

# CHAPTER 1

## Introduction and Literature Review

### 1.1 Introduction

Coal is one of the major energy resources, contributing nearly 40% of the electricity production throughout the world. Current estimates are 926 billion tones of total proved coal reserve in the world (Energy Information Administration, 2009). Presently, total coal consumption has reached around 7 billion tones (World Coal Institute, 2010); expectedly much of this expansion will occur in China and India. Because coal is abundant and relatively cheap, there will be increasing utilization over the next 25–50 years and hence mining.

The contribution of coal as the primary source of energy is much higher in India than that of the world (Figure 1.1). At present the total proved coal reserve in India is nearly 109 billion tones (CMPDI, 2010). According to Coal India Vision-2025, production of coal is expected to grow from 411 million tones (Mt) in 2007–08 to 1267 Mt in 2024–25. Due to rapid increase in coal production, generation of huge amounts of mine waste will lead to various environmental consequences.

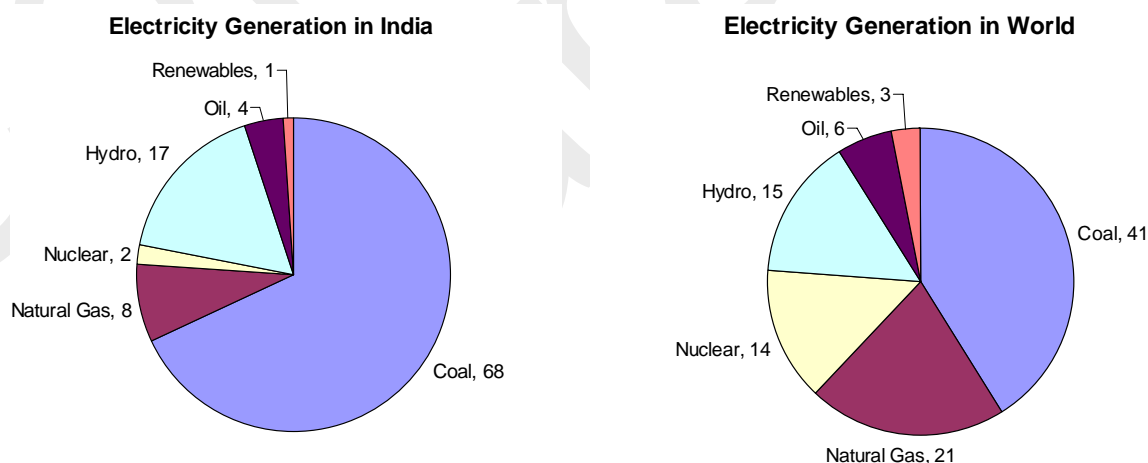


Figure 1.1: Electricity generation in India as compared to the World (as of 2007)

Source: International Energy Agency (2009); <http://www.iea.org/stats/index.asp>

India has nearly 50 coalfields ranging in area from a few square kilometers to more than 1500 km<sup>2</sup> (Tiwary, 2001). All these coalfields belong to the Gondwana and Tertiary ages, and most of them are non-coking with high ash and low calorific value whereas only 15% are of coking quality. The majority (90%) of Indian coals is sub-bituminous to bituminous and is found in the central and eastern parts of the country. These coals were deposited under freshwater conditions during Gondwana age while the Tertiary coals deposited under marine environment are mostly lignite to sub-bituminous in variety and are scattered in their occurrences.

A number of adverse environmental effects arise out of coal mining, *viz.* generation of mine waste, dust, land subsidence, deforestation, spontaneous combustion of coal, etc. Sulphide rich overburden produces acid mine drainage (AMD) which contaminates surface and groundwater, soil and sediment leading to various adverse consequences. AMD problem is even more severe in the case of coals of marine origin (Caruccio and Ferm, 1974; Campbell et al., 2001). The extent of environmental problems due to coal mining depends on many factors, *viz.* mining process, coal quality, characteristics of intervening strata, topography of the area and climate, etc.

Among all the above problems associated with coal mining, AMD is one of the serious issues caused due to the presence of high concentrations of sulphide minerals, *viz.* pyrite, pyrrhotite and marcasite in coal and/or overburden. Improper mining practices and excavation exposes sulphide minerals to atmospheric oxygen and water leading to the generation of very low pH mine discharge. Due to its acidic nature, this discharge can get highly enriched with metals, well beyond their allowable limits, resulting in water and soil pollution and subsequent health hazards in the surrounding and downstream areas. In some instances, the mine discharge is also neutral to alkaline containing low concentrations of metals (Younger, 1995). This variation in pH is mainly controlled by the minerals in coal and coal bearing strata which consume the acid generated subsequent to oxidation of sulphides (Perry and Brady, 1995; Sherlock et al., 1995).

Subsequent dilution and/or interactions with various minerals, particularly carbonates increase the pH of AMD leading to deposition of a wide range of minerals along the steam bed in form of ochre — orange-red-yellow precipitates of hydrated Fe-oxide (Alpers et al., 1994). The ochre thus precipitated from the acid mine water plays a

vital role in controlling the mobility of metals through scavenging and/or releasing elements under varying physicochemical conditions (Chapman et al., 1983; Cornell and Schwertmann, 1996).

The concentrations of various elements in both coal and coal measure rocks and their leaching behavior are critical to understand the impact by AMD. The sulphides in coal host many metals; therefore, their modes of occurrences provide insight into the post-oxidation leaching behavior besides the basic information on the likely environmental impact during and after mining (Liu et al., 2007).

Most of the northeastern Tertiary coalfields discharge acid mine water whereas Gondwana coalfields are mostly free of AMD (Tiwary and Dhar, 1994; Tiwary, 2001). Therefore, this study attempts to understand the control of mineralogy of coal and coal measure rocks in AMD generation, the resultant impact on water, soil and sediment, and metal mobility in the surrounding area of Makum coalfield (MCF), the largest Tertiary coal deposit in Assam, India.

## 1.2 Study Area

Makum coalfield situated along the outermost flank of the Patkai range covers approximately 150 km<sup>2</sup> on Survey of India toposheet No. 83M/11 and 83M/15 bound by longitude 95° 40'E–96° 5'E and latitude 27° 15'N–27° 25'N. The coalfield has two open cast (Tikak and Tirap) and three underground (Baragolai, Ledo and Tipong) collieries (Figure 1.2). The southern and southeastern sides of the colliery are flanked by hills rising to 300–500 m above the floodplains of the Burhi Dihing and Tirap rivers.

Mining in this coalfield began in 1882 by the Assam Railways & Trading Company at Ledo. As of April 2008, reserve of 315.91 million tonnes of coal up to a depth of 600 m was estimated by the Geological Survey of India ([http://www.portal.gsi.gov.in/gsiDoc/pub/Coal\\_INV\\_2008.pdf](http://www.portal.gsi.gov.in/gsiDoc/pub/Coal_INV_2008.pdf)). Assam contributes nearly 40% of the total coal production from northeastern part of India, of which MCF alone contributes approximately 84%.

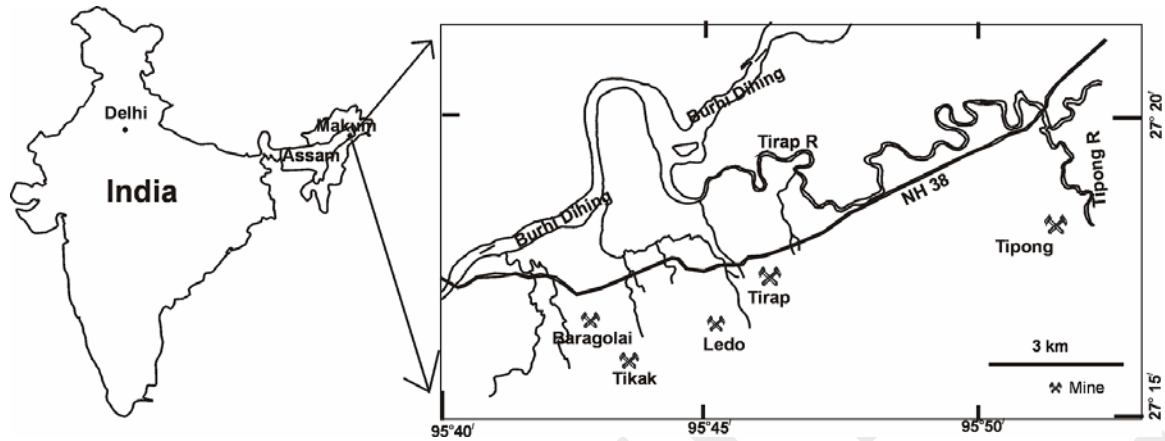


Figure 1.2: Location map of the study area

### 1.2.1 Physiography

The Burhi Dihing, Tirap and Tipong rivers constitute the main drainage system in the study area (Figure 1.2). A number of perennial streams, *viz.* Namdang, Ledopani and Lekhapani, originate at the outer hill ranges in the south and dissect the coalfield before joining the Burhi Dihing river. The northern part of the area is dominated by agricultural land with scattered settlements while the southern part is covered mostly by dense mixed forest. There are a number of tea gardens around the coalfield *viz.* Ledo, Namdang and Powai.

### 1.2.2 Climate

The area experiences humid summer during May-June with maximum temperature around 36 °C and a fairly cold winter during December-January with minimum temperature falling to 4 °C. The area experiences very high precipitation from 300 to 425 cm annually; the bulk occurring from April to September. The average relative humidity range is 87–91% during the wet months.

### 1.3 Geological Setting

Makum coalfield is situated along an active mobile belt and has experienced intense tectonic disturbances resulting in a series of imbricate overthrust known as the

belt of Schuppen. The coalfield is bounded northerly by the regional Margherita and southerly by Haflong Disang thrusts. The thrusting was accompanied by folding and interlocked slicing of Tertiary strata (Mishra and Ghosh, 1996; Ahmed, 1996).

The coalfield belongs to the Assam-Arakan basin and consists of five workable seams, out of which two are 18 m and 6 m thick persisting across the coalfield whereas others are random in occurrence. All the coal seams occur in the Oligocene Tikak Parbat Formation (uppermost member of the Barail Group) comprising of alternating sandstone, siltstone, mudstone and carbonaceous shale underlain by the Borgolai and Naogaon Formations.

#### **1.4 Characteristics of Makum Coal and its Depositional Environment**

The Makum coals are sub-bituminous and contain high sulphur (2–7%), volatile matter (30–50%) with strong (18–30) caking index (for coking coals) and high calorific value (6500–8000 kcal/kg). The ash content is usually low (3–15%) and mostly less than 5% while moisture content is low to medium, rarely exceeding 5% (Mukherjee and Borthakur, 2003a; Chandra et al., 1984).

Sulphur in these coals occurs in both organic and inorganic forms. While the majority of inorganic sulphur occurs in very finely disseminated sulphides, usually pyrite; these coals are also rich (75–90%) in organic sulphur (Chandra et al., 1980). Total as well as both pyritic and organic sulphur increases from the floor to the roof in a particular seam while upper seams reportedly contain more sulphur than the lower ones. The lithologic characteristics of these formations are summarized in Table 1.1.

The Tertiary sedimentation in this belt commenced in an external trough near the platform corresponding to a miogeosynclinal belt. Along this belt, rapid subsidence and detrital supply resulted in a >2000–6000 m thick pile of Tertiary sediments. During Barail (Oligocene) sedimentation intermittent phases of emergence allowed development of widespread coal facies (Mishra, 1992). The coal bearing sediments of Oligocene Tikak Parbat Formation are preceded by marine and followed by fluvial sedimentary sequences. The Barail Group encompasses a wide spectrum of lithofacies deposited under shallow marine, lagoonal, deltaic and fluvial environments.

Table 1.1: Stratigraphy of Oligocene Barail Group (Raja Rao, 1981)

Formation	Thickness (m)	Lithology
Tikak Parbat	600	Grayish to yellowish white massive fine grained sandstone, sandy shale, siltstone, mudstone, sporadic dolomitic limestone and several coal seams.
Boragolai	3500	Grayish to bluish grey or yellowish mudstone, massive sandstone, sandy shale, carbonaceous shale, clays and thin coal seams.
Naogaon	3000	Hard massive medium grained sandstone, dark grey splintery shale with sandstone alternations.

Deltaic and lagoonal environments for these coals were depicted based on high sulphur and volatile contents and perhydrous nature and very fine clastic units (Rajarithnam et al., 1996). The presence of foraminifera in association with sediments clearly suggests the marine influence (Raja Rao, 1981). Framboidal pyrites, generally forming near marine-influenced zones in lagoons having negligible currents and wave actions are also found in these coals (Rajarithnam et al., 1996). These coal seams are formed under tropical to subtropical climate during rapid decomposition of mangrove, costal palms and transitional angiosperm vegetations (Rajarithnam et al., 1996). During Oligocene, the Assam-Arakan basin contained terrestrial plants and mangroves and had tropical to subtropical climate (Ranga Rao, 1983). Mehrotra (2000) identified two new fossil fruits from the shale of Makum coalfields which support the existence of evergreen to littoral and swamp forests during the Oligocene. Mishra (1992) reported the presence of angiospermous evergreen forest vegetation that grew under humid tropical conditions during the Palaeocene and Oligocene.

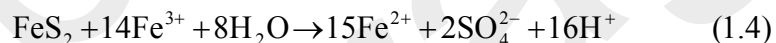
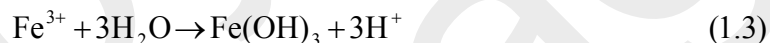
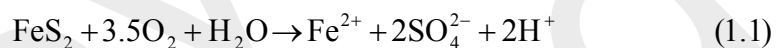
## 1.5 Literature Review

### 1.5.1 Characteristics of Mine Discharge

The composition of natural water is influenced by various geochemical processes; pyrite oxidation is one of them that control the sulphate concentration. The term “acid

rock drainage” was coined by Nordstrom and Alpers (1999) for water quality hazard caused due to pyrite oxidation and named as acid mine drainage (AMD) if generated from mining activities. Although acid drainage is mostly associated with mining activities (Younger, 1995), it can also occur due to natural processes (Schwertmann et al., 1995; Kawano and Tomita, 2001). Jambor and Blowes (1998) have reported that materials containing >0.3 wt% pyritic sulphur can produce acid upon weathering. Association of AMD with coal mining has been reported and well studied in various countries, e.g. England (Younger, 1995; Worrall and Pearson, 2001), USA (Larsen and Mann, 2005), Korea (Chon and Hwang, 2000; Kim and Chon, 2001), Iran (Shahabpour et al., 2005), Germany (Rolland et al., 2001) New Zealand (Weber et al., 2006) and South Africa (Geldenhuis and Bell, 1998).

AMD generation involves complex geochemical processes caused by both organic and inorganic mechanisms. The basic principle of oxidation of pyrite is well understood (Singer and Stumm, 1970; Nordstrom, 1982) and summarized through the following four reactions important for acid production:



The reaction (1.2) is the rate-limiting step. There is a cycle between reactions (1.2) and (1.4); where  $\text{Fe}^{3+}$  produced in reaction (1.2) oxidizes pyrite in reaction (1.4), and  $\text{Fe}^{2+}$  thus produced is further oxidized in reaction (1.2). As the process is limited by pyrite oxidation, the surface area available for oxidation determines the reaction rate (Gottschlich et al., 1986). The  $\text{Fe}^{3+}$  is hydrolyzed to form Fe-hydroxide (reaction 1.3) releasing more  $\text{H}^+$  into the aquatic environment reducing pH. The oxidation of pyrite can be accelerated in presence of bacteria, viz. *Thiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Acidithiobacillus ferrooxidans*, etc at low pH and is much faster than the inorganic processes.

Reaction (1.4) dominates at  $\text{pH} < 4$  in presence of bacteria and is faster than reaction (1.1). Pyrite and other sulphide minerals are widely distributed in rocks and sediments and the above reactions represent the most widely accepted acid producing

reactions in nature (Appelo and Postma, 2005). Clearly, dissolved oxygen and  $\text{Fe}^{+3}$  are the most important oxidants for the production of acid drainage.

AMD is a major source of water pollution in and around the present and abandoned mines and continues long even after mining activities have ceased (O'Bara and Estes, 1985). These discharges are characterized by low pH, high  $\text{SO}_4^{2-}$ , high total dissolved solids and metals such as Fe, Al, Ni, As, Cr, Pb, Zn, Cu, etc. This low pH allows metals to be more mobile than under neutral conditions (Stumm and Morgan, 1996). Metal concentrations in AMD from coal mines are controlled by three factors: oxidation rate of pyrite, mineralogy of the country rock and pH of the leachate (Yue and Zhao, 2008). Acidic water generated by the oxidation of pyrite reacts with the country rock dissolving minerals and releasing elements beyond their allowable limits (Sullivan and Yelton, 1988).

### **1.5.2 Effects of Mine Discharge**

Various effects from AMD have been schematically elaborated by Gray (1995). The influx of untreated AMD into streams can severely degrade habitat and water quality, often producing environment unsuitable for most aquatic life and unfit for use (Kimmel, 1983). It has been estimated that about 19,300 km of rivers and streams in the USA have been seriously affected (Kleinmann, 1989). Agricultural, industrial, and potable of water supplies along with recreational uses and aquatic organism habitat have been greatly affected. Acidic nature of the mine drainage leads to corrosion of man-made structures such as pipes, well screens, dams, bridges, water intakes, and pumps. AMD may contaminate the shallow groundwater system, and in turn the soil water zone; thus affecting the vegetation. Cooper and Wagner (1973) studied the distribution of fish in Pennsylvania streams affected by acid mine drainage and found fish species being severely impacted at pH 4.5 to 5.5 and that pH of 4.5 and total acidity of 15 mg/L accounted for complete loss of fish in 90% of the streams studied. In USA, 10 million fishes were killed during 1961–1975 from the effect of mining activities (Biernacki, 1978) and 47,100 fishes were killed by mine drainage at one site during a 7-days period in January, 1967 in California (Nordstrom et al., 1977). Most plants cannot tolerate low pH water because the high concentration of hydrogen ions causes inactivation of



enzymatic systems and restricts respiration and root uptake of mineral salts and water (Bradshaw et al., 1982). Accordingly, the acidity of the seepage water and the high concentration of total dissolved solids adversely affected vegetation locally. All plants were killed due to low pH in approximately 3 ha land around the Witbank coalfield, South Africa (Bell et al., 2001). Precipitation of various oxyhydroxysulphates from mine discharges may result in a complete blanketing of the stream bottom and adversely affect both macroinvertebrates and fish (Hoehn and Sizemore, 1977).

### 1.5.3 Ochreous Precipitates from AMD

Weathering of pyrite and other sulphide minerals leads to precipitation of various crystalline to poorly-ordered secondary metal-oxyhydroxides and sulfates (reaction 1.3). These precipitates primarily composed of Fe compounds, yellow-red-brown in color have long been referred to as “yellow boy” by North American miners (Bigham and Nordstrom, 2000). The “yellow boy” imparts orange or red color to the acidic runoff in the streams and covers the stream bed with slimy coating. Therefore, it becomes the visual indicator of occurrence of AMD. These precipitates are environmentally significant since they add to the suspended sediment and bed load of receiving streams, and play a major role in element mobility.

Formation of ochre and its solubility has been extensively studied (Alpers et al., 1994; Bigham and Nordstrom, 2000). Precipitation can occur at the surface of a mineral undergoing incongruent dissolution, or can take place through various processes such as oxidation, dilution, mixing, evaporation and neutralization (Alpers et al., 1994). However, depending on pH, concentrations of  $\text{SO}_4^{2-}$  and iron various secondary minerals such as jarosite, schwertmannite, goethite and ferrihydrite form from AMD (Bigham et al., 1992; Bigham et al., 1996; Bigham and Nordstrom, 2000).

The ochreous precipitated at AMD impacted sites forms the basis for the sorption process. The large adsorption potential of iron oxyhydroxides with respect to both cations and anions is well documented (Cornell and Schwertmann, 1996). Schwertmannite has the capacity to retain metal ions because it is poorly crystalline and has a large specific surface area. Some studies have reported the importance of ochreous precipitates in the regulation of potentially toxic trace elements through adsorption/coprecipitation

(Chapman et al., 1983; Winland et al., 1991; Schroth and Parnell, 2005; Kumpulainen et al., 2007). Both the formation and the dissolution of precipitates affect the composition of water associated with AMD (Hochella et al., 1999; Gagliano et al., 2004). In recent years, some work has been done on the adsorption of metals onto the surface of natural and synthetic schwertmannite (Webster et al., 1998; Carlson et al., 2002; Jönsson, et al., 2006). Metal adsorption by ochreous precipitates at the AMD impacted site is influenced by the specific mineral phase, solution pH, ternary surface complexation with  $\text{SO}_4^{2-}$  and bacterial mediation of precipitation (Webster et al., 1998; Swedlund and Webster, 2001). Influence of dissolved organic matter on the adsorption of metal onto ochre was also reported (Jönsson et al., 2006). Hochella et al. (1999) have emphasized the importance of the secondary minerals formed from sulphate-rich water in scavenging of metals and their role with variation in pH whereas Schroth and Parnell (2005) stressed the attenuation of mobility of various metals and their partitioning with transformation of schwertmannite to goethite. Webster et al. (1998) suggested that trace metals in ochre do not occupy binding sites associated with adsorption but get incorporated into the structure either through diffusion with time or by active ongoing precipitation with the oxides.

Schwertmannite being metastable with respect to goethite (Bigam et al., 1996) will re-dissolve with time and transfer to goethite with increasing pH. Gagliano et al., (2004) observed goethite as the only final product of transformation at the base of ochre deposits in 6-10 years old wetland in Ohio, USA. Schwertmann and Carlson (2005) have noticed from laboratory observations that this is a 1:1 transformation assuming that decomposition of schwertmannite follows the hydrolytic reaction:



#### 1.5.4 Acid Base Accounting

Assessment of acid drainage potential is one of important parameters in management of overburden and mine spoil generated during mining, especially if containing significant amounts of sulphide minerals (Jambor et al., 2003). Acid base accounting determines the amount of acidity or alkalinity that could be produced upon weathering or leaching of overburden (Skousen et al., 2002) and is the most common method for predicting post mining water quality and is widely adopted technique for

characterization of overburden (Perry, 1985; Sobek et al., 2000; Skousen et al., 2002). The first approximation for acid base accounting was the development of a two by two matrix (Table 1.2) for qualitative interpretation of overburden analyses. The four fields were broadly categorized into low neutralization potential (NP), high NP, low and high sulphur fields. The boundaries between the four fields were not numerically defined and the matrix served as a conceptual approach (Perry, 1985). This study involves the determination of acid production potential (APP) and NP of the waste, overburden and coal.

Table 1.2: Conceptual decision matrix for AMD potential used in early 1980's

	Low Sulphur	High Sulphur
Low NP	Evaluate Additional Data	Probable Denial
High NP	Probable Issuance	Possible Issuance or Denial

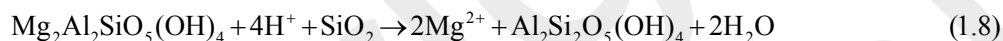
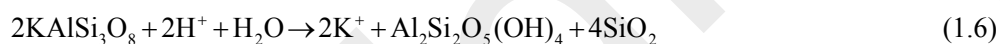
(Source: Brady and Hornberger, 1990)

NP is a measure of the amount of neutralizing compounds present in coal and overburden and is calculated from the amount of acid neutralized by the samples and is expressed in metric tons/1000 metric tons (parts/1000) of overburden (Kania, 1998). Maximum acid potential was based on the measure of total sulphur content of the rock. The presumption is that this accurately represents the amount of acid generating sulphide minerals. Sulphur in coal and coal bearing rocks occurs in sulphide, sulphate and organic forms. Sulphides, mainly pyrite, are the principal source of acid generation while sulphate exists in many forms, *viz.* gypsum, jarosite, melanterite and alunite. However, they are usually associated with weathered spoil or refuse but absent in fresh overburden and hence may or may not produce acid. Organic sulphur is considered non-acid forming (Casagrande et al., 1989), and is found in coal, carbon-rich shale and partings. Both AP and NNP are also expressed in parts/1000 (ppt).

The role of carbonates and silicates in consuming acid generated during oxidation of sulphides in determination of post-mining water chemistry is well established (Sherlock et al., 1995). Carbonate minerals determine post-mining water chemistry and neutralize acidity generated by oxidation of pyrite besides inhibiting pyrite oxidation (Perry and Brady, 1995). NP of various carbonate and aluminosilicate minerals and other diverse rock types have been measured (Jambor et al., 2002, 2007). The carbonate minerals, calcite and dolomite, have maximum acid consuming potential due to their

relatively high reactivity but NP generated from weathering of siderite is zero (Skousen et al., 1997). Silicate minerals such as pyroxene, amphibole, feldspar, mica, chlorite and clay show insufficient NP whereas olivine, serpentine and wollastonite have relatively higher NP. Therefore, distribution, amount, and types of minerals, particularly carbonates and sulphides, at any mine sites determine the potential for post-mining environmental problems.

The dissolution of silicate minerals consumes acidity through the following reactions:



### 1.5.5 Mineralogy of Coal

Mineral matter of coal is essentially composed of rock-forming minerals such as quartz, calcite, dolomite, clays and iron sulphides (Gluskoter, 1981; Finkelman, 1982; Swaine, 1990). The approximate quantitative distribution of mineral matter in coal in decreasing order of significance is generally: silicates > carbonates > oxyhydroxides > sulphides ≥ sulphates > phosphates > others; although the amounts of these inorganic vary considerably (Vassilev and Vassileva, 1996). These inorganic constituents are also responsible for numerous environmental problem related to coal use (Vassilev and Vassileva, 1996).

Quartz, kaolinite, illite and mixed-layer clays have been reported as major minerals in coal (Ward, 1991). Calcite and gypsum are deposited as fracture fillings and surface coatings. Siderite often a common constituent in coal (Maes et al., 2000) and is related to the depositional environment and the geochemical conditions existed during the first stages of coalification (Gluskoter et al., 1981).

The occurrence, distribution and grain size of iron sulphides influence the acid generating potential of coal (Finkelman and Gross, 1999). Forms of iron sulphide present in coal were described by Wiese and Fyfe (1986). Out of the various forms, finely disseminated pyrite framboids in coal and associated strata decompose rapidly to produce

severe AMD (Caruccio and Ferm, 1974). Other types such as euhedral, coarse grained massive and joint filled pyrite decompose at a relatively slow rate and the amount of acidity produced is generally low and can easily be neutralized by any alkaline solutions derived from carbonate minerals found in the associated rocks and/or coal. It has been observed that waste from marine coals in New Zealand is highly acid producing than that of fresh water environment (Campbell et al., 2001), and is attributed to the presence of high concentration of reactive disseminated pyrite, which has much larger surface area, allows more intense acid generation.

### 1.5.6 Oxidation Products of Pyrite

The formation of hydrated iron sulfates in the form of efflorescent from iron sulphide-bearing coals and associated strata is the first step in a sequence of chemical reactions during the formation of acid waters in coal mines, mine spoils and waste dumps, and in coal storage areas (Wiese et al., 1987). The precipitation and dissolution of these secondary sulphates have been identified as significant factors contributing to highly acidic water (Alpers et al., 1994, 2003; Nordstrom and Alpers, 1999). These soluble minerals store iron,  $\text{SO}_4^{2-}$  and potentially hazardous elements as well as acidity. Copiapite-group of minerals is relatively common in oxidized sulphide deposits and mine-waste environment (Jambor et al., 2000) and their chemical compositions are listed in Table 1.3.

Table 1.3: Minerals in the copiapite group (Mandarino, 1999)

Minerals	Ideal Formula
Copiapite	$\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Magnesiocopiapite	$\text{MgFe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Cuprocopiapite	$\text{CuFe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Calcicopiapite	$\text{CaFe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Zincocopiapite	$\text{ZnFe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Ferricopiapite	$\text{Fe}_{2/3}^{3+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$
Aluminocopiapite	$\text{Al}_{2/3}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$

### 1.5.7 Elements in Coal

The concentration of an element in geologic materials such as coal is commonly used as a measure of the material's potential environment and human impacts (Finkelman and Gross, 1999). However, the concentration of an element provides just partial information of its potential impact. Therefore, importance of mode of occurrence to assess the potential environmental and human health impact of elements through mobilization has been stressed (Finkelman and Gross, 1999).

Raask (1985) have reported that P and Ti associated mainly as organometallic complexes in coal substance; K and Pb bound to aluminosilicate mineral matter; Mn residing in carbonates and Cd, Co, Cu, Cr, Pb and Ni with sulphides in Coal. Major elements are usually associated with mineral matter, except in low rank coal. Trace elements, in coal with ash < 5%, are likely to be associated with organic matter (Finkelman, 1982) and Swaine (1992) reported the important organic functional groups responsible for binding these elements.

The elements in Indian coal owe their origin either to organic matter decomposed at high P-T conditions during the Lower Gondwana and Tertiary periods, or to the inter-banded silicate matrix, clay partings, sulphide and carbonate minerals comprising the inorganic fraction. Nickel, Co and Cr are associated with organic fractions whereas Pb and Cu show affinity for both organic matter and sulphides while Mn with the organic and mineral matter in Tertiary coals of India (Mukherjee et al., 1992).

In Assam coals Mg, Ca, Pb and Mn are significantly organic bound while Fe, Co, Ni, Cu and Zn are preferentially associated with minerals and Cd and Cr are bound to both organic and mineral matter (Baruah et al., 2003, 2005).

### 1.5.8 Soil and Sediment Contamination

The contamination of soil and sediment by metals from various sources is a subject of increasing concern in recent times. Heavy metal contamination is mainly caused through anthropogenic activities including mining, metallurgical processing and waste disposal (Pahraj et al., 2003). The presence of heavy metals in sediments of aquatic system represents one of the most important environmental problems, especially

if we take into account that the sediments of these systems represent an important reservoir of these elements (Ridgway and Shimmiel, 2002). Although many elements in certain amounts are essential for biological activities, most become toxic at higher concentrations. AMD is one of the important causes of heavy metals in the environment leading to considerable contamination of soil, water and sediments. Metals loading into the sediments and soil due to AMD are well known, for example at Tino and Odiel rivers, Spain (Nieto, 2007) and around Adam mines, Sweden (Bhattacharya et al., 2006). The Huelva estuary in Spain is the most contaminated in the world caused by AMD affected Tino and Odiel rivers. High concentration of arsenic (up to 219 mg/L) in the stream sediments close to the Xingren coalfield, Southwest China has recently been reported by Wu et al. (2009).

From the streams impacted by AMD, dissolved metals can be removed by adsorption on, or precipitated with, Fe and Al phases (McKnight et al., 1988). Heavy metals in sediments can easily be re-dissolved by physical and chemical changes in aquatic environments that may result in water pollution. Though many studies dealing with metal contamination in soil systems are concerned with total metal concentrations, limited information about their bioavailability and mobility can be drawn from their total concentration (Li and Thornton, 2001). The mobility and bioavailability of metals depends on the retention capacity of soil and on the geochemical phases with which they are associated (Veeresh et al, 2003). The processes of metal retention by solid phases in soil are controlled by different mechanisms: adsorption onto active surfaces of mineral and humic constituents (ionic exchange, specific adsorption), diffusion in the primary and secondary mineral structures and precipitation as carbonates, hydroxides, phosphates (Reed and Cline, 1994). Acidification of soil changes its chemistry resulting in mobilization, leaching and re-adsorption of base cations within the soil profiles (Blake et al., 1999).

Moreover, the risk assessments of heavy metals in soils for surface and ground water contamination or other environmental issues are based on their chemical 'lability' in soils rather than on their total contents. 'Bioavailability' or chemical 'lability' of heavy metals strongly depends on their specific chemical forms or speciation (Kabata-Pendias, 1993) and, consequently on soil physicochemical characteristics (Planquart et al., 1999).

However, the most important geochemical components considered to control bioavailability of metals in sediments include organic matter and Fe-Mn Oxides (Campbell and Tessier, 1989).

Sediments are the most favorable sink for heavy metals in polluted environments and readily attenuate the contaminants owing to their high sorption capacity (Prusty et al., 1994). Heavy metals associated with different fractions of soil and sediments have different impacts on the environment (Tam and Wong, 1996). Metals are known to be retained by different sorption mechanisms and are fractionated into various geochemical components such as exchangeable, organic, carbonate, Fe-Mn oxides and residual. Determination of the fractionation of metals into various components is necessary for understanding their mobility in soils and sediments. Heavy metals bound to exchangeable, carbonates, organic and Fe-Mn oxides are considered to be more prone to remobilization and pose a greater environmental hazard than those associated with the residual fraction (Förstner et al., 1989; Lopez-Gonzalez et al., 2006); the former pose a greater potential hazard to the environment.

### **1.6 Status of Mine Drainage Studies at Makum Coalfield**

A lot of work has been carried out on sulphur variation, its removal from coal (Sain et al., 1991; Mukherjee and Borthakur, 2003a, b), leaching of coal and its kinetic study (Baruah et al., 2006), coal petrology and mineralogy (Ahmed, 1996; Mukherjee and Srivastava, 2005), and depositional environment (Mishra, 1992; Mukherjee et al., 1992) of the Makum coalfield. Recently, Dutta (2006) studied the land use and land cover changes due to coal mining activities using remote sensing technique. However, little emphasis has been given to the distribution of metals in these coals and their mode of occurrences, except in some studies (Mukherjee et al., 1992; Baruah et al., 2003; Mukherjee and Srivastava, 2005) carried out on very restricted samples.

AMD was reported by Rawat and Singh (1982), but only the water quality of the mine discharges (Rawat and Singh, 1982; Singh, 1987; Tiwary, 2001), removal of trace metals by the application of limestone (Singh and Rawat, 1985), and the role of bacteria in the formation of AMD (Rawat and Singh, 1982) have been studied so far. However, no study on the impact of mine discharge on the surrounding water, sediment and soil has



yet been reported. Acid base accounting, which is very critical for predicting the post mine water quality (particularly of sulphide rich overburden), and a geochemical study of the ochreous precipitates from the highly acidic saturated solution have not been done.

### 1.7 Objectives

Based on the foregoing review and considering the information gap on the geochemical characterization of mine drainage vis-à-vis the coal and overburden and the resultant contamination scenario, the present study attempts to work on the following aspects around Makum coalfield:

- 1) Hydrogeochemical characterization of AMD and its impact on the surrounding water systems.
- 2) Geochemical characterization of the ochreous precipitates from AMD and their role in the mobilization of elements.
- 3) Role of mineralogy of the overburden and coal in AMD generation.
- 4) Evaluation of metal mobility from overburden and coal.
- 5) Assessment of metal contamination in soil and stream bed sediments.