Acid Base Accounting of Overburden and Coal

A REPORT SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

**Bachelor of Technology
In
Mining Engineering**

By

NIRAJ AGARWAL
107MN031

Department of Mining Engineering
National Institute of Technology
Rourkela-769008
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Under the Guidance of
Dr. Sk. Md. Equeenuddin

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CERTIFICATE

This is to certify that the thesis entitled, "**Acid Base Accounting of Overburden and Coal**" submitted by **Mr. Niraj Agarwal** in partial fulfilment of the requirement for the award of Bachelor of Technology Degree in Mining Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any University/Institute for the award of any Degree or Diploma.

Prof. Sk. Md. Equeenuddin
Department of Mining Engineering
National Institute of Technology
Rourkela – 769008

ACKNOWLEDGEMENT

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An assemblage of this nature could never have been attempted without reference to and inspiration from the works of others whose details are mentioned in reference section. I acknowledge my indebtedness to all of them.

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Niraj Agarwal
Department of Mining engineering
National Institute of Technology
Rourkela – 769008

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ABSTRACT

Acid-Base Accounting (ABA) is an analytical procedure that provides values to help assess the acid- or alkaline-producing potential of overburden rocks prior to coal mining. This procedure was developed at West Virginia University in the late 1960s. After the passage of laws requiring an assessment of surface mining on water quality, ABA became the preferred method to predict post-mining water quality, and permitting decisions for surface mines are based on the values determined by ABA. In order to predict the post-mining water quality, the amount of acid-producing rock is compared to the amount of alkaline-producing rock, and a prediction of the water quality at the site (whether acid or alkaline) is obtained.

Samples were collected from the coalfields of Jindal Steel and Power Limited, Raigarh. Maximum potential acidity (MPA), net neutralization potential (NNP), neutralization potential (NP), and NP/MPA ratios were determined for each site based on ABA.

Neutralization potential of overburden ranges from 8.1 to 27.0 ppt while in coal it varies from 2.4 to 12.0 ppt. ABA is a good tool to evaluate overburden quality during leaching before mining and to forecast post-mining drainage quality after mining.

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CHAPTER-1

INTRODUCTION

1.1 Acid Base Accounting:

Acid-Base Accounting was established at West Virginia University by Richard M. Smith and associates in the year of 1971 (Skousen et al., 1990). The method developed from early attempts at categorizing mine spoils for revegetation potential on the basis of their potential for acidity or alkalinity.

Acid-Base Accounting (ABA) is a selection procedure whereby the acid-generating potential and acid-neutralizing potential of rock samples are determined, and the difference, net neutralizing potential, is calculated. The ratio of neutralizing potential to acid-generation potential, and/or net neutralizing potential is compared with a fixed value or set of values to split samples into categories that require, or do not require, further determinative acid potential generation test work.

Acid-Base Accounting is the balance between the acid neutralization and acid generation properties of any geologic material. Coal and overburden contains some sulphide minerals, mostly pyrite, react with water and oxygen to gives sulphuric acid. Hence, decrease the pH in the mine discharges. Acid leaches metals from coal and overburden, and introduces them into environment. Therefore, ABA is considered as a mechanism for evaluating post-mining water quality throughout the world. Its utility is enhanced when used along with other pre-mining information including previous mining, water quality, examination of and evaluation of geologic and hydrologic conditions.

The part of carbonates and silicates in consuming acid produced during oxidation of sulphides in defining the post-mining water chemistry is well established and reviewed (Sherlock et al., 1995). Carbonate minerals decides the post-mining water chemistry and neutralise acidity created by oxidation of pyrite, and inhibit pyrite oxidation (Perry and Brady, 1995). Jambor et al. (2002, 2007) have performed static tests in order to measure the NP of various carbonates and aluminosilicate minerals and various rock types. The carbonate minerals or calcite and dolomite

have maximum acid consuming potential due to their relatively high reactivity. Silicate minerals such as amphibole, feldspar, pyroxene, mica, chlorite and clay show insufficient NP whereas olivine, serpentine and wollastonite have relatively higher NP value. NP generated from the weathering of $FeCO_3$, siderite is zero (Skousen et al., 1997). Therefore, distribution, amounts and types of minerals, particularly, occurrence of carbonates and sulphides, at any mine sites defines the potential for post-mining environmental problems.

1.2 Some Acid Producing Reaction:

Pyrite

FeS_2 (s) + (7/2) O_2 (g) + H_2O = Fe^{2+} (aq) + 2 H+ (aq) + 2 SO_4^{2-}(aq)

Pyrrhotite
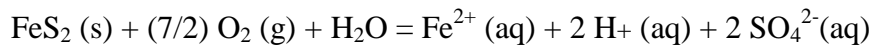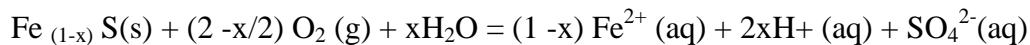
$Fe_{(1-x)}$ S(s) + (2 -x/2) O_2 (g) + xH_2O = (1 -x) Fe^{2+} (aq) + 2xH+ (aq) + SO_4^{2-}(aq)
Where x ranges between 0.000 and 0.125.

1.3 Some Acid-Generating Sulphides:

1. Pyrite (FeS_2)
2. Pyrrhotite ($Fe_{1-x}S$)
3. Enargite (Cu_3AsS_4)
4. Marcasite (FeS_2)
5. Arsenopyrite (FeAsS)
6. Tennantite ($Cu_{12}As_4S_{13}$)
7. Orpiment (AsS)

1.4 Alkali Minerals

1. Carbonates: - Calcite ($CaCO_3$), Dolomite ($Ca,Mg(CO_3)_2$)
2. Hydroxides: - $Fe(OH)_3$, $Al(OH)_3$
3. Silicates
4. Clays

1.5 Acid Neutralization Reactions

$CaCO_3(s) + H+(aq) = HCO^{3-}(aq) + Ca^{2+}(aq)$ (above pH 6.4)

$CaCO_3(s) + 2H+ (aq) = H_2CO_3(aq) + Ca^{2+}(aq)$ (below pH 6.4)

            Or

$CaCO_3(s) + H_2SO_4 = CaSO_4(s) + CO_2(g) + H_2O$
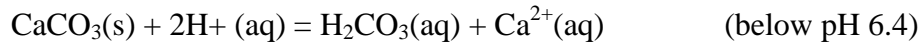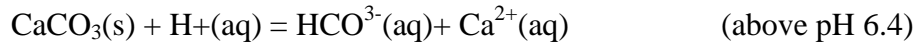
Other mineral dissolution reactions (chlorite, biotite, other silicates) produce less neutralization and have lower solubility at moderate pH.

1.6 Effect of siderite

$FeCO^{3+} + H_2SO_4 = Fe^{2+} + H_2CO_3 + SO_4^{2-}$

        And

$4Fe^{2+} + O_2 + 4H+ (aq) = 4Fe_{3+} + 2 H_2O$

        But

$FeS_2(s) + 14 Fe^{3+} + 8 H_2O = 15 Fe^{2+} + 2 SO_4^{2-} + 16 H+ (aq)$

CHAPTER-2

LITERATURE REVIEW

2.1 Principles of Acid-Base Accounting:

ABA was established and used in Pennsylvania, comprises of computing the acid generating and acid neutralizing potentials of different rock sample. Values of Maximum Potential Acidity (MPA) and Neutralization Potential (NP) are subtracted to attain a Net Neutralization Potential (N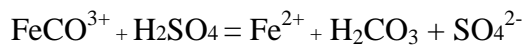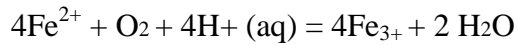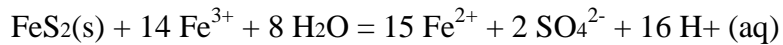NP), or net Acid-Base balance for the rock. The results are typically reported in tons per thousand tons of overburden or parts per thousand (ppt). The units designation imitates the agronomic origins of ABA.

The constituents of ABA measurements are occasionally stated to by other terms, as they have been attuned for use in metal mining and other uses (Miller and Murray, 1988). The term "Acid Production Potential" (APP) is equivalent to MPA, "Net Acid Producing Potential" or NAPP is the same as NNP and Acid Neutralizing Capacity" (ANC) is equivalent to NP.

2.2 Neutralization Potential:

The neutralization potential (NP) is evaluated by digesting a part of the prepared sample in hot acid, and then titrating with a base to determine how much of the acid the sample digested. NP denotes carbonates and other acid neutralizers and usually expressed in relations of tons $CaCO_3$ per 1000 tons of overburden (Kania et al., 1998).

2.3 Maximum Potential Acidity (MPA):

Extreme potential acidity is based on a measure of sulphur content of the rock. The presupposition is that this accurately signifies the amount of acid generating sulphur minerals. Sulphur in overburden occurs in sulphate, sulphide, or organically bound forms. Metal sulphides, mainly pyrite, are the principal source of acid generation and the dominant sulphur form in Appalachian overburden (Smith, et al., 1976). Acid-base accounting stoichiometry adopts that the sulphur is all present as pyrite, and complete oxidation and acid generation occurs.

2.4 Acid and Neutralization Potential:

The intention of these tests is to produce an APP value (Acid Production Potential) and/or an NP value (Neutralization Potential).

Net Neutralization Potential: NNP = NP -APP

         And

Neutralization Potential Ratio: NPR = NP/APP

The unit of measurement is kg $CaCO_3$ per ton, or equivalently parts per thousand $CaCO_3$.

2.5 Paste pH:

A share of the prepared sample is mixed with deionised water, and then tested with a pH probe after one hour (Sobek et al., 1978; Noll et al., 1988). Coal and Overburdens with paste pH less than 4 are generally classified as acid producing whereas paste pH > 6 indicates non-acid forming.

2.6 Study Area

Acid base accounting study was carried out at Jindal Power Limited, Raigarh which is situated in Chhattisgarh.

2.6.1 Geomining Condition in JSPL

In general, area of the coal block - Jindal Steel and Power Limited Open Cast Coal Mine is almost flat with small undulations from surface. The lithological section comprises about 3-4 m unconsolidated loose soil/alluvium. Below the top soil there is weathered shale/sandstone up to 6–8 m depth. The weathered shale/sandstone is comparatively loose in nature and can be excavated without blasting. Below weathered zone (which varies from 3 – 10 m), the rock is hard, compact and massive in nature and can be excavated only after blasting. Thus the average depth of the excavation of these excavations, which can be removed, is about 16 m.

The Mand Raigarh basin is a part of IB River - Mand - Korba master basin lying within the Mahanadi graben. The sub-block IV/2 & IV/3 of Gare-Pelma area is structurally undisturbed except one small fault (throw 0-15 m) trending NE-SW with westerly throws. The strike of the bed is NW-SE in general with dip varies from 2° to 6° southwesterly. The strata shows rolling dip. In the sub block IV/2 & IV/3 total 10 number of persistent coal seams have been established. They are seam X to I in descending order. Seam I is im-persistent due to metamorphism in the central and eastern part of the block. The lithology of the seams is given in Table 1.

Table 1: Lithology of the seams

Seam No/ Parting	Thickness range(m)	Lithology
X&XA	2-3	Coal,Shaly coal & carbonaceous shale
Parting	38-52	Fine to coarse grain sandstone with shale and shaly coal band.
IX	4-4.5	Parting
Parting	4-6	Fine to medium sandstone with shale band
VIII	4-4.5	Coal,Shaly coal & carbonaceous shale band
Parting	6-9	Fine to medium sandstone with shale band
VII	5-5.5	Coal, Shaly coal & carbonaceous shale with grey shale band

The Mand Raigarh Coal Field of Raigarh district, Chhattisgarh forming a part of Son Mahanadi master basin, is situated between IB- Himgir Coal field in the south east and Korba Area (SECL) in the North West, in between these coal fields, a large part of intervening terrain is covered by Kampthi sediments. The Mand- Raigarh coal field extending over an area of more than 900 sq. km. is bounded between latitude 21°45' and 22°42' north and between longitude 83°01' and 83°44' east. Collectively these basins form a broad asymmetrical syncline on an approximately NW-SE axis passing through Hati, Kida, Bhalmori, Taraimal etc. Within the main syncline,

several sub units are well defined. In the Mand valley proper, the coal measure lying between Kharsia and Dharamjaigarh display a broad synclinal structure with its axis running just south of Sithra. The northern limb of the 11 land river basin is exposed to the north in the Sithra — Dharamjaigarh where the Barakar beds are found to strike broadly in a NW- SE direction from the Talchir contact. In the southern limb the strike is approximately NW-SE with minor variations and the beds dip towards North West. The other structural elements in this basin comprise normal gravity faults. The stratigraphic succession is given in the Table 2.

Table 2: Stratigraphic succession of the Raigarh Coalfield

Formation	Lithology
Kamthi	Coarse to medium grained cross-banded sandstone, frequent Ferruginous, red siltstone and shale.
Ranigan	Fine to medium grained sandstone, sandy shale, carbonaceousus shale and mirror coal seams.
Barren Measures	Grey shale, sandy shale, fine grained sandstone with ripple marks and their alternation with ferruginous bands.
Barakar	Alternate units of fine grained sandstone and shale carbonaceous shale and coal seams. Medium to coarse frequently very coarse grained arkosic-sandstone, carbonaceous shale and coal seams.
Karharbari	Mottled micaceous sandstone frequently associated with angular pebbles of quartzite, granites etc.
Talchir	Mostly fine rained sandstone, khaki green to cement grey shale and sillstone diamictite.
~~Non conformity~~~~~~~~~~~~~~~~~~~~~~~~~	
Metamorphics	Granite, gneisses, schists and quartzite.

2.8 Percentage of Pyritic Sulphur:

Add 45 ml of distilled water with 5 ml of concentrated nitric acid to each flask. Vacate the flask on the steam bath for 90 min. Vacuum screens the blend in each flask through a 25 mm filter. Wash the residue with distilled water and discard the residue. Calculate the iron leached from the sample by the nitric acid using flame atomic absorption spectrometry at the following conditions: 248.3 nm, 0.2-nm slit width, hollow cathode lamp, and an air-acetylene flame (oxidizing lean, blue).

Calculate the percentage of pyrite sulphur as follow:

$FeS_2 = Fe^{2+} + S_2 = (2 \times S) = \dfrac{64.128}{55.847} = 1.148$ $\qquad$ Atomic Weight of S = 32.064 amu

$\qquad\qquad\qquad\qquad\qquad$ Fe

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ Atomic Weight of Fe = 55.847 amu

Weight of Sample taken = 0.500gm

Percentage of Fe as pyrite in sample = ppm Fe x $\dfrac{0.0001}{0.500}$ = ppm Fe x 0.0002

Dilution Factor = 200

Percentage of pyritic Sulphur = ppm Fe x 0.0002 x 200 x 1.148 = ppm Fe x 0.0459

CHAPTER-3

METHODOLOGY

3.1 SAMPLE COLLECTION

Overburden and coal samples were collected from the coalfields of Jindal Steel and Power Limited (JSPL), Raigarh, Chhatisgarh as shown in figure 1.

Figure 1 A view of sample collection from JSPL

3.2 SAMPLE PREPARATION

- Samples were crushed into powder form and were sieve through the sieve of mesh size 200 mm and 230 mm.
- The powder samples were collected in a container.
- 230 mm mesh size sample is used for X-Ray Diffraction Test to know about the mineralogy of the sample with help of X-Ray Diffractometer.
- 200 mm mesh size sample is used for Acid Base Accounting test.

3.3 X-RAY Diffraction Analysis:

X-Ray powder Diffraction investigation is an influential method by which X-Rays of a known wavelength are distributed through a sample to be acknowledged in order to identify the crystal structure. Wave nature of the X-Rays means diffraction by the lattice of the crystal to give a exclusive pattern of peaks of 'reflections' at differing angles and of different strength, just as light can be diffracted by a grating of suitably spaced lines. The diffracted beams from atoms in sequential planes cancel unless they are in stage, and the condition for this is given by the BRAGG relationship.

$$n\lambda = 2\ d \operatorname{Sin} \theta \text{ (Bragg's Equation)}$$

λ = wavelength of the X-Rays

d = distance between different plane of atoms in the crystal lattice.

θ = angle of diffraction.

X-Ray detector travels around the sample and measures the strength of these peaks and the position of these peaks [diffraction angle 2θ]. The uppermost peak is well-defined as the 100% x peak and the strength of all the other peaks are measured as a percentage of the 100% peak.

3.4 Acid Babe Accounting

Acid Base Accounting Test was carried out using Sobek Method (Sobek et al., 1978).

3.4.1 Sobek method (Standard ABA method): The earliest and still much-used method guesses the acid potential based on the sulphur content each mole of sulphur produces two moles of acid neutralized by one mole of calcium carbonate

Assumption:

- oxidation of pyrite by oxygen
- The mole ratio of sulphur to calcium carbonate is therefore 1:1.

The weight ratio is then:

100 g $CaCO_3$/mole $CaCO_3$: 32g S / mole S

or

31.25 % $CaCO_3$ per % S (‰is same as kg/ton) in standard AP units

3.4.2 Neutralization Potential by reaction with acid and back-titrating:

- The NP in the Sobek test is determined by treating the sample with HCl, and back-titrating with NaOH.
- The strength and amount of HCl to use is assessed with a "fizz test."
- Introduces a large vagueness in the final NP calculated.
- With a stronger amount of initial acid, the solution reacts at a lower pH and involves phases that would not react at the more realistic pH of the real situation.
- Therefore, the simple Sobek test tends to misjudge the NP of a material, and this affects the AP/NP ratio. The presence of siderite (iron carbonate) can significantly affect the laboratory determination of NP.

3.4.3 Fizz Rating:

- The significance of the fizz rating on ABA results is much underrated. The fizz rating can be used to check the NP determination (Kania et. al. , 1998)

- The fizz test is executed by toting one to two drops of 25% HCl to a small amount of the prepared sample (Sobek et al., 1978). The degree of reaction is watched and recorded, according to a four-tiered system where the reaction is judged to be none or 0, slight or 1, moderate or 2, strong or 3.

CHAPTER-4

RESULTS AND DISCUSSION

Some minerals have expected tendency to generate acidity upon chemical weathering while some consume the acidity. Therefore, it is essential to characterize the overburden and coal in terms of their mineral assemblages which mainly controls their acid drainage potential (Perry, 1985; Sobek et al., 2000; Skousen et al., 2002). Further, acid base accounting study also plays a decisive role in the decision-making during environmental assessment, mine plan, waste management and closure of any mine where either the ore or the host rock or both contain high amounts of sulphide minerals. The evaluation of acid drainage potential is one of the major steps in the management of sulphide rich subsurface materials (Jambor et al., 2003).

4.1 Mineralogy of Overburden:

The overburdens are mainly composed of quartz, kaolinite, calcite, dolomite, siderite, pyrite, and muscovite. Quartz and kaolinite are major mineral phases whereas other occurs as minor to trace quantity. The X-ray diffractograms of the overburden are shown in Figure 2 and 3. The dominant peaks at 4.28 and 3.35 Å in all the samples are assigned to quartz along with its other lower order peaks. In some samples prominent peak at 3.2-3.18 Å is assigned to plagioclase; whereas intermediate to small peaks in most of the samples at 2.77-2.8 Å and 1.72Å are identified as siderite. Most of the samples showed small peaks of dolomite at 2.88-2.90 Å. The overburden from seam IX colliery is rich in kaolinite. A very small peak at 2.68 Å is assigned to calcite. In a few samples from seam X prominent peaks observed at 1.64 and 2.72 Å have been attributed to pyrite along with lower order peaks at 2.43, 2.22, 1.92 and 3.14 Å. Intermediate peaks at 7.18, 4.48 and 3.58 Å in all the samples are assigned to kaolinite. Pyrite present in the shale as shown in figure 4. Some of the overburden materials show a prominent but less intense peak of Muscovite at 9.9Å**.**
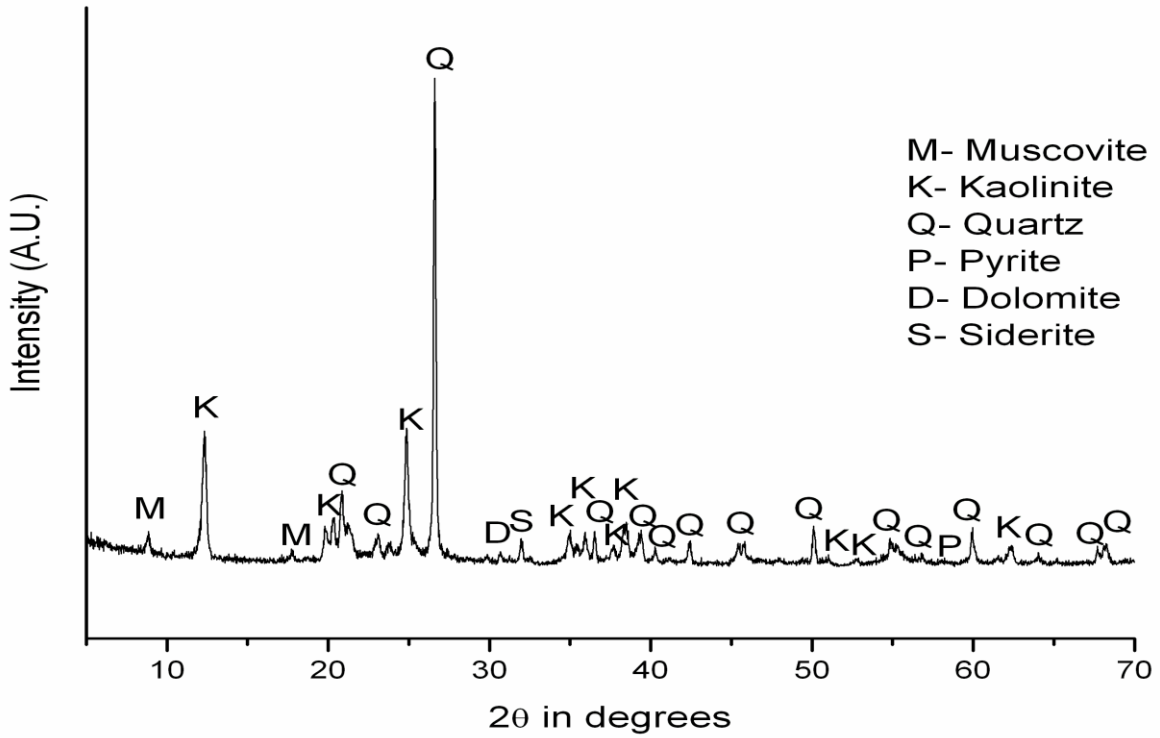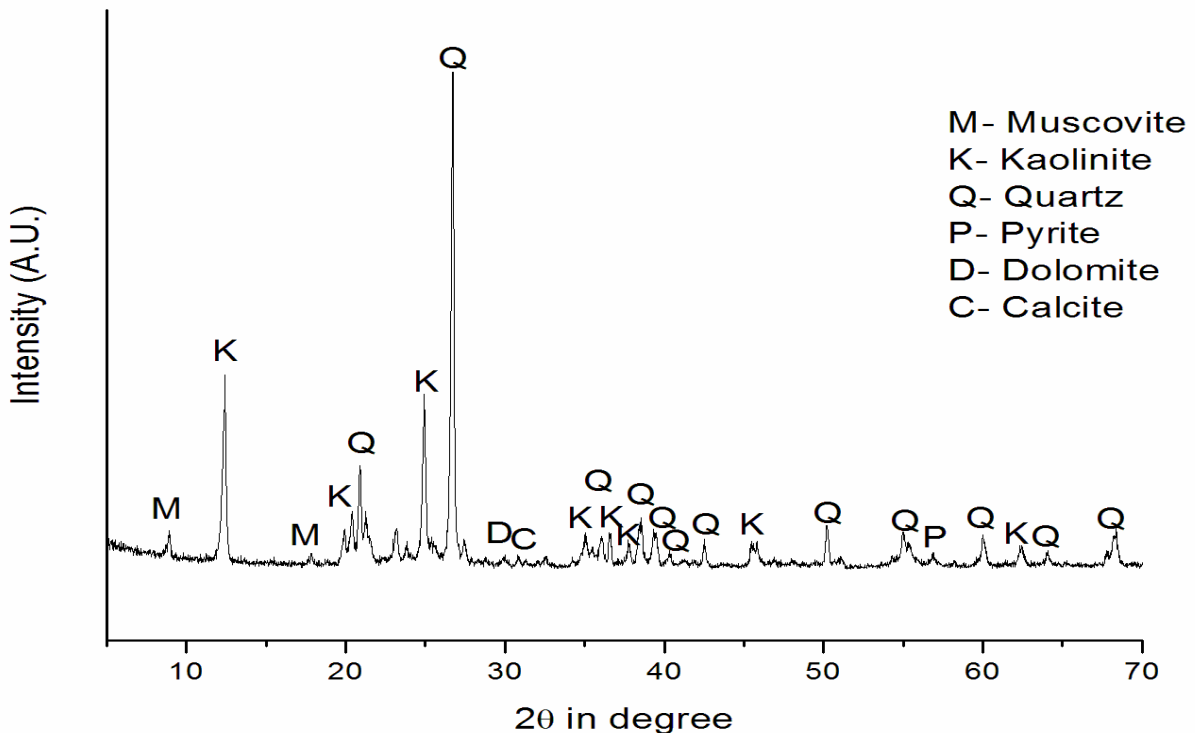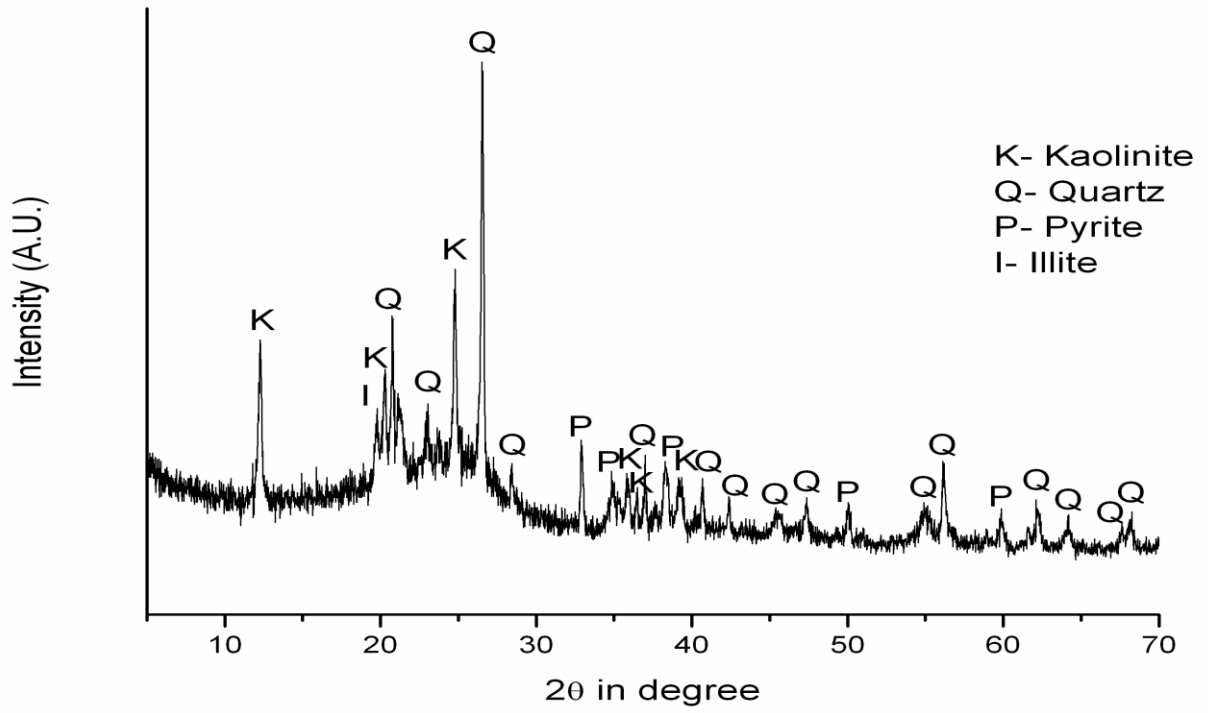
Figure 2 X-Ray Diffractograms of Overburden-1

Figure 3 X-Ray Diffractograms of Overburden-2

Figure 4 Present of Pyrite in Shale

4.2 Mineralogy of Coal:

Quartz, kaolinite and pyrite were identified as major mineral phases in the X-ray diffractograms of most coal samples. The X-ray diffractograms of the coal is shown in Figure 5. The dominant peaks at 4.28 and 3.36 Å in all the samples are assigned to quartz along with its other lower order peaks. In some samples prominent peak at 4.50 Å is assigned to illite. Most of the samples showed small peaks of kaolinite at 7.21 Å but a few showed the highest intensity peak at the same position along with other lower order ones at 4.39, 3.51, 2.50, 2.46, and 2.30 Å. The coal from seam IX is rich in pyrite. A very small peak at 3.04 Å is assigned to calcite. In a few samples, prominent peaks observed at 1.64 and 2.72 Å have been attributed to pyrite along with lower order peaks at 2.43, 2.22, 1.92 and 3.14 Å. Pyrite present in coal as shown in figure 6.

Figure 5 X-Ray Diffractograms of Coal Sample

Figure 6 Pyrite present in Coal

4.3 Acid Base Accounting Results:

Acid Base Accounting results of overburden and coal are given in Table 3. Neutralization potential of overburden ranges from 8.1 to 27.0 ppt while in coal it varies from -2.4 to 12.0 ppt. Very low NP is possibly due to absence of carbonate minerals like calcite and dolomite, more abundance of quartz, and kaolinite. The negative value of NP is due to the presence of higher quality of pyrite. Acid production potential of overburden varies from 0.18 to 3.75 ppt where as in coal it varies from 5.3 to 19.7 ppt. Therefore it indicates that coal has more potential to generate acid in comparison to the overburden.

Table 3: Various Results of the Acid Base Accounting of Overburden and Coal

| Sample	Type	Paste pH	NP(ppt)	Pyritic Sulphur	APP(ppt)	NNP(ppt)	NPR
R-1	Sandstone	5.80	16.00	0.032	1.00	15.00	16.00
R-2	Sandy Shale	5.20	27.00	0.043	1.34	25.66	20.14
R-3	Coaly Shale	3.10	8.10	0.120	3.75	4.35	2.16
R-4	Sandstone	5.50	21.00	0.057	1.78	19.22	11.79
R-5	Coal	1.90	-2.40	0.630	19.68	-22.08	-0.121
R-6	Coal	4.70	12.00	0.170	5.30	6.70	2.26
R-7	Coal	4.50	10.00	0.22	6.87	3.13	1.45
R-8	Alternative Sandstone Shale	7.40	18.00	0.006	0.180	17.82	100
R-9	Shale	6.90	23.00	0.070	2.180	20.82	10.55

Table 4: Criteria for the characterization of post mining water quality

| Water Quality	NNP (ppt)	NP/MPA	Study Source
Net Acid	<0	<1	(Brady et al.,1994; Perry and Brady, 1995)
Either acid, neutral or alkaline	0 to 12	1 to 2	(Brady et al.,1994; Perry and Brady, 1995)
Net Alkaline	>12	>2	(Brady et al.,1994; Perry and Brady, 1995)

NNP and NPR depict the post-mining discharge quality more accurately than both NP and APP (Skousen et al., 2002). Hence, both NNP and NPR have been used as criteria for evaluating mine discharge quality (Table 4). It is deduced that, the coal has acid generating potential while most overburden can generate either acidic or alkaline discharges since their NNP ranged between 0 and 12 ppt.

Based on NPR value, most overburden are found to generate net alkalinity, whereas coal (R-5) which is enriched with pyrite and therefore give negative NPR and more acid generating in nature.

The relationship between paste pH, NNP and NPR are shown in Figure 7 and 8. The NPR has good relationship with paste pH because overburden with paste pH > 6 also have NPR > 2 indicating them nearly non-acid generating. Therefore, NPR is considered to provide better information than NNP about the post-mining discharge quality (Skousen et al., 2002).
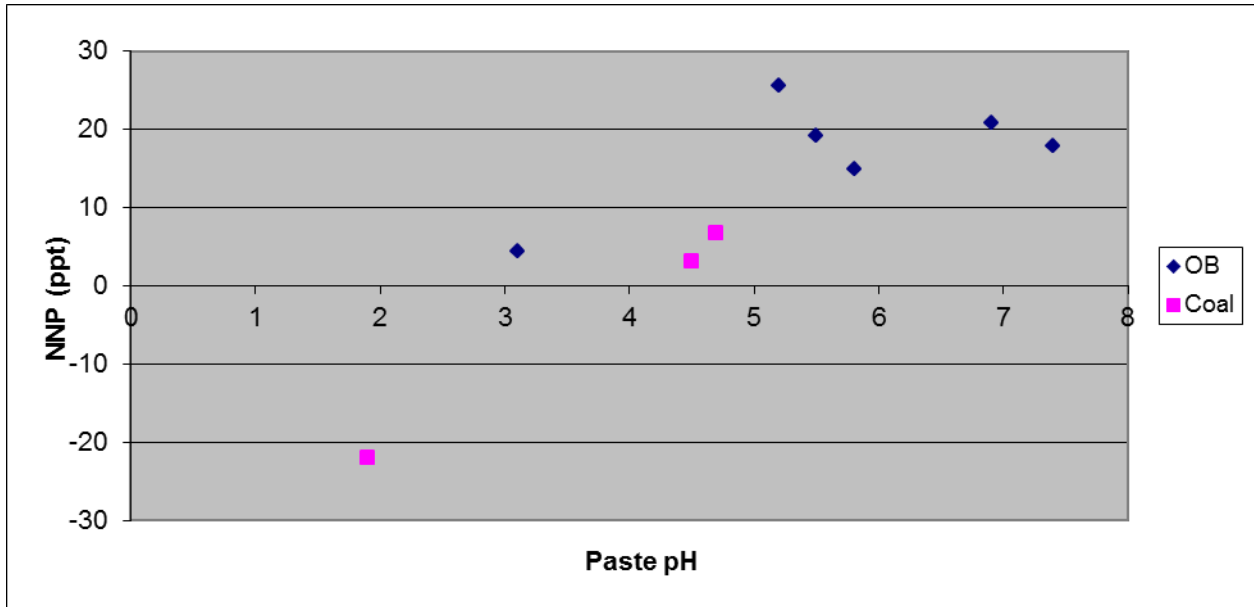
Figure7 Relationship between Paste pH and Net Neutralization Potential of Coal and Overburden
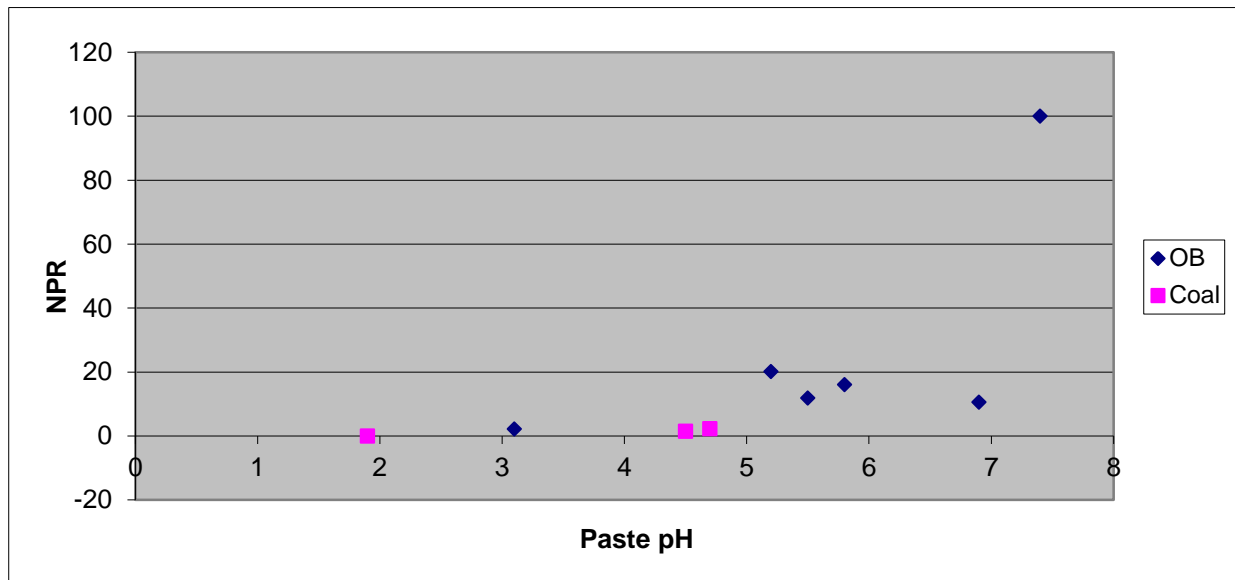
Figure 8 Relationship between Paste pH and Net Potential Ratio of Coal and Overburden

CHAPTER-5

CONCLUSION AND RECOMMENDATION

Conclusion

1. Quartz and kaolinite are the dominant mineral phases in both coal and overburden while pyrite occurs as traces. However, in few coal pyrites also occur as major phases.
2. Acid base accounting result indicates that some overburdens have potential to release alkaline discharge whereas some overburden and coal have categorized as uncertain i.e. can produce either acid or alkaline upon leaching. However only few coal samples has the capacity to generate acidic discharge.

Recommendation

1. Acid base accounting study must be carried with more number of samples
2. Direct mine discharges water quality should be incorporated
3. Acid base accounting study can be done through Kinetic methods.

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