

# ANALYSIS OF HYDROGEOCHEMICAL AND MINERALOGICAL CHARACTERISTICS RELATED TO HEAVY METAL ATTENUATION IN A STREAM POLLUTED BY ACID MINE DRAINAGE: A CASE STUDY

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**Abstract** - Acid mine drainage discharged from the mine may be harmful for the environment as well as for the human beings. The study area comprises of underground metal mine working and the Banas river which flows nearby the mining area. In this study, chemical characteristics of the water samples, mineralogy of the AMD sediments and heavy metal attenuation are discussed on the basis of mineral analysis, chemical analysis and sequential extraction techniques. The chemical characteristics of the acid mine drainage and sulfide minerals from the mine tailings are determined in order to study the impact of acid mine drainage on the river water. The water samples are classified as affected and unaffected water. The affected water has low pH value, high  $(SO_4)^{2-}$  ions and high heavy metal concentration. The concentration of heavy metals and sulfide ions decreases and the pH increases downstream. The acid mine drainage water chemistry is controlled by the transformations and mineral precipitates of  $Fe^{3+}$  minerals.

**Key Words:** Acid mine drainage, Sediments, Mineralogy, Attenuation, Sequential extraction, Heavy metal

## 1. INTRODUCTION

Mining has been an important part in human world. It provides various minerals and coal that has been used in regular basis e.g. Thermal Power Plants, Cement Industry etc. But there exist various problems like Acid Mine Drainage. It is one of the major problems polluting the water as it pollutes around 27 billion of water per year. Human health has been a major issue which surrounds the mine area.

A mine draining acid can destroy streams, rivers, and aquatic life for hundreds of years. Oxidation and liberation of sulfur present in rocks in the form of sulfide minerals generates sulfuric acid. This is one of the major impacts of coal and metal mining activity. Acid Mine Drainage (AMD) is a problem that initiates within short time in sulfide rich mines. When these sulfide minerals come in contact with oxygen or oxygenated waters, breakdown of these minerals leads to acid generation and leaching of metals.

Acid mine drainage leads to the problems like contaminated drinking water, disrupted growth and reproduction of aquatic plants and animals and the

corroding effects of the acid on infrastructures such as bridges, etc. Treatment of AMD by conventional methods include various physicochemical methods, which involve excessive use of chemicals and capital. Biological treatment has come out as efficient, cost-effective, and eco-friendly alternative for remediation of AMD. Biological treatment methods involve use of microorganisms such as bacteria and fungi. Biotechnological approaches can prove an asset in developing techniques that can treat AMD in an effective way without affecting the environmental sustainability.

Heavy metal contamination has slowly become a common and important concern world-wide. The most common heavy metals are iron, copper, zinc, lead, nickel, arsenic, mercury and cadmium. Heavy metals are distributed in the aquatic environment as sedimentary phases, suspended forms, colloids and water-soluble species. Heavy metals are an important category of pollutants as they can have a significant harmful effects on both human health and the health of terrestrial and aquatic communities and ecosystems. A number of heavy metals have been commonly studied as pollutants due to high environmental concern, such as Cd, Cu, Cr, Hg, Pb, Ni, and Zn.

The danger of heavy metal pollution can be understood by three fundamental reasons. They are not biodegradable, so they remain indefinitely in the environment, unless transported to other environments. They can be retained by organic tissues through bioaccumulation and then transmitted to other species in a higher level of the trophic chain, thus causing biomagnifications. Some of them such as copper, zinc and manganese are necessary micronutrients for some plants and animals, but they can become lethal above certain concentration levels. However, organisms need these metals within an optimal level, under which conditions of want appear and over which we find toxicity.

The mine in the study area has been extensively mined with massive tailings left behind and the surroundings have borne the effects of AMD contamination. Production of AMD continues in the tailing reservoir. AMD discharge from the mine has caused severe environmental pollution and human health problems.

## 2. METHODOLOGY

### 2.1 Field Work

Thirty five water samples were collected across the river in the region of mining area. A composite sample was formed at each sampling site by collecting three sub-samples. On the basis of the geological conditions and hydrodynamic relationships, water samples are classified into two groups: affected water and unaffected water.

Nine sediment samples were collected which include tailing dam sediment, waste dump sediment and streambed sediments along the Banas river. The surface water sampling sites were co-located with the sediment sample locations. A composite sample was formed at each sampling site by collecting five top layer sediment samples of thickness 10 cm within the area of 5 m<sup>2</sup>.

### 2.2 Laboratory Work

Temperature, pH, Electrical conductivity (EC), oxidation-reduction potential (ORP), total dissolved solids were measured in the laboratory were measured in-situ with portable instrument (thermo orion 4 star). The concentration of the dissolved ions were measured using conventional methods. The concentration of heavy metals were determined by inductively coupled plasma – optical emission spectrometry (ICP-OES). Mineralogy was determined by field emission scanning electron microscopy (FE-SEM), powder x-ray diffraction (XRD) and fourier transform infrared (FT-IR).

## 3. FIELD AND LABORATORY INVESTIGATIONS

### 3.1 Analysis of Dissolved Ion Concentrations and TDS

Conventional methods were used for determination of dissolved ion concentrations. Alkalinity was determined by acid – base titration method with HCl solution (0.025 mol/L) at a pH of 4.5 – 4.6, within 24 hours after the sample collection. Triplicate analysis was performed to test the precision and accuracy of the computed results. TDS was measured in-situ with portable instrument (thermo orion 4-star meter).

### 3.2 Determination of pH, Electrical Conductivity (EC) and ORP

pH, electrical conductivity (EC) and oxidation-reduction potential (ORP) were measured in-situ with the portable instrument, thermo orion 4-star meter.

### 3.3 Analysis of Heavy Metals and Trace Elements

Inductively coupled plasma – optical emission spectrometry (ICP – OES) was used to measure the concentrations of trace

elements and heavy metals. Other metals analysis procedures are listed in table 1.

**Table-1: Analysis methods of different metals**

Metal	Analysis Method
K, Na, Ca and Mg	Atomic absorption spectrometry
Fe and Fe <sup>2+</sup>	Colorimetry
As	Atomic fluorescence spectrometry

### 3.4 Analysis of Mineralogy of AMD Sediments

Before the analysis, sediment samples were pulverized. Mineralogy was determined by field emission scanning electron microscopy (FE-SEM), powder X-ray diffraction (XRD) and fourier transform infrared (FT-IR).

### 3.5 Sequential Extraction Method

0.2 gm of dry sediments were taken and sequential extractions were performed. The details of the analysis procedure are shown in the table 2.

**Table-2: Sequential extraction procedure used in this study**

Fraction	Extraction (dilution)	Procedure
Exchangeable fraction	1 mol/L MgCl <sub>2</sub> (pH = 7)	Continuous shaking for 2 hours (room temperature)
Adsorbed carbonates	1 mol/L NaOAc (pH = 5)	Continuous shaking for 3 hours (room temperature)
Fe-Mn oxides	0.04 mol/L NH <sub>2</sub> OH-HCL	Heat in water bath 96°C for 6 hours
Organic matter	0.04 mol/L HNO <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> and 3.2 mol/L NH <sub>4</sub> OAc	30% H <sub>2</sub> O <sub>2</sub> added twice to samples with 0.04 mol/L HNO <sub>3</sub> , shaking in water bath 85°C for 3 hours, cool to room temperature, then added 3.2 mol/L NH <sub>4</sub> OAc for 30 minutes
Residual	HCl-HNO <sub>3</sub> -HClO <sub>4</sub>	Sample digested with HCl, HNO <sub>3</sub> and HClO <sub>4</sub> in a microwave digester

## 4. RESULTS AND DISCUSSION

### 4.1 Chemical Characteristics of Water

The main characteristics of the affected water are high concentrations of  $(SO_4)^{2-}$  and TDS.

**Table-3: Geochemical parameters of water samples**

Property (mg/L)	Affected water (n = 27)				Unaffected water (n = 8)			
	Max.	Min.	Mean	Median	Max.	Min.	Mean	Median
TDS	1517	14	343.40	168.73	297	21	94.37	56
$(SO_4)^{2-}$	2117	2.76	296.35	78.67	19.38	2.23	6.57	4.61
$Cl^{1-}$	13.76	0.18	2.13	0.96	2.16	0.17	0.84	0.46
$(HCO_3)^{1-}$	129.60	4.09	44.12	27.13	309.4	22.70	72.42	46.30
$K^+$	25.24	0.19	3.65	1.65	4.7	0.23	1.34	1.23
$Na^+$	9.34	0.14	2.33	1.37	7.63	0.35	1.84	1.43
$Ca^{2+}$	488	0.76	67.58	34.61	79.24	5.31	19.27	8.93
$Mg^{2+}$	202.30	0.45	36.81	8.73	13	1.09	3.18	1.87

The concentrations of  $HCO_3^3-$ ,  $(SO_4)^{2-}$ ,  $(Cl)^{1-}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$  varies in affected water and changed uniformly with distance from the source of AMD. The concentration of  $Ca^{2+}$  was abundant in affected as well as unaffected water.

The average concentration of  $HCO_3^3-$  (44.12 mg/L) in the study area was significantly lower in affected water as compared to unaffected water (71.42 mg/L). On the contrary, the average concentration of  $(SO_4)^{2-}$  ions is more in affected water. This shows that more  $(SO_4)^{2-}$  is received in the affected water from the mine tailings.

### 4.2 pH, Electrical Conductivity (EC) and ORP

Generally, the chemical processes of AMD is mainly influence by the pH. In unaffected water, the highest pH value measured was 7.08 while in affected water, the lowest pH measured was 2.86. The pH value in the study area increased downstream of the Banas river because unaffected water flowed into the affected water.

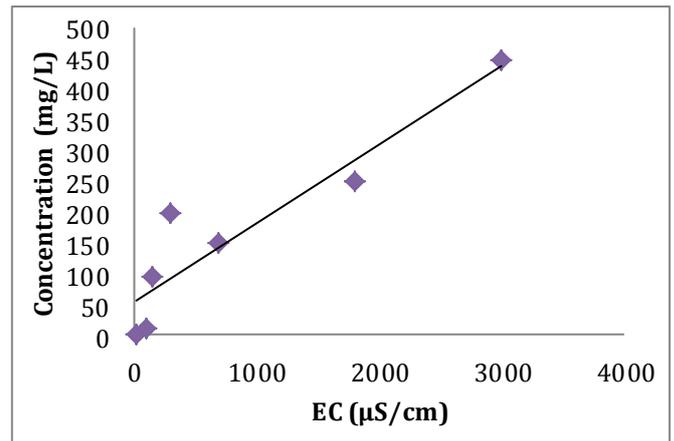
**Table-4: pH, EC and ORP parameters of water samples**

Property	Affected water (n = 27)				Unaffected water (n = 8)			
	Max.	Min.	Mean	Median	Max.	Min.	Mean	Median
pH	7.16	2.86	5.14	5.55	7.08	6.23	6.53	6.51
EC ( $\mu S/cm$ )	3080	26.78	697.27	343.40	586	41.32	193.4	110.30
ORP (mV)	692.7	273.5	470.62	390.65	516.4	268.3	351.1	324.30

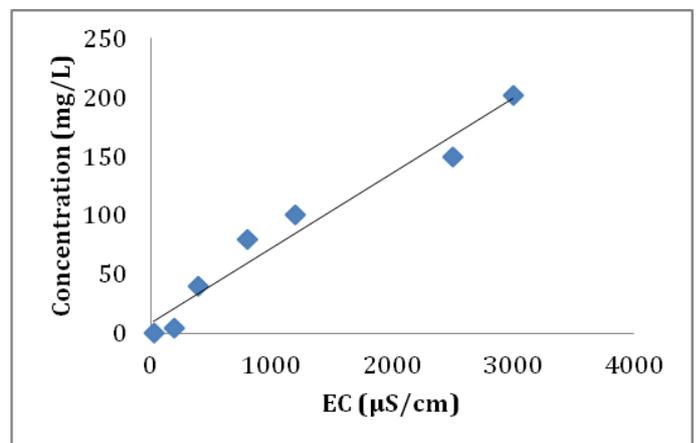
The higher EC values in affected water shows that affected water contain more minerals as compared to unaffected water. EC values have good correlations with  $Ca^{2+}$ ,  $Mg^{2+}$  and  $(SO_4)^{2-}$  concentrations as shown in the chart 1, 2 and 3 respectively.

**Table-5: Correlation values of EC with different ions**

Ions	Correlation with EC
$Ca^{2+}$	0.85
$Mg^{2+}$	0.95
$(SO_4)^{2-}$	0.94



**Chart-1: Correlation plots of EC vs  $Ca^{2+}$**



**Chart-2: Correlation plots of EC vs  $Mg^{2+}$**

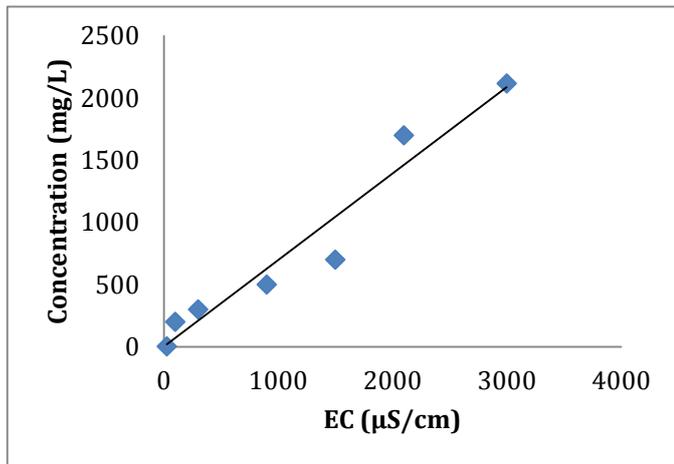


Chart-3: Correlation plots of EC vs (SO<sub>4</sub>)<sup>2-</sup>

### 4.3 Heavy Metals and Trace Elements

As AMD is discharged at mining sites, sediment is an important factor. In understanding the environmental activities of trace elements and heavy metals in AMD, sediment geology and mineralogy are very helpful.

The affected water contains high concentrations of Cu and Zn with low concentrations of Cd, As and Pb.

Table-6: Heavy metal concentrations

Property (mg/L)	Affected water (n = 27)				Unaffected water (n = 8)			
	Max.	Min.	Mean	Median	Max.	Min.	Mean	Median
Cu <sup>2+</sup>	7.65	0	1.73	0.28	0.01	0	0	0
Pb <sup>2+</sup>	0.71	0.03	0.31	0.18	0	0	0	0
Cd <sup>2+</sup>	0.26	0	0.09	0.07	0	0	0	0
Zn <sup>2+</sup>	35.65	0	6.87	1.33	0.77	0.02	0.17	0.06
Total As	0.03	0	0.01	0.01	0.02	0	0.01	0
Total Fe	116.53	0.03	12.93	2.55	0.42	0.01	0.17	0.08
Al <sup>3+</sup>	63.62	0	13.17	2.52	0.18	0.04	0.10	0.07

Cadmium exists in sphalerite along with Zn and the geological characteristics of Cd and Zn are similar. The concentrations of Cd and Zn were well correlated in affected water (R<sup>2</sup> = 0.97, n = 27).

The correlations between other elements and Al were also significant and are shown in the table 7. This indicates that at the mine site, these elements originated from the same minerals.

Table-7: Correlation of Al with other elements

Elements	Correlation (R <sup>2</sup> )
Al:Zn	0.98
Al:Cu	0.94
Al:Pb	0.97
Al:Cd	0.97
Al:Mn	0.85

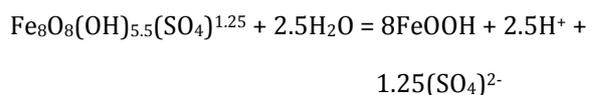
### 4.4 Mineralogy of AMD Sediments

The sediments of Fe minerals were found at tailing dam, waste dumps and river in the mining area. The sediments on riverbanks in AMD affected areas consist of Fe phases precipitated from Fe dissolved in AMD which comes from pyrite at the mine site.

The minerals of AMD sediments consist of amorphous hydroxides and oxyhydroxysulphates, such as as schwertmannite and goethite. As the AMD leaches from the mine, secondary minerals are formed.

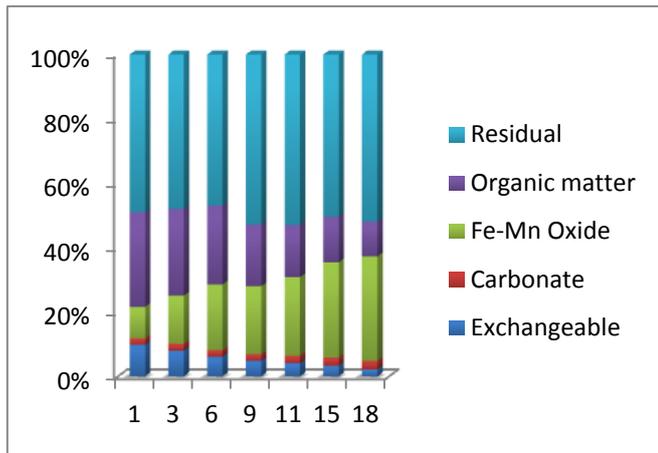
Schwerrtmannite is the dominant mineral at waste dump site and tailing dam because of the continuous injection and slow movement of AMD. Goethite and quartz with low amount of schwertmannite are present at riverbanks. This shows that the minerals changed from schwertmannite to goethite and the amount of goethite increases with increase in distance from the mine tailings.

The transformation occurs via the following reaction:



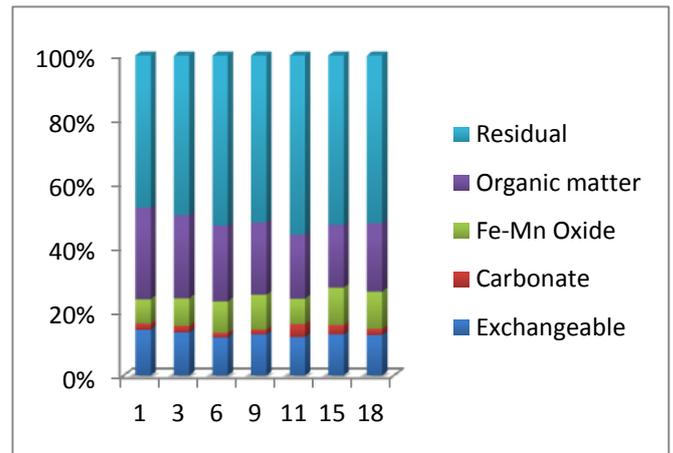
### 4.5 Sequential Extraction of Sediment

The exchangeable and organic matter fraction of Zn decreased and carbonate & Fe-Mn oxide increased downstream in the river. The residual phase of Zn dominated in the Banas river sediments. Organic matter phase dominate near the mine site while Fe-Mn oxide became the main phase as we moved away from the mine.



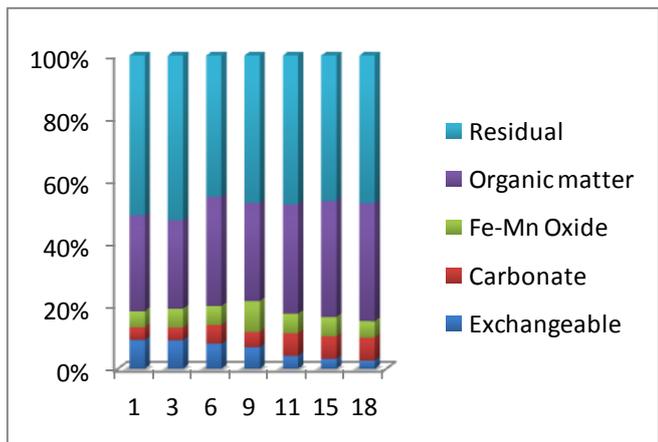
**Chart-4: Sequential extraction of Zn**

The organic matter and carbonate phases increased while exchangeable fractions decreased downstream of the river. Fe-Mn phase of Cu increases upto 9<sup>th</sup> sampling location and then decreases downstream of the river. Organic matter was the major fraction for Cu throughout the sampling locations.



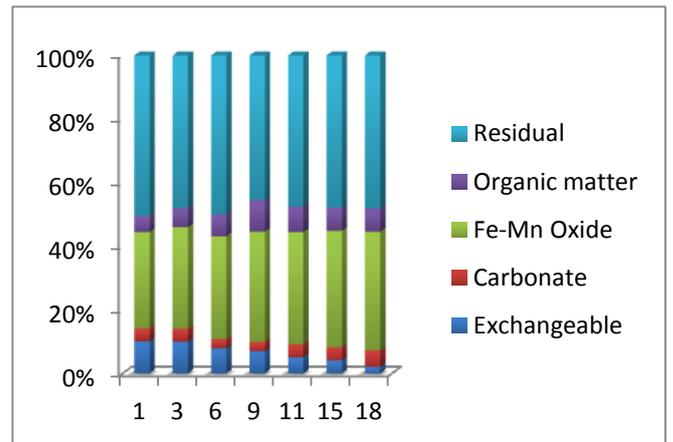
**Chart-6: Sequential extraction of Cd**

The organic matter fraction for Pb increases and then decreases as we move away from the mine site. Carbonate and Fe-Mn oxide phases increased while exchangeable phase decreased downstream in the river. Fe-Mn oxide is the dominant fraction for Pb.



**Chart-5: Sequential extraction of Cu**

Cd was mainly found in residual phase (silicate) and Fe oxide phases. The organic and exchangeable fractions of Cd decreased while carbonate and Fe-Mn oxide fractions increased as we moved away from the mine site. The fraction of residual phase for Cd was highest as compared to that of Zn, Pb and Cu.



**Chart-7: Sequential extraction of Pb**

#### 4.6 Attenuation of Heavy Metals in AMD

Heavy metals in AMD can be removed by adsorption, deposition, co-precipitation and bioremediation. The adsorption, deposition and co-precipitation are physiological processes and their removal efficiency of heavy metals is affected by the pH values.

Fe or Al hydroxide minerals plays important role in the removal of heavy metals and other ions by adsorption and co-precipitation process. Fe hydroxides surface can adsorb Cu, Zn and Pb. Al hydroxides or hydroxysulphates can adsorb Cu, Zn, Pb and Ni.

AMD can be neutralized by dissolution of carbonate minerals. Initially, AMD of the mine is strongly acidic

because sulphide oxidation results in the liberation of H<sup>+</sup> ions. As the AMD moves away from the mine tailings, carbonate minerals buffer the acidity produced by sulfide minerals resulting in increase of the pH and decrease of concentrations of heavy metals in the water.

Due to the above natural attenuation processes such as adsorption and co-precipitation of secondary minerals and buffering by carbonate minerals, the hydrogeochemical characteristic of the affected water become similar to the unaffected water of the Banas river.

### 3. CONCLUSIONS

In the surrounding of study area, the chemical characteristics of the affected water are controlled by sulfide minerals rather than belonging to carbonate type. AMD is characterized by low pH and high concentrations of heavy metals and high concentrations of SO<sub>4</sub><sup>2-</sup>. Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> were the major ions present in the affected water while concentrations of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>3-</sup> dominated in the affected water.

The concentrations of heavy metals and SO<sub>4</sub><sup>2-</sup> decreased downstream in the river while pH increases. The results of XRD, FT-IR, FE-SEM and sequential extraction experiment revealed that secondary Fe minerals were precipitated in the affected water. At the waste dump site, schwertmannite was the major minerals while goethite was the major mineral at the tailings dam and riverbanks.

The exchangeable and organic matter fraction of Zn decreased and carbonate & Fe-Mn oxide increased downstream in the river. The organic matter and carbonate phases Cu increased while exchangeable fractions decreased downstream of the river. Cd was mainly found in residual phase (silicate) and Fe oxide phases. The organic and exchangeable fractions of Cd decreased while carbonate and Fe-Mn oxide fractions increased as we moved away from the mine site. The organic matter fraction for Pb increases and then decreases as we move away from the mine site. Carbonate and Fe-Mn oxide phases increased while exchangeable phase decreased downstream in the river. Fe-Mn oxide is the dominant fraction for Pb.

The attenuation of heavy metals are are very complex processes in acid mine drainage. Further study is required in this region to analyse the adsorption and co-precipitation of heavy metals on other minerals such as aluminium and manganese minerals. A detailed study of the mineral transformations in the affected area should also be initiated.

### ACKNOWLEDGEMENT

I take it to be proud privilege to avail this opportunity to express my sincere and deep sense of gratitude to my major advisor Dr. Anupam Bhatnagar, Professor and Head, Department of Mining Engineering, College of Technology

and Engineering, MPUAT, Udaipur for this stimulating guidance, constructive suggestion, keen and sustained interest and incessant encouragement bestowed during the entire period of investigation, as well as critically going through the manuscript.

I am gratified to record sincere thanks to the member of the advisory committee Dr. S.C. Jain, Professor, Department of Mining Engineering, CTAE, Udaipur; Dr. Bheru Lal Salvi, Associate Professor, Department of Mechanical Engineering, CTAE, Udaipur; Dr. Manjeet Singh, DRI Nominee and Assistant Professor, Department of Soil and Water Conservation Engineering, CTAE, Udaipur for this generous gestures and valuable suggestion in planning and execution of this study.

With respect and deep sense of gratitude, I hereby express my thank to Dr. P.K. Singh, Dean, College of Technology and Engineering, Udaipur for providing necessary facilities to carry out my work.

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