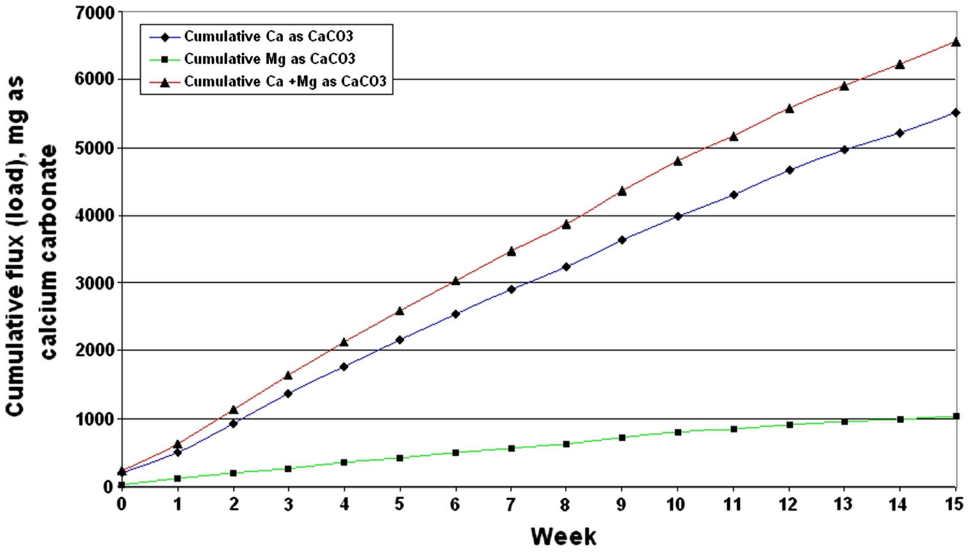

Fig. 6 Cumulative flux of calcium, magnesium and (Ca + Mg) expressed as calcium carbonate

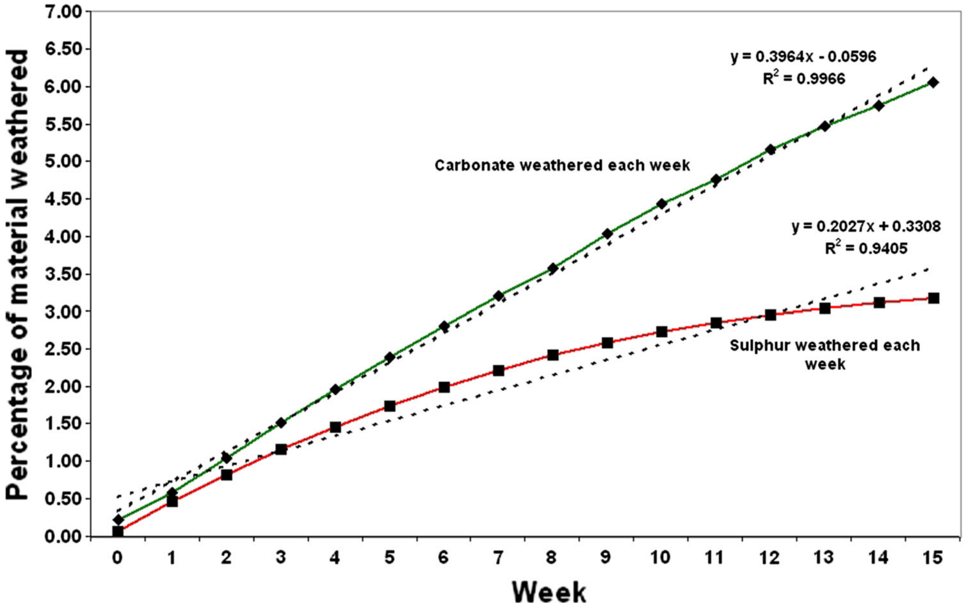

Fig. 7 Percentage of carbonate and sulfur weathered through the course of the humidity leaching cycle with simulated rain water

concentration varied between 23.7 and 141.7 with a mean of 75.03 mg/l. Sulfate accumulated at an average rate of 754.53 mg/l per week with a total accumulation of 1125.40 mg/l in the 15 week period. Acidity ranged between 23.5 and 90.8 mg/l, completing the low pH level with mean acidity of 50.70 mg/l. The iron content ranged between 0.8 and 5.8 mg/l with a mean of 2.51 mg/l. The weathering rate was 21.87 mg/l per week, while the total iron leached from the sample was 37.60 mg/l. The calcium concentration varied between 277.80 and 466.90 mg/l, while the total accumulation was 5,417.50 mg/l. The average weathering rate was 3,020.92 mg/l/per week. Magnesium concentration ranged between 1.67 and 9.78 mg/l with a total accumulation of 54.97 mg/l and a weekly weathering rate of 30.48 mg/l. In the final, OB-M4S3-N12, the pH value ranged between 4.22 and 7.89 with average of 6.70. The sulfate concentration varied between 9.3 and 76.9 with a mean of 33.77 mg/l. Sulfate weathered at an average rate of 359.96 mg/l per week with a total leached material of 506.6 mg/l in the 15 week period. Acidity ranged between 19.8 and 89.5 mg/l with a mean of 39.78 mg/l. The iron content ranged between 1.6 and 6.4 mg/l with a mean of 3.85 mg/l. The weathering rate was 30.12 mg/l per week, while the total iron leached from the sample was 57.8 mg/l. The calcium concentration varied between 329.8 and 643.9 mg/l, while the total accumulation was 7,165.3. The average weathering rate was 3,934.23 mg/l/per week. Magnesium concentration ranged between 1.87 and 11.8 mg/l with a total accumulation of 84.7 mg/l and a weekly weathering rate of 52.90 mg/l.

The production rates of the analytes (Fe^{3+}, SO_4^{2-}, Ca^{2+}, Mg^{2+}) plotted against time (week) are given in Fig. 4a–d. All the analytes showed a decreasing production rate with sharp decline during the first 3 weeks and gradual and slow till the last week. Stability was reached after the 9th week in all samples. The overall average SO_4^{2-} production for the leaching period was 18.31 ± 29.55 with a range of 1.19 and 113.95 mg/kg/week. Sample wise, the average 15 week production rate of sulfate ranged between 11.66 and 23.58 mg/kg/week. The minimum production rate ranged between 0.62 and 1.58, while the maximum rate varied between 76.90 and 141.70 mg/kg/week. There is sharp fall in the production rate within the first 4 weeks with stability reaching after the 10th week. The average Fe^{3+} production for the leaching period was 0.67 ± 0.69 with a range of 0.11 and 3.35 mg/kg/week. Sample wise, the average 15 week production rate of iron ranged between 0.55 and 0.84 mg/kg/week. The minimum production rate ranged between 0.06 and 0.12, while the maximum rate varied between 2.40 and 3.60 mg/kg/week. The average Ca^{2+} production for the kinetic test period was 94.65 ± 98.65 with a range of 22.18 and 365.28 mg/kg/week. Sample wise, the average kinetic test cycle production rate of calcium ranged between 80.82 and 106.23 mg/kg/week. The minimum production rate ranged between 19.23 and 23.56, while the maximum rate varied between 289.90 and 422.90 mg/kg/week. There is sharp fall in the production rate within the first 3 weeks with stability reaching after the 9th week. The overall average Mg^{2+} production for the leaching period was 12.26 ± 16.65 with a range of 2.01 and 67.13 mg/kg/week. Sample wise, the average 15 week production rate of magnesium ranged between 7.10 and 14.96 mg/kg/week. The minimum production rate ranged between 1.26 and 2.05, while the maximum rate varied between 41.60 and 89.60 mg/kg/week. There is sharp fall in the production rate within the first 3 weeks with stability reaching after the 9th week.

The cumulative carbonate and sulfur weathering rate data are given in Table 5. Comparison of the cumulative weathering rates shows which species will be exhausted initially and whether the material is likely to produce acid or alkalinity drainage in the near future. The Fig. 5 represents the accumulative mass of sulfates (oxidation product) in the leachate plotted against the accumulative mass of calcium and magnesium (carbonate dissolution products) in mg/kg, averaged for the four samples. This oxidation–neutralization curve demonstrates the geochemical evolution of the acidic and neutralization potentials during the kinetic tests (Blodau 2006; Méndez-Ortiz et al. 2007). The best fit linear ($R^2 = 0.98$) relation between the neutralizing and acidification agents in the system suggests that neutralizing capacity exceeds the oxidizing capacity by almost at a ratio of 2.5:1. It can be said that the neutralizing capacity of the samples from the RCF area is greater than the oxidation capacity based on the kinetic test in this study period. This is indicative of a high neutralizing capacity of the mine site materials, from where samples were taken for this study.

The cumulative fluctuation (average of 4 samples, 15 week leaching) of Ca^{2+}, Mg^{2+} and combined (Ca^{2+}, Mg^{2+}) is given in Fig. 6. It is observed that the cumulative of (Ca^{2+}, Mg^{2+}) is more dependent on the Ca^{2+} content of the samples. The magnesium content was observed to be much lowered and is unlikely to take part in the neutralization process of the acid drainage. The Fig. 7 represents the comparative weathering rates of the carbonate and sulfur through the 15 week leaching period. For the results, it can be said that the rate of carbonate weathering is much higher than that of sulfur. The study is indicative that high carbonate weathering and dissolution into the aqueous system is neutralizing the acidity, but since this carbonate weathering is occurring at high rate, the chances of its gradual exhaustion from the system is very high, leaving the oxidative materials to generate high acidic drainage in these areas.

Conclusion

The present study was aimed at assessing the potential of acid drainage of collected coal mine overburden samples from a large coalfield area in India. The samples were subjected to overburden analysis and further static test using acid base accounting. Based on the finding of the acid base accounting, samples showing high acid generation potential were subjected to the kinetic test using humidity cell. The leaching with simulated rain water was conducted for a period of 15 weeks. The result of the kinetic test was used for prediction of acid mine drainage using the data of neutralizing and oxidative capacity of the samples. Based on weathering rate and the oxidative-neutralizing curve, it can be said that the carbonate content will deplete away faster than the acid generation species, hence will result in acid mine drainage, which will be produced in the absence of the neutralizing materials in the system. In reference to Fig. 5, it can be said that the neutralizing capacity of the samples is although greater than the oxidation capacity, but due to the higher leaching and dissolution rate, they will be exhausted earlier from the system. This would be detrimental, as demonstrated in the Fig. 7, that due to this early exhaustion of carbonate species, the neutralizing capacity will tend to cease in the near future, leading to acid drainage generation from that point of time.

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