LEACHATE TRANSPORT FROM FLY ASH SLURRY POND

A THESIS

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by

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **LEACHATE TRANSPORT FROM FLY ASH SLURRY POND** in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy and submitted in the Department of Water Resources Development & Management of the Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during the period from July 2006 to May 2010 under the supervision of Dr. Deepak Khare, Professor, Department of Water Resources Development & Management and Dr. G. C. Mishra, Retired Professor Department of Water Resources Development & Management, Indian Institute of Technology Roorkee, Roorkee. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institute.

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ABSTRACT

Huge quantities of fly ash, generated from combustion of low rank coal at various thermal power plants, are being disposed off on large piece of land. Utilization of fly ash is the one way to solve the problem of its disposal, but only 30% of fly ash is being utilized in India and rest of the unused fly ash is dumped in the ash pond. Fly ash contains several toxic elements such as Pb, Zn, Cd, Ni, Co and As. Leaching of these toxic elements in ash pond poses great environmental hazard due to its potential toxicity. The adverse impact includes contamination of surface and subsurface water with toxic heavy metals present in the coal ashes, loss of soil fertility around the plant sites. Water infiltrating through ash pond dissolves such heavy metals and soluble salts and carries it downward through the unsaturated zone. Such pollutants traveling through the unsaturated zone join the water table and may affect the water quality adversely. The problem of safe disposal of large quantities of ash which remain unutilized has received little attention in the past and is area of focus of this research work.

The physical and chemical properties of coal ashes are dependent on coals geological origin, combustion conditions, efficiency of particulate removal and degree of weathering before final disposal. Mineralogy along with morphology gives an important index about utilization of fly ashes or it can be also useful to monitor post disposal scenario. Physical and chemical properties are characterized with the help of various instruments such as XRF, XRD, SEM, AFM, SEM-EDAX and Laser Particle size Analyzer.

To study to the field leaching behavior of fly ashes cascade leaching test has been performed at pH= 7 (120 hours) and pH= 4 (288 hours). Cascade leaching test simulates natural leaching of fly ash. The leaching trend was observed as, an initial or early peak concentration of the metals in leachate followed by an exponential decrease of concentration with increase in time or L/S ratio or pore volumes. Scanning electron Micrographic studies of post leached fly ashes reveals that surface of fly ash particles is etched. Single and composite exponential decay models were fitted between two parameters, i.e. metal concentrations in leachate and 'n' stage of leaching, and can be used for the prediction of concentrations of metals in leachate. Based on the desorption

phenomenon and laboratory experiments performed, leachate prediction model is formulated where it is assumed that distribution coefficient is constant but, it is observed that it is not constant and it decreases exponentially with 'n'. A model considering that the distribution coefficient, changes from stage to stage of leaching has been developed. The distribution coefficient is linearly proportional to the leacahte concentration and it decreases with decrease in leachate concentration.

Soil column leaching tests conducted in the laboratory showed that the pH of the effluent is persistent for the study period of 44 days. The release of metals appears to be adsorption controlled, due to which attenuation of heavy metals took place. Attenuated heavy metals, however, are not biodegradable. They are stored in the soil and may be remobilised and migrate into groundwater when the soil's adsorption capacity is exceeded or its properties are changed. To protect unsaturated zone and groundwater provision of liners is essential.

Top soil layer of surrounding of the Nashik ash pond is occupied by fly ash and it may be due to wind blown particles of fly ash. Analysis of groundwater from open dugwells at Kotamgaon and Hinganvedhe village found that the groundwater quality is deteriorated due to the presence of fly ash ions such as Fe, Mn Cd and Ni. Apart from input from ash pond, use of ash pond effluent for irrigation, seepage from Eastern and Southern effluent channel and leaching of top soil (contaminated due to fly ash dispersal) contributes to groundwater. There is significant potential exists for environmental impacts from uncontrolled seepage of rainwater and slurry water through ash deposits in the absence of liner, once the operating life of ash pond is over. Provision of low cost liner is necessary to protect the groundwater contamination from ash pond.

The past several decades have seen considerable progress in the conceptual understanding and mathematical description of water flow and solute transport processes in the unsaturated zone. Mathematical models can be used to predict changes in ambient soil and water quality due to transport of pollutant through the underlying unsaturated zone below the ash pond. Once the leachate joins the water table, the solute transport would take place through advection and dispersion. Predicting water quality impact of a single discharge , that is due to storage of flyash slurry, can be done quickly and sufficiently accurately with simple models. In this study, using Green and Ampt infiltration theory, the arrival time of the pollutants at water table has been derived for the case when a low permeable liner is placed at the bottom of the ash pond. Provision of liner is essential. The brick lining is inadequate for restricting leachate infiltration. A liner having conductivity of the order of $3.6\times10^{-4}\ cm/hour$ is preferable to brick lining. Once the operating life of ash pond is over, gradual reclamation of ash pond should be practiced.

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ABBREVIATIONS USED

AAS	Atomic Absorption Spectroscopy
ADRE	Advection Dispersion Reaction Equation
BFA	Bhatinda Fly Ash
BTPS	Bokaro Thermal Power Station
CCP	Coal Combustion Product
CFB	Circulated Fluidized Bed
CPCB	Central Pollution Control Board of India
CTPS	Chandrapura Thermal Power Station
DFA	Dadri Fly Ash
DI	De Ionized Water
DSC	Dynamic shape Characterization.
DST	Department of Science and Technology
EC	Electrical Conductivity
EP Tox	Extraction Procedure for Toxicity
EPA	Environmental Protection Agency
EPCC	Environmental Pollution Control Committee
EPMA	Electron Microprobe Analysis
EPRI	Electric Power Research institute
ESP	Electrostatic Precipitator
FAUP	Fly ash Utilization Programme
GWT	Groundwater Table

H_{ex}	External Hazard Index
ICP-MS	Inductively Coupled Mass Spectroscopy
IEA	International Energy Agency
IPP	Indraprastha Power Plant
LOI	Loss on Ignition
L/S	Liquid to Solid Ratio
LDPE	Low Density Poly Ethylene
MEP	Multiple Extraction Procedure
MOEF	Ministry of Environment and Forest,
MW	Mega Watts
NEERI	National Environmental Engineering Research Institute
NFA	Nashik Fly ash
NTPC	National Thermal Power Corporation
PC	Pulverized Coal
PM	Total Particulates
PSA	Particle Size Analysis
Ra_{eq}	Radium Equivalent Activity
RPH	Rajghat Power House
RSD	Relative Standard Deviation
SAB	Science Advisory Board.
SEM	Scanning Electron Microscopy
SEM-EDAX	Scanning Electron Microsopy- Energy Dispersive X-ray Analysis
SFA	Suratgarh Fly Ash

SPLP	Synthetic Precipitation Leach Procedure
TCLP	Toxicity Characteristics Leaching Procedure
TDS	Total Dissolved Solids
TEM	Transmission Electron Microscopy
TERI	Tata Energy Research Institute
TIFAC	Technology Information Forecasting
TVA	Tennessee Valley Authority
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
XRD	X ray Diffractometer
XRF	X –ray Fluorescence Spectroscopy

MODEL ABBREVIATIONS USED

V	Influx volume of leachant in liters
$C_i(n)$	Concentration of the i^{th} element in the leachate at n^{th} stage of leaching (gm/l)
ρ	Residual mass in grams
k	Distribution coefficient (gm/lit)
$M_i(n)$	Mass of the i^{th} element at per unit residual mass n^{th} stage (gm)
$\rho M_i(0)$	total mass in the i^{th} element before leaching in gm
S	Stripping coefficient
n	Stage of leaching

CHAPTER 1

INTRODUCTION

1.1 PREAMBLE

Power is the key to the affluence and development of the nation. Coal is the most important and abundant fossil fuel in India and as a result it has proved to be most dominant fuel for electricity generation. Currently 68% of its electricity is generated from coal. India is the sixth largest electricity generating country in the world and accounts for 4% of global annual electricity generation (Bhattacharya B. C., 2007). The total installed capacity in India including the captive power plants has increased to 137,552 MW in 2005 compared to 131,424 MW in 2004. Total Installed Capacity is 1,47,966 MW, a capacity addition of 41,110 MW comprising 14,393 MW hydro, 25,417 MW thermal and 1,300 MW nuclear power has been fixed for the Tenth Five Year Plan. However India is still facing power shortages in terms of overall and peak demands. The country has very optimistic projection of generation and supply of power. The Central Electricity Authority has estimated the need for creating additional capacity of 100,000 MW by 2012. In long term projection rate of increase in electricity consumption is estimated to be as much as 8%-10% annually and India is expected to be one of the highest in the world by 2020. According to the International Energy Agency (IEA) projection, coal will remain the dominant fuel in India's energy mix through 2030. During coal combustion, most of the carbon present in the source coal is converted to CO_2 and emitted through the stack, while the mineral fraction of the coal is converted to form the matrix of the coal ash. Due to variation in source coal composition and combustion conditions, the composition of bottom ash and fly ash can vary widely, with fly ash typically being more enriched in trace elements.

Coal ash consists of two components: bottom ash, or slag, that is removed from the bottom of the furnace, and fly ash that is suspended in the flue gases during combustion and collected by electrostatic precipitators or bag filters. A small percentage of the fly ash generated by power plants in the India is used beneficially, for cement production and embankment and other construction activities. However, the majority of coal ash is disposed by wet disposal scheme.

Land disposal of any solid residue is possible source of contaminating surface and underlying water because these residues contain several inorganic constituents that may impact plants, animals and human health. Typically fly ash is disposed by dry and wet disposal method. Even in Israel some portion of ash is dumped in to sea (Nathan, Y., 1999). Between these two, the wet method of disposing fly ash slurry into ash pond, lagoons or ash dykes has been widely practiced by most of the power plants in India. Both bottom ash and fly ash are stored temporarily in silos prior to transporting them to the disposal areas in either wet or dry form and then used as construction material, binder in stabilizing ground, and embankment construction. In wet disposal method, fly ash is typically mixed with 70-80% of water or liquid to solid ratio of 10:1 and 3.5:1 (Sear, L. K. A., 2001) and then transported through pipes for storage into ponds or lagoons or ash dykes. Here ash particles settled by sedimentation process, resulting in very soft deposits. The supernatant liquid is collected and drained off into nearby stream or river if effluents standards are satisfied for such disposal. Leaching of trace elements and their environmental impacts on surface water, groundwater, and soil is a concern when disposed in ash pond or used in highway applications. Previous studies have shown that Ag, As, B, Ba, Cd, Cr, Co, Cu, Hg, Mg, Ni, Pb, Sb, Se, and Zn leach from coal combustion by products (Kim, et al., 2002 ; Praharaj, et al., 2002).

1.2 ISSUES AND CHALLENGES ASSOCIATED WITH FLY ASH DISPOSAL

Disposal of fly ash has become an increasing problem in many countries of the world. In India 30% of ash was being utilized which is very less compared to all other countries in the world (Asokan, et al., 2005). In India 130 million tonnes of fly ash was generated in 2007 and it is expected to cross over 175 million tonnes by the end of 2012. Since low ash high-grade coal is reserved for metallurgical and other industries, thermal power plants have no choice but to use low grade coal having ash content up to 55% ash (Kumar, V. et al., 2000), and out of which 80% is fly ash and balance 20% is bottom ash.

The estimates prepared by Ministry of Power as well as Planning Commission up to the year 2031-32 indicated that the coal requirement and generation of fly ash during the year 2031-32 would be around 1800 million tonnes and 600 million tonnes respectively (Fly Ash Mission). The production of increasing amounts of fly ash resulting from coal fired power plant is major pursuit due to its environmental impact. The management of such a large amount of fly ash will be huge task. In India little attention has been paid to the selection of area, operational cost, health hazards and air, water and land pollution due to disposal of fly ash from power generating industries. Environmental pollution due to non-degradable inorganic fractions of fly ash and interactions of these with soils, including their solubility, mobility and bioavailability, has become a matter of increasing concern in the recent years due to the potential effects on human health, agriculture and natural ecosystems (Khandekar et al., 1999).

Fly ash represents a significant hazard to population situated around thermal power plants and ash deposits. There may be air pollution from fugitive dust, when ash deposits dry without water or vegetation cover. Typically, most of the area of ash ponds or ash dikes is not covered by water. The ash dries up and is an excellent source for fugitive dust emissions. Fugitive emissions from poorly managed ash disposal areas can contribute to increased local concentrations of respirable particulates, and adversely impact human health. Direct inhalation of coal fly ash can cause potential health problems related either to the presence of particles in the lungs or due to presence of heavy metals in ash.

Dumping of dry fly ash may produce particulate pollution. Fly ash affects directly through deposition on plant surfaces or indirectly through accumulation in the soil. Vegetation at site receiving higher pollution loads have reduced total chlorophyll content, leaf area and higher specific leaf area as well as increased contents of sulfate and trace elements (Agrawal, M., et al., 1993). Soil pollution at the surrounding of power plant or ash pond is caused by two ways namely atmospheric fallout of fly ash and through the seepage of ash pond decant water (due to the leaching of soluble salts present in ash). The particulates fallouts enriched in more volatile metals return to the earth surface and join the leachates from ash dumps. The physicochemical and mineralogical properties of the soil profile in the predominant wind direction are found to be modified compared to the background and other soil profile (Mandal, A., et al., 2006, Praharaj , T., et al., 2003,). The World Bank has cautioned India that by 2015 land disposal of coal ash would require for about 1000 km^2 or 1 m^2 of land per person. The construction of large ash disposal ponds results in resettlement issues, loss of agricultural production, grazing land and habitat, as well as other land use impacts from diversion of large areas of land to waste disposal.

In India ash pond effluent is discharged in to nearby stream or adjoining river, which often does not meet effluent water quality standards. These rivers and their tributaries are the largest source of drinking water for population that lives the down stream. Many rivers are polluted and their ecological balance is disturbed in India due to wet disposal of fly ash are; Yamuna (Mehra A. et al., 1998, Walia A., et al., 1998), Jamuna river (Fulekar, M. H., 1989), Pandu river a tributary of Ganga river (Ravi Chander, D. V., 1994), Konar and Damodar river (Prasad B., 2004), Paravannar river (Khan et al., 2005), Brahmani and Nandira river (Rath, P., et al., 2009), Ganga river (Dwivedi, S., et al., 2006). Disposal of fly ash in unlined surface ash pond is not environmentally safe due to leaching of soluble salts and surface associated trace metals.

Many times ash dams/ ash ponds are filled up to their full capacity and even then plant authorities continue to dispose ash slurry in to the unlined ash pond. There are chances of failure of ash dam due to excess capacity fill up, which in turn is responsible for fly ash spill in surrounding area. It is reported in literature that in the year 2003, a breach in the embankment of a fly ash slurry pond at the Kolaghat Thermal Power Station West Bengal, India, caused fly ash spill. Recently the largest coal ash spill in U S (United States) history was recorded on December 22, 2008. The retaining wall broke on a waste retention pond at the Tennessee Valley Authority (TVA) Kingston Fossil Plant, Tennessee, United States of America.

1.3 LEACHING OF FLY ASH

Leaching of fly ash begins as soon as dry ash is mixed with water inside the power plant for wet disposal. Interaction with rainwater will also cause the leaching of trace metals, which will produce leachate. Leachates from the coal combustion byproducts contain metals which can contaminate the groundwater (Choi, S. K., et al., 2002, Twardowska I., et al., 2003). The elements that may leach from the ash in high concentrations, when in contact with an aqueous phase may include Ba, Br, Ca, Cl, F, Fe, K, Mg, Na, Mn, P and S (Abbas et al., 2003; Hansen et al., 2001; Nugteren et al., 2001; Steenari et al., 1999; Twardowska and Szczepanska, 2002; Wang et al., 2001). Similarly elements that are in relatively low concentrations but extremely mobile will leach, these may include As, B, Be, Bi, Cd, Co, Cr, Cu, Ga, Li, Mo, Ni, Pb, Sb, Se, V, W, and Zn (Bav'erman et al., 1997; Cheeseman et al., 2003; Minnesota Office of Environmental Services. 1997; Nable et al., 1997; Nugteren et al., 2001; Praharaj et al., 2002; Steenari et al., 1999; Twardowska and Szczepanska, 2002: EIA 2007; Daniels and Das, 2006). Possibly rare earth elements such as Eu, Sc and Sm present in some ashes may be mobile (Zhang et al., 2001). Because the mobile elements are non-degradable, their long-term fate is a matter of concern from the viewpoint of pollution and sustainability. It has been found that these major and trace elements have the potential to adversely affect the groundwater quality, if released into the subsoil in sufficient amounts.

There is a need to accurately assess the mobilization of elements that results from the weathering of these wastes and to understand those chemical processes in the ash/water systems that dictate the concentrations of these elements in the leachate (Fetter 1993; Kunungo and Mohapatra, 2000; Kyper 1992; Wassay 1992). A range of reactions may take place which control the speciation and the mobility of metal contaminant. These reactions include acid or base, precipitation or dissolution, oxidation or reduction, and sorption or ion exchange. Reactions like precipitation, sorption, and ion exchange can hinder the movement of metal contaminants in groundwater. These reactions depend on different factors like pH, Eh, conductivity, moisture content, and organic matter present. Groundwater flow characteristics also influence the transfer of metal contaminants.

In view of a wide range in leaching behavior by ashes, the question of what is acceptable emerges. For a proper determination of what is suitable, one should apply leaching tests that practically reflects the leaching behavior in the field and one should have a standard for suitability. The difference between leach tests and field conditions has been the driving force for the recent development of alternative experimental leaching protocols and numerical models.

There are more than hundred leaching tests available (Kim, A. G.,2008), choice of method depends upon the purpose to which it is employed, like environmental impact assessment effect under disposal or utilization scenario, to study leaching characteristics or to monitor post disposal scenario.

Purposes of carrying out leaching test on coal fly ash are as follows;

1. To classify fly ash as hazardous or non hazardous.
2. To determine the maximum amount of contaminants that can be leached out from fly ash.
3. To estimate the likely concentration of solutes in the supernatant of a wet disposal system and it can be used for risk assessments on time scale.
4. To assess the release potential of contaminants under specified reuse or disposal condition.

1.4 PROBLEM IDENTIFICATION

Power generating units are mega project, which require, not only huge capital investment but also various natural resources like, fossil fuels, water and land for disposal, thus create an impacts on environment and generates stress on local ecosystem. Disposal of fly ash is a major concern due to huge land requirement for construction of ash pond/ash lagoon/ash dam. Acquiring open lands for disposal in developing countries such as India is difficult, where land to population ratio is small. At present 26355 ha of land occupied by ash ponds in India. The requirement for land disposal of fly ash slurry would increase with the addition of more power plants. It was expected to go up to about 80,000 acres by the turn of century. About 2% of capital cost of thermal power goes towards fly ash disposal system i.e. approximately Rs. 200 Million in a 210 MW plant (Kumar, V. 2003). The Badarpur, Indraprastha and Rajghat power plants, Delhi together use 1.426 Million of water per day, of which almost 50 per cent is wasted in fly ash disposal. The other half is used for cooling in boilers. The Environment Pollution Control Committee (EPCC), set-up by the Supreme Court of India has recommended to the Delhi government, to reduce wastage by recycling and through disposal of dry fly ash. Water requirement for a coal-based power plant is about 0.005-0.18 m^3/kwh.The land requirement per mega watt of installed capacity for coal-based power plant is 0.1-4.7 ha (NEERI Report, 2006). In addition to this huge expenditure is done on road transportation just for dumping the fly ash and also on operation and maintenance of ash slurry discharge and storage system.

Fly Ash Mission was initiated in 1994 to promote gainful and environment friendly utilization of the ash in India. In a regulation issued by the Ministry of Environment and Forests (MOEF) in 1999, it was stipulated that all new coal thermal power plants should be able to use 100% of the fly ash they produce within the first nine years of operation. For existing power plants, MOEF has set a time period of 15 years for 100% fly ash utilization from the date of issue of the regulation. But the 100% utilization of fly ash as enforced by MOEF does not appear to be practically feasible, obviously wet or dry disposal of fly ash is bound to happen.

In view of the importance of fly ash disposal in India, it was decided to collect fly ash samples from four power plants for study purpose (not yet reported in literature) are Guru Hargobind Thermal power plant (Lehra Mohabat) Bhatinda Punjab state, Dadri Thermal Power Plant Uttarpradesh, Nashik Thermal Power Plant Eklahara, Maharashtra State and Suratgarh Super Power Plant, Rajasthan State of India. It was found that in the Guru Hargobind Thermal Plant Lehara mohabat, Bhatinda 49.58% of fly ash was being used in the year 2003-2004, at Nashik thermal power station 25% in 2003-2004, 7.55% in 2004-2005 and 22.2% in 2005-2006 respectively being used. At Dadri power plant, National Thermal Power Corporation (NTPC) has established for first time in Asia, a 100% dry ash extraction-cum-disposal system in the form of ash mound. Similarly ash utilization at Suratgarh Thermal Power Station is also encouraging, 22.85% utilization of generated ash have achieved during the year 2003-04. Less utilization of fly ash in the selected power plant enhances the possibility of the wet disposal of fly ash, which is a great environmental hazard.

Dry disposal of fly ash is responsible for air pollution. Wet disposal of fly ash causes the soil contamination, groundwater pollution and river pollution and creates health hazards. Both are equally harmful. Experimental work along with field investigation will represent true field condition and environmental predictions. Therefore Nashik ash pond was selected for field investigations based on accessibility to the area. Field survey is carried out at Nashik ash pond and adjoining Darna river for problems encountered due to wet disposal of fly ash. Farmers around Nashik ash pond complained about water quality of dug wells which is the only source of drinking water for them. They also pointed that water from dug well is not suitable for cooking, drinking and even for cleaning of vehicles and created health related problems such as gastrointestinal disease, kidney stone etc. Farmers lay a major share of the blame on the Nashik Thermal Power Plant for air borne fly ash particles for change in crop pattern, particularly grapes which they use to grow 15 years back.

Most of the ash ponds are unlined in India. Leachates from such ash pond are responsible for contamination of groundwater due to its toxicity. Therefore provision of liner is necessary. Presently there are no specific guidelines available in India from environmental regulating agencies for design and installation of impermeable liner for ash pond or the parameters or specification for impervious liner has been defined. There is need to monitor groundwater quality regularly for the presence of heavy metals due to wet disposal of fly ash. Fly ash leachate will contaminate first unsaturated zone and later join groundwater table. Thus the very first target of fly ash leachate is unsaturated zone Travel time to wells, background concentrations, sorption and degradation properties of contaminants determine the final concentration in the filtrate (Ray, C. et al., 2006). Provision of liner will serve two purposes, namely collection of leachate via leachate collection system at the top of the barrier (which protects unsaturated zone from contamination) and protection of groundwater. Flow and transport of leachate in the unsaturated zone often control the amount of contamination in the unsaturated zone. Leachte travel time via unsaturated zone to groundwater table is one such important parameter which will highlight need of low permeable liner and it will be also useful in remediation process or cleanup operations and ash pond management.

The successful management of solid waste arising from the combustion of low rank, high ash coal for power generation presents significant engineering and environmental challenge in India. Based on a detailed review of literature pertaining to the above aspects and problems identified, the present study has been directed towards the following objectives.

1.5 OBJECTIVES AND METHODOLOGY

The following objectives are considered for the present work

1. To carry out physical and chemical characterization of fly ash.
2. To perform cascade leaching test on fly ash to simulate field leaching behavior of fly ash.
3. To formulate mathematical model for prediction of metal concentrations in leachate.
4. To study the leachability or transport of metals through soil column.
5. To conduct metal analysis of immediately disposed ash slurry water, ash pond effluent, ash pond surface water and groundwater for pollution due to fly ash disposal around one of the thermal power plant.
6. To derive the leachate arrival time at the groundwater table including a low permeable liner using Green and Ampt infiltration theory.

A block diagram, as shown in Fig. 1.1 indicates the methodology adopted to achieve these objectives.

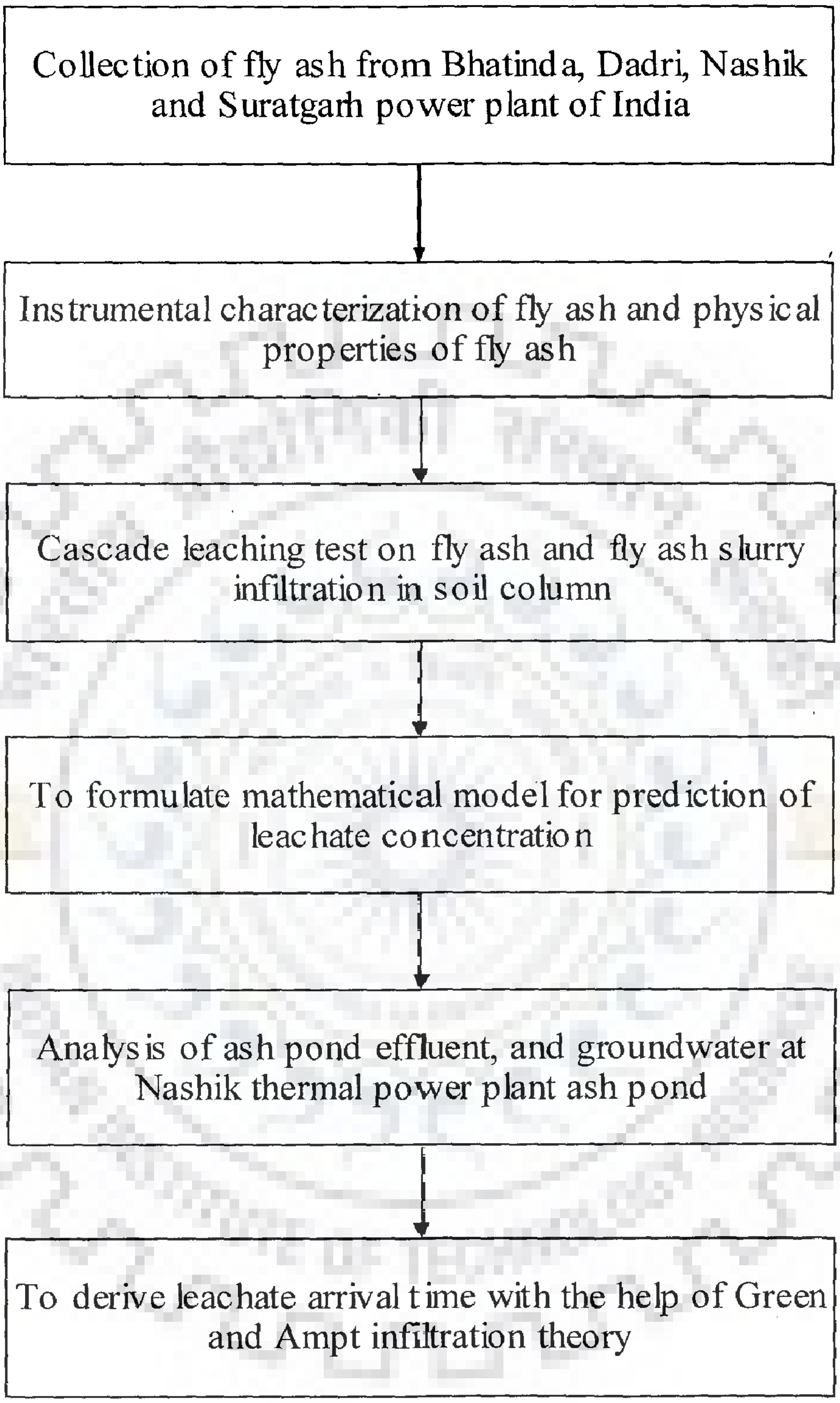


Fig.1.1 Block diagram of methodology

1.6 ORGANIZATION OF THE THESIS

The thesis has been organized into ten chapters. The contents of each are briefly described below:

Chapter 1 introduces the issues and challenges associated with fly ash disposal followed by purpose of carrying out leaching test, and environmental aspects of fly ash disposal. The objectives of the study and methodologies followed for the study are outlined. The organization of the thesis describes the details of each chapter of the thesis.

Chapter 2 presents literature review on the characteristics of fly ash, analytical techniques/instrumental techniques used for characterization of fly ash, properties of fly ash, leaching behavior of fly ash, environmental effects of fly ash disposal particularly on surrounding soil, surface water, groundwater and river. Review of potential mechanisms which control the release of metals and metalloids from coal combustion byproducts during leaching process, types of liners used for disposal facility.

Chapter 3 describes the analytical techniques used for the characterization of fly ashes. It also describes in detail of experimental set-up used in the laboratory and various protocols used for the experimental investigation.

Chapter 4 elaborates Instrumental characterization of fly ash and investigation of physical as well as chemical properties and other useful properties. Atomic force micrographs of fly ash are reported for the first time in Indian context.

Chapter 5 presents the laboratory cascade leaching test performed at pH =7 and pH= 4, and which gives cumulative percentage of metals leached at pH = 7 and pH= 4 in fly ash transport or pore water.

Chapter 6 illustrates the model developed for the prediction of leachate concentration and same is used for prediction of leachate concentrations.

Chapter 7 deals with laboratory open percolation column soil leaching test, which was carried out on Bhatinda and Nashik fly ash.

Chapter 8 presents metals analysis of ash pond surface water, immediately disposed slurry water, effluent samples and groundwater at Kotamgaon and Hinganvedhe villages near to Nashik ash pond. Physical observations made through actual site visit are also elaborated.

Chapter 9 contains the derivation of leachate arrival time at water table for considering a low permeable liner is placed at the bottom of the ash pond using Green and Ampt infiltration theory.

Chapter 10 presents the conclusions of the research work and future scope of work. Towards the end, list of references has been made.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

Power generation is one of the thrust areas for the economic growth and overall development of a country. Thermal power stations using pulverized coal as fuel generate large quantities of ash as a byproduct. Disposal of coal ash is posing a serious threat to environment. The Indian coal has a low calorific value of 3000-4000 kcal/kg and since low ash high-grade coal is reserved for metallurgical and other industries, thermal power plants have no choice but to use low grade coal having ash content up to 55%. Further, the deteriorating quality of coal will aggravate the situation, if clean coal technologies are not adopted at large scale.

About 130 million tonnes of ash is being produced annually in the country presently, which may be doubled in the next 10 years. It is most important and in the best national interest to utilize coal ash or disposal be done in safe manner, so as to save environment from pollution and agricultural land from destruction. Utilization of ash solves two problems with one effort viz., elimination of a solid waste problem on one hand and availability of the most needed construction material on the other. In view of large-scale generation of fly ash, lot of Research and Development work is going on across the country on utilization of ash for the construction of road and railway embankments, as backfill in underground or open cast mine openings and low lying areas, soil stabilization and agricultural use, etc. The major potential adverse impacts of ash disposal on terrestrial ecosystems include leaching of potentially toxic trace metals from ash into soils and groundwater; reductions in plant establishment and growth, changes in plant elemental composition and increased cycling of potentially toxic metals through food chain (Carlson C L., et al., 1993).

In the present chapter, a detailed literature review is presented on fly ash classification, mineralogy, morphology, physical and chemical properties of fly ash, leaching behavior of fly ash, various leaching tests used. The effect of ash disposal on soil, water and ecosystem and its health aspects are described. Liners are used in ash pond for containment of pollutants from land-filled ash pond, so the types of liners and their importance are also highlighted in this chapter.

2.2 COAL ASH

Coal ash is a waste material produced by the burning of coal in coal fired thermal power stations. The process of combustion produces two types of residue, one which settles at the bottom of the furnace called as bottom ash and the other which is carried away by the fuel gases to be collected by electrostatic precipitators (ESP) called as fly ash. Bottom ash is typically in the range in size from fine sand to gravel and is sub-angular in shape with glassy texture and porous structure. Fly ash is a silt-sized material composed primarily of glass spheres together with some crystalline material and varying amount of unburned carbon. Formation of unburned carbon depends on coal properties (reactivity/burning profile), pulverized coal fineness (milling), and operational parameters (primary/secondary air ratio, O_2 level, burner tilt, flame turbulence/air-fuel mixing, furnace temperature, fuel residence time etc) (Mandal, P. K., 2008).

In thermal power plant, the disposal of coal ash is done by a wet system or a dry system. In wet system, fly ash and bottom ash are mixed with water to form slurry and the entire mixture is hydraulically transported to ash pond. In the ash pond, the ash is allowed to settle by sedimentation and the clear water is decanted off. The ash stored in pond is called as pond ash (Dayal et al., 1999, and Reddy et al., 1999). In dry disposal system, the fly ash collected from various electrostatic precipitators is pneumatically conveyed to a silo, where it is conditioned with water before loading on to trucks or a conveyer belt for transportation to an ash mound. The dry ash disposal system is highly eco-friendly and has many advantages over wet disposal system. Therefore, all new thermal power stations are adopting dry disposal system.

The physical and chemical properties of ash are dependent on type (e.g. anthracite, bituminous, sub-bituminous, and lignite) and source of coal, method and degree of coal preparation, cleaning and pulverization, type and operation of power generation unit, ash collection, handling and storage methods, etc.

2.3 COAL ASH FORMATION AND LEACHING POTENTIAL

During coal combustion, most of the carbon present in the source coal is converted to CO_2 and emitted through the stack while the mineral fraction of the coal is converted to form the matrix of the coal ash. Due to variation in source coal composition and combustion conditions, the composition of bottom ash and fly ash can vary widely, with fly ash typically being more enriched in trace elements. The elements found in coal can be divided into three classes based on their behavior and partitioning during combustion which is controlled by the volatility and boiling point of the element, and its associations in the coal.

Class I elements include Al, Ca, Ce, Dy, Eu, Fe, Hf, K, La, Mg, Mn, Nd, Rb, Sc, Si, Sm, Ta, Tb, Th, Ti and Yb and are not volatilized during combustion. Instead, they form a melt of relatively uniform composition that becomes the matrix of both the fly ash and the bottom ash and do not exhibit a significant change in enrichment with changing fly ash particle size (Klein et al., 1975; Coles et al., 1979). Trace elements in this category include lithophilic elements which are associated with the aluminosilicate matrix in coal and are expected to be distributed within the aluminosilicate matrix of the fly ash. However, due to reactions with surface-formed H_2SO_4 they may also be found in surface-associated sulfate crystals and exhibit an increased solubility (Coles et al., 1979).

Class II includes chalcophilic and siderophilic elements such as As, Cd, Ga, Mo, Pb, Sb, Se, W and Zn, which are somewhat volatile during combustion (Klein et al., 1975; Coleset et al., 1979). Boron also is likely to belong in this group (Davison et al., 1974). During the initial stages of combustion, reducing conditions presumably cause the bonds between the trace elements and either sulfide or the organic matrix to break, allowing these elements to form volatile species. A fraction of the sulfur is volatilized as SO_2 during combustion and the remainder is retained in the ash, primarily as sulfate minerals including gypsum (Clemens et al., 1999). The behavior of the chalcophilic trace elements is not analogous to that of the iron in the pyrite minerals and so it appears to depend on the volatility of the specific elements and compounds rather than the association with sulfide alone (Martinez-Tarazona and Spears, 1996). In the gas stream, class II elements are oxidized to form less volatile species that condense on or are adsorbed to fly ash particle surfaces as the gas cools (Klein et al., 1975). They tend to have higher enrichment on smaller sized particle fractions within the fly ash due to increased surface area (Coles et al., 1979; Martinez-Tarazona and Spears, 1996). The behavior of some elements including, Ba, Be, Co, Cr, Cs, Cu, Na, Ni, Sr, U, and V is generally between classes I and II (Klein et al., 1975; Coles et al., 1979).

Class III elements, including Hg, Cl, and Br, are very volatile and remain almost completely in the gas phase (Klein et al., 1975). These elements are typically emitted through the stack almost exclusively and only minor concentrations are found in either the fly ash or the bottom ash. The potentially toxic trace elements, such as As, Pb, Cd, Cr, Zn, are commonly associated with the nonmagnetic fraction of fly ash in glass phase, and are distributed on the surface of the ash particles as shown in Table 2.1 with their higher dissolution characteristics (Smith et al.,1979; Meserole et al.,1979; Natusch et al.,1974). Cu, Mn, Co, Ni, etc. are distributed in the magnetic fraction, with poor dissolution characteristics, and Fe occurs in both phases of fly ash (Murarka et al.,1992; Ram et al., 1996; Smith et al., 1979)

Table 2.1 Fraction of Total Metals Associated with the Surface of Fly Ash Expressed as Percent of Total Metals (Theis et al.,1982).

Species	Range	Average
Arsenic	65 - 100	93
Cadmium	<2 - 58	25
Chromium	15 - 84	44
Copper	25 - 75	48
Lead	5 - 40	8
Nickel	5 - 42	11
Zinc	10 - 70	30

2.4 FLY ASH CLASSIFICATION

Fly ash is fine powder like material collected from electrostatic precipitator or bag house and most of the particles are spherical in shape either solid or hollow and mostly glassy (amorphous) in nature. The color of fly ash varies from tan to grey to black, depending on the amount of unburned carbon present in fly ash. Lighter the color, lower the carbon content. The American Society for Testing and Materials (ASTM) classifies fly ash into two categories i.e. Class F and Class C, based on the physical and chemical properties of fly ash (Table 2.1) (ASTM C 618-99). Class F fly ash is produced from burning of anthracite and bituminous coal and Class C is produced from lignite and sub bituminous coal and is usually contains a significant amount of lime (CaO).

Table 2.2 Chemical requirements for fly ash classification.

Properties	Fly ash class	
	Class F	Class C
Silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and iron oxide (Fe_2O_3), min, %	70.0	50.0
Sulfur trioxide (SO_3), max, %	5.0	5.0
Moisture content, max, %	3.0	3.0
Loss on ignition, max, %	6.0	6.0

2.4.1 Properties of fly ash

Information regarding the physical, chemical and engineering properties of coal combustion byproducts are required before these materials can be safely and effectively used. Physical and engineering properties are very useful for application of coal combustion byproduct in utilization. Fineness of fly ash (Chai,J., et al.,1999) is important in fly ash cement mortar and it plays major role in pozzolanic reactions as well (Theerawat S., et al., 2006). Information pertaining to the chemical composition is important for addressing the potential of coal combustion byproducts utilization and disposal (Walker, H. W., et al., 2002).

2.4.2 Physical Properties

A summary of specific gravity and particle size distribution of fly ash, bottom ash and pond ash produced in some of the thermal power stations in India is given in Table 2.3 (a), (b), and (c) respectively. In general, specific gravity of coal ash is around 2 but varies to a large extent (1.6 to 2.6) (Pandian et al., 1998). The variation of specific gravity of coal ash is due to combination of various factors like gradation, particle shape, and chemical composition (DiGioia and Nuzzo, 1972, and Skarzynska et al., 1989). The low specific gravity of fly ash resulting in low unit weight as compared to soils is an attractive property for its use in geotechnical applications. The low value of specific gravity is due to presence of a high proportion of cenospheres or hollow ash particles (Gray and Lin, 1972). The higher value of specific gravity is attributed to high iron (Fe_2O_3) content (Seals et al., 1972, Singh, 1996, and Trivedi et al., 2002).

The particle size distribution of ash provides considerable insight into its properties and behaviour. The fly ash is typically a uniform silt size material and the grain size of bottom ash varies between sand to fine gravel. The particle size of pond ash falls between sand to silt size. Because of spherical shape, small surface area, uniform size of particles, most ashes have no plasticity (Gray and Lin, 1972, Martin et al., 1990, DiGioia and Brendel, 1998, and Dayal and Sinha, 2000).

Table 2.3 (a): Physical Properties of Fly Ash

Thermal Power Plant	Specific Gravity G	Particle Size Distribution (%)					Reference
		Sand Size 4.75-0.075 mm	Silt Size 0.075-0.002 mm	Clay Size < 0.002 mm	Uniformity Coefficient C_u	Coefficient of Curvature C_c	
Rajghat	2.19	20	77	3	5.65	0.9	Kaniraj and Gayathri, (2003)
Gulbarga	2.58	5	95	0	2.43	0.84	Prashanth et al., (2001)
Raibareli	2.05	34	65	1	5.88	0.75	Sridharan et al., (2001)
Korba	1.98	34	63	3	6.0	1.14	--do--
Vijayawada	1.95	27	70	3	5.7	0.61	--do--
Ghaziabad	2.31	7	91	2	8.0	2.9	--do--
Ramagundam	2.18	12	83	5	1.59	1.09	--do--
Neyveli	2.55	27	70	3	9.0	3.16	--do--

Table 2.3 (b): Physical Properties of Bottom Ash

Thermal Power Plant	Specific Gravity G	Particle Size Distribution (%)						Reference
		Gravel >4.75 mm	Sand Size 4.75-0.075 mm	Silt Size 0.075-0.002 mm	Clay Size < 0.002 mm	Unifo. Coeffi. C_u	Coeffi. of Curva. C_c	
Dadri	2.01	0	76	19	5	2.3	15.4	Vittal et al., (2003)
Raibareli	1.66	0	88	11	1	7.8	3.7	Sridharan et al., (2001)
Korba	2.15	1	92	6	1	4.7	2.1	--do--
Vijayawada	1.82	14	86	0	0	6.55	1.36	--do--
Ghaziabad	2.01	1	64	34	1	7.5	1.4	--do--
Badarpur	1.95	6	82	11	1	9.09	1.03	--do--
Ramagundam	2.08	15	73	11	1	8.02	1.6	--do--
Neyveli	2.08	0	88	9	3	5.2	2.05	--do--
Singrauli	2.45	0	89	11		7.14	0.83	Swami et al., (2000)

Table 2.3 (c): Physical Properties of Pond Ash

Thermal Power Plant	Specific Gravity G	Particle Size Distribution (%)						Reference
		Gravel >4.75 mm	Sand Size 4.75-0.075 mm	Silt Size 0.075-0.002 mm	Clay Size < 0.002 mm	Unifo. Coeffi. C_u	Coeffi. of Curva. C_c	
Raibareli	1.93	0	65	34	1	4.57	1.59	Sridharan et al., (2001)
Korba	1.91	0	89	10	1	3.60	1.80	--do--
Vijayawada	2.01	2	90	7	1	3.00	0.79	--do--
Badarpur	2.00	0	77	22	1	9.40	1.64	--do--
Ramagundam	2.15	1	97	1	1	3.37	1.41	--do--
Neyveli	2.50	3	82	13	2	9.67	1.93	--do--
Singrauli	2.24	40		60		9.00	0.69	Swami et al., (2000)
Ropar	1.86	0	64	36	0	-	-	Pathak et al., (1999)

2.4.3 Chemical Composition

Coal ash is derived from a natural material, and as such, its composition depends upon the type of coal used in thermal power stations. The main chemical components of coal ash are identified as silica, alumina, iron oxide, and alkalis. A typical range of chemical composition of ashes from different parts of the world along with Indian fly ash is given in Table 2.4. and Table 2.5 which show the range of various chemical components of pond ash and bottom ash respectively. The free lime (CaO) and unburned carbon contents affect the engineering and physical properties of ash. Free lime influences age hardening properties while unburned carbon content affects compaction and strength characteristics (Gray and Lin, 1972, DiGioia et al., 1977, and Achoubi et al., 1987). Leaching characteristics mainly depends on amount of free lime present in fly ash (Pandian, N. S., 2004).

Table-2.4: Chemical Composition of Fly Ashes

Chemical Components	British Ash[a] (%)	American Ash[a] (%)	Swedish Ash[a] (%)	Polish Ash[a] (%)	Indian Ash[a] (%)
SiO_2	38-58	30-58	30-53	43-52	55-71
Al_2O_3	20-40	7-38	14-33	19-34	20-27
Fe_2O_3	6-16	10-42	10-14	0.7-10.7	1.7-4.8
CaO	2-10	0-13	0.9-6.1	1.7-9.4	0.5-5.6
MgO	1-3.5	0-3	4-6	1-2.9	0.2-0.9
Na_2O, K_2O	2-5.5	0.4-2	1.6-3.5	0.4-0.9	0.7-0.81
SO_3	0.5-2.5	0.2-1	0.4-1.5	0.3-0.8	0.1-0.5
Unburned Carbon	NA	0-4.8	0.9-3.3	1.9-9.9	0.2-0.6

[a] Trivedi and Sud, (2004)

NA- Not available

Table-2.5: Chemical Composition of Pond Ash and Bottom Ash

Chemical Components	Indian Pond Ash[a] (%)	Indian Bottom Ash[a] (%)	Turkey Bottom Ash[b] (%)	USA Bottom Ash[c] (%)
SiO_2	47-75	50-72	15-58	20-60
Al_2O_3	11-33	13-27	8-28	10-35
Fe_2O_3	3-11	4-11	3-20	5-35
CaO	0-0.6	0-0.8	2-24	1-20
MgO	0-0.8	0-0.7	0.92-4.5	0.3-4
Na_2O, K_2O	0.1-1	0-1.4	0.68-10.87	1-4
SO_3	NA	NA	Trace-13.2	0.1-12
Unburned Carbon	0-8	1-13	0-1.03	NA

[a] Sridharan et al., (2001) ; [b] Kayabali and Bulus, (2000) ; [c]Seals et al., (1972)

Coal produced in India has low sulphur content but high ash content, whereas coal produced in USA is rich in sulfur and it contains less ash. Environmental impacts associated with certain trace elements, e.g., As, Se, Cr, Cd, Ni, and Pb, are found to be more concentrated in the smaller fly ash particles as the result of volatilization-condensation and adsorption mechanisms (Natusch, D. F.S., et al., 1974). The pH of coal ashes can vary over a wide range from extremely low to high value. 50% of Indian fly ashes are alkaline in nature; about 67% of Indian pond ashes are alkaline. Almost all Indian bottom ashes are dominantly alkaline (Shridhran et, al., 2007).

2.5 MINERALOGY OF FLY ASH

The adverse effects of ash as well as its probable utilization are largely dependent on its mineralogical and other physico-chemical properties. Ash mineralogy has strong bearing on environmental impacts and use of the fly ash (Sahu K.C., 1999). The inorganic oxides in fly ash may be in crystalline or glassy phases. The relative amounts of crystalline and glassy phase materials in fly ash depend largely on the combustion and glassification process used at the particular power plant. When the maximum temperature of the combustion process is above 1200°C and the cooling time is short, the ash is mostly glassy phase material (McCarthy et al.,1987).

When a more gradual cooling of the ash particles occurs, crystalline-phase calcium compounds are formed. The minerals present in the coal dictate the elemental composition of the fly ash, but the mineralogy and crystalline nature of the ash are dictated by the boiler design and operation. The primary factors that influence the mineralogy of a coal fly ash are chemical composition of the coal, coal combustion process including coal pulverization, combustion, flue gas clean up, fly ash collection operations, and the additives used during combustion, including oil additives for flame stabilization and corrosion control additives (Baker, 1987). Hydration and leaching properties of fly ash are significantly influenced by the mineralogy of the fly ash, which includes the relative proportion of the spherical glassy phase and crystalline materials, the size distribution of the ash, the chemical nature of glass phase, and the type of crystalline material (Roy et al., 1985).

The major elements contained in fly ash are Ca, Al, Si, and Fe, along with lesser amounts of Mg, S, and C, as well as trace amounts of metals and metalloids, e.g., As, Ba, Cd, Cr, Se, and Hg, (Tishmack., J.K., 2004, Adriano, D. C., 1980). These elements, mostly originating from coal, react with oxygen in the flue gases and form both crystalline and non-crystalline compounds through condensation or/and crystallization within melt droplets (Klein, D. H., 1975). Quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), tricalcium aluminate ($Ca_3Al_2O_6$), melite ($Ca_2(Mg,Al)(Al,Si)_2O_7$; merwinite ($Ca_3Mg(SiO_4)_2$); C_3S(Ca_3SiO_5); C2S(Ca_2SiO_3); ferrite spinel ((Mg,Fe) ($Fe,Al)_2O_4$); magnetite (Fe_3O_4), hematite (Fe_2O_3), lime(CaO); anhydrite($CaSO_4$); periclase (MgO);and alkali sulfates ($(Na,K)_2SO_4$) are mineral components normally found in fly ash (Tishmack., J.K., 2004). Fly ash is basically an amorphous ferro-aluomino silicate which is also characteristically high in Ca, Na, Mg and K (Adriano, D. C., 1980). Among these minerals, quartz is believed to originate from silt and clay particles in the coal (Tishmack., J.K., 2004). Mullite does not occur naturally in the coal, it is assumed to form during combustion by the thermal decomposition of naturally occurring aluminosilicates such as kaolinite (White S. C., et al., 1990). Formation of mullite is likely due to re-crystallization of molten clay minerals, e.g., quartz-albite-kaolinite mixtures, at temperatures higher than 1000°C during the combustion process (Tishmack., J.K.,2004, Glasser., F. P., 2004).

The decomposition reactions for kaolinite are:

$$Al_2O_3, 2SiO_2\,2H_2O \quad 500^\circ C \longrightarrow Al_2O_3, 2SiO_2 + 2H_2O$$

Kaolinite ⟶ Metakaoline +Steam

$$3(Al_2O_3, 2SiO_2)\ 980^\circ C \longrightarrow 3Al_2O_3\ .\ 2SiO_2 + 4\ SiO_2$$

Metakaoline ⟶ Mullite + Silica

Presence of hematite and magnetite in fly ash might be due to the oxidation of Fe-bearing minerals; e.g., FeS_2, in the coal. The amorphous glass fraction of fly ash is formed during the cooling of the melt phase (Tishmack., J.K., 2004). The glass content in high calcium fly ash was more than low calcium fly ash and mullite is absent in high calcium fly ash (Das, S. K., et al., 2005).

Khanra, S., et al., (1998) obtained XRD pattern of pre and post leached four Indian fly ashes as α-quartz, mulite, magnetite, rutile and other phases. Shorter burning span favoured the formation of magnetite. Presence of both hematite and magnetite in all investigated fly ashes suggest that different fly ash particles have different residence time in the combustion zone. Iron is distributed in magnetic and nonmagnetic phases of fly ash. They concluded that concentration profile of toxic trace elements in leachates of fly ash will follow the similar trend to that of iron. Mineralogical phases identified with X-ray diffraction analysis for some Indian fly ashes are shown in Table 2.6

Table-2.6: Minerals observed in Indian fly ashes through XRD studies

Sr no	Reference	Thermal power plant	Minerals identified
1	Ravi Chander D. V. et al., (1994)	Panki thermal power plant, Kanpur, Uttarpradesh, India	Quartz, Chlorite,Illite, Kaolinite, and Mullite.
2	Trivedi. A., et al., (2002)	Ropar thermal power plant , Punjab, India	Quartz, Mullite, hematite and magnetite.
3	Kolay. P. K., et al., (2001)	Dhanu thermal power plant, Maharashtra, India.	Alumina, Quartz, Mullite, Sillmanite and magnetite.
4	Kaniraj S. R., et al., (2004).	Dadri thermal power plant, Uttarpradesh, India	Quartz, Mullite, Sillmanite Gehlanite, hematite and Melilite.
5	Gaikwad P. G., et al., (2009)	Bhatinda thermal power plant, Punjab, India	Quartz, Mullite, hematite and magnetite.
6	Suresh I V., et al., (1998)	Vijaywada thermal power station, Andhra Pradesh, India	α Quartz, Mullite, Magnetite.

2.6 MORPHOLOGY OF FLY ASH

Morphology can affect physical and chemical properties of the ash which in turn relate to environmental and technological aspects of fly ash disposal and utilization. Morphology of a fly ash particle is controlled by combustion temperature and cooling rate. The chemical and physical properties of fly ash particles are function of the mineral matter in the coal, the combustion conditions and post combustion cooling. During the combustion process, the heat causes the inorganic minerals to become fluid or volatile or to react with oxygen. During cooling, it may form crystalline solids, spherical amorphous particles or condense as coatings on the particles (Kutchko,B. G., et al., 2006).

Results of many morphological examinations on coal fly ash have been published by various researchers and have included observations of solid sphere (Gutierrez et al.,1993), plerosphers (Goodarzi et al.,2009), cenosphers (Kolay P. K., et al., 2001), irregular particles (Schure, M. R., et al.,1985) micron and submicron particles (Kaufherr N., et al., 1984). Torrey S (1978) reported that the word cenosphere is derived from two Greek words, kenos (hollow) and sphaira (sphere). These ash particles get their hollow spherical shape due to cooling and solidifying around a trapped gas (generally CO_2 and N_2) from the molten droplets of inorganic coal residue. The amount of cenospheres or plerospheres in an ash normally depends on its carbon and iron content (Kolay P. K., et al., 2001). Norton G. A., et al., (1986) found the internal morphology of iron rich fly ash fractions is both complex and diverse.

Light microscopy was (Fisher G. L., et al., 1978) used to define 11 major classes of coal fly ash particles (a) amorphous nonopaque (b) amorphous opaque (c) amorphous mixed opaque and nonopaque (d) rounded, vesicular, nonopaque (e) rounded, vesicular, mixed opaque nonopaque (f) angular lacy opaque (g) nonopaque, cenosphere (hollow spheres); (h) nonopaque plerosphere (sphere packed with other spheres) (i) nonopaque, solid sphere (j) opaque sphere and (k) nonopaque sphere with either surface or internal crystals.

Scanning Electron Microscopy (SEM) is one of the most useful and well known analytical techniques for ash characterization (Kutchko,B.G.et al., 2006). Diamond, S., et al.,(1986) used SEM for internal and external morphological characterization of low calcium fly ashes. Scanning electron micrographs revealed that ash contained a variety of particles with different shapes and compositions. Some of the particles were glassy spheres both solid and hollow (cenospheres), also clinker-like (holey) and irregular particles were observed. Platy particles occasionally stacked were also observed by (Leonards, G. A., et al., 1982).

SEM-EDX (Scanning Electron Microscope/Energy Dispersive Using X-Ray) analysis provides fast and accurate results on the morphology, chemical composition and microstructure of ferrospheres of fly ash particles (XUE, Q., et al., 2008), which in turn helpful to understand environmental issues related to the disposal and utilization of fly ashes. Various investigation using SEM- EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy) (Kutchko,B.G.et al., 2006), SEM-EDX (Sarkar, A., et al., 2005, Goodarzi, F. 2006 and XUE, Q., et al., 2008), reported in literature for morphological characterization and various phases of fly ash. Gieré, P., et al., (2003) observed micro and nanochemistry of fly ash from USA power plant by using SEM, Transmission Electron Microscope (TEM), Electron Microprobe Analysis (EPMA) and XRD.

Scanning Force Microscopic (SFM) image of fly ash was first reported by Vempati R. K., et al., (1994). The surface topology of the composite fly ash imaged by 10 μm scanner was uneven and contained a few protuberances indicative of an amorphous phase. Based on three dimensional parameters, the image may be of either of plerosphere of cenosphere surface. A conchoidal fracture of quartz was observed. SEM gives a sufficient general overview of particle shape in the case of relatively coarser material, which is necessary for evaluation of the heterogeneity of the larger particles whereas AFM (Atomic Force Microscopy) gives significant information about surface texture of fine particles of fly ash (Papadakis, V. G., 1999). For fly ash particles, AFM showed two types of spheres, dark, large ones (approximately 100 μm) with numerous craters on their surface and clear, small ones (approximately 10 μm) with smooth roughness (Demanet C.M., 1995). Kutchko,B. G. et al., (2006) observed that quartz and aluminosilicates are found as crystalline and a amorphous particles.

Iron rich particles exist as mixed iron oxide/alumino-silicate particles. Calcium is associated with sulfur or phosphrus, not with the alumino-silicate. Goodarzi, F. (2006) examined total particulates (PM) and size fractions $PM_{>10}$, PM_{10}, and $PM_{2.5}$ with SEM-EDX to check the impact of particulates on human health. Sarkar, A., et al., (2005) used SEM-EDX mainly for morphological analysis and for determination of chemical composition of fly ash. Result obtained through this study was used to check the suitability of fly ash as construction material or extraction process. They found that data obtained through various instrumental analyses is helpful in understanding the potential of environmental and health impacts associated with fly ash disposal. Micro and nanochemical examination is also useful for study of ash-fluid interaction process, which in turns can be useful to take decision regarding disposal strategy (pre disposal ash treatment washing to dissolve surface deposits, magnetic removal of Fe rich particles).

2.7 LEACHING OF FLY ASH

For many coal combustion byproducts utilization and to know the environmental consequences of disposal, it is necessary to understand the leaching behavior of these materials. When ash water interaction takes place the final product is called as leachate.

$$\text{Fly ash} + \text{water} \longrightarrow \text{Leachate}$$

(Leachee) (Leachant)

The smaller particles have larger specific surface area, making a larger area susceptible to hydrolysis (Fischer, 1978). Studies have shown that only about 1-3% fly ash material is soluble in water with lignite fly ashes having a higher proportion of water soluble constituents.

2.7.1 Leaching Mechanisms

When a porous matrix containing heavy metals is exposed to an aqueous medium, the pore water becomes contaminated due to desorption of metals or/and dissolution of metal compounds. The process of desorption of metals or dissolution of metal compounds in the pore water is called "solubilization" (Conner, 1990). The difference in chemical potential between the pore fluid and the fluid surrounding the porous matrix induces diffusion of metals through pore fluid and causes leaching. When the aqueous solution or water passes through the porous matrix, contaminant transport occurs due to advection along with dispersion (which includes molecular diffusion) of contaminants through pore water (Fetter 1993; Fleming et al., 1996).The main mechanisms that cause leaching are shown in Figure 2.1. Release of trace metals from coal combustion byproduct is mostly controlled by adsorption-desorption and dissolution (Bin-Shafique et al., 2006; Mudd et al., (2004); Murarka et al., 1991; Wang et al., 2004). Desorption phenomenon was adopted by Chapelle, F. H., (1980), in order to model the process of leaching from a coal fly ash matrix and entering aqueous phase. Murarka et al., (1991) suggests that leaching of trace elements from fly ash is solubility controlled. Edil et al., (1992) observed typical leaching curve for release of metals from class C fly ash as: first flush response, lagged flush response.

First flush leaching pattern generally corresponds to adsorption- controlled release under conditions where pH and redox potential (Eh) remain relatively constant and can be described mathematically by the advection- dispersion- reaction equation (ADRE) with instantaneous, linear, and reversible sorption (Bin-Shafique et al., 2006). Lagged leaching response can be attributed to a variety of geochemical processes and generally cannot be described using a single function (Li, L., et al., 2006). Metal partitioning is a function of pH, the liquid-to-solid ratio, and the physical and chemical characteristics of the fly ash and soil (Kosson et al., 2002; Wang et al., 2004; Bin-Shafique et al., 2006).

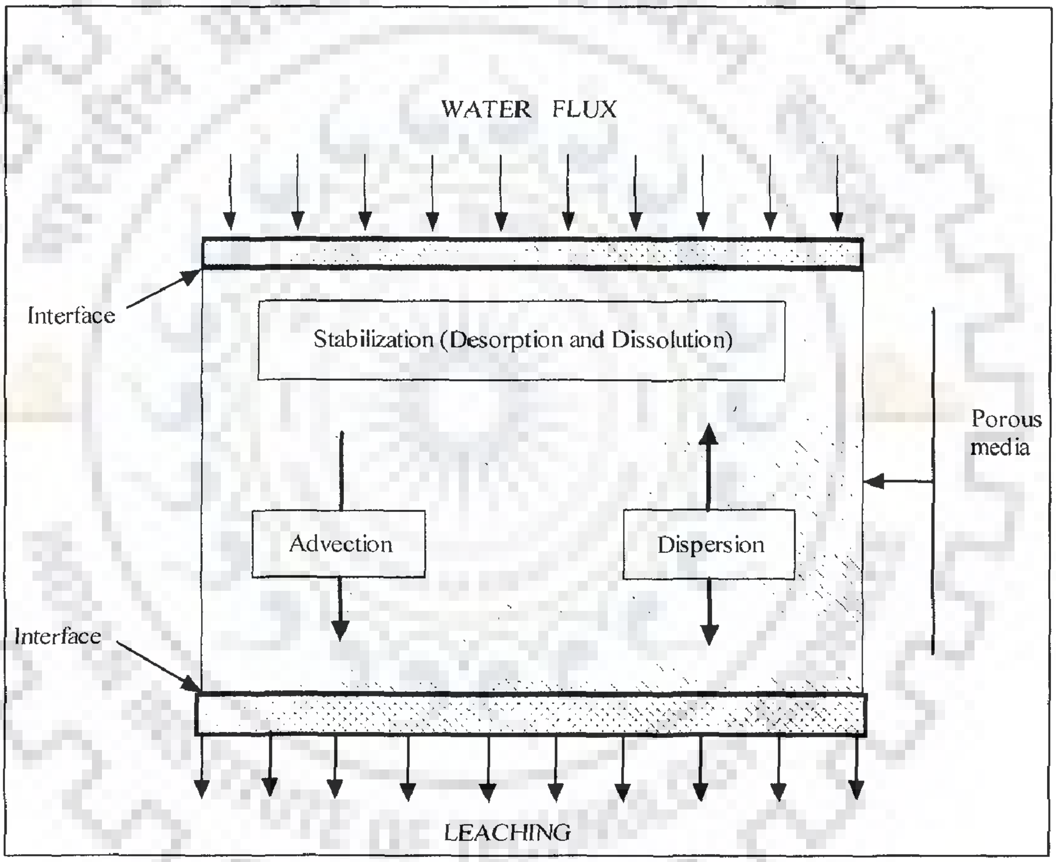


Figure 2.1: Schematic of leaching mechanisms (Cote et al., 1985)

2.7.2 Factors affecting leaching

There are number of factors that can influence the rate at which constituents are dissolved from material matrix. These can be divided into physical, chemical and biological factors. The typical physical factors that include material characteristics such as particle size, shape, and surface area exposed to leaching, homogeneity/heterogeneity, permeability of material during test/field, temperature during leaching, flow rate during leaching, porosity of solid matrix, hydrogelogical conditions. Chemical factors includes: equilibrium or kinetic control of release, potential leachability of constituents, pH of material or that imposed by the surrounding (e.g.CO_2 effects), complexation with inorganic or organic compounds, redox condition of the material or that imposed by the surroundings, sorption processes, biologically generated factors capable of affecting pH, redox and complexation with organic matter. It was found that pH is the most controlling factor in the leaching behavior of fly ashes. Roy (1984) reported that the mechanism responsible for the change in pH of initially acidic system remains enigmatic. Number of physical and chemical factors that can influence leaching behavior of fly ash are porosity of fly ash, particle size, leaching time, liquid to solid ratio, temperature, chemical composition of fly ash, phase composition of fly ash, leachant type, pH and redox potential (Zandi M., 2007).

2.8 TYPES OF LEACHING TESTS

Types of leaching tests include agitated extraction tests, serial batch tests, flow through tests, flow around tests, etc. These tests address different aspects of leaching fluid, the kinetics of leaching, leaching as a function of time, etc. Some of the uses of leaching tests include regulatory purposes, environmental impact assessment, scientific studies and waste management (Sorini, S. S., 1996).

2.8.1 Standard leaching test

Leaching or extraction tests are often used as expedient means to evaluate the potential of a material to release contaminants to the environment. The material is exposed to a leachant (typically water) and the amount of contaminant in the leachate is measured and compared to an established standard (USEPA 1994). Some of the widely used standard leaching tests with their corresponding extraction conditions are shown in Table 2.7.

Table-2.7: Extraction Conditions for Different Standard Leaching Tests

Test Procedure	Method	Purpose	Leaching Medium	L/S ratio	Particle Size	Time of extraction
Water Leach Tests	ASTM D3987-85	To provide rapid means of obtaining an aqueous extract	Deionized water	20:01	Particulate or monolith as received	18 hr
TCLP	EPA SW-846 Method 1311	To compare toxicity data with Regulatory level. RCRA Requirement.	Acetate buffer	20:01	<9.5 mm	18 hr
Extraction Procedure Toxicity (EP TOX)	EPA SW-846 Method 1310	To evaluate leachate concentration RCRA Requirement.	0.04 M acetic acid (pH=5.0)	16:01	<9.5 mm	24 hr
Multiple Extraction Procedure	EPA SW- 846 Method 1320	To evaluate waste leaching under acid condition.	Same as EP Toxicity, then pH=3.0	20:01	<9.5 mm	24 hr Extraction per stage
Synthetic Precipitation Leach Procedure	EPA SW- 846 Method 1312	For waste exposed to acid rain	DI water, pH adjusted to 4.2 to 5.0	20:01	<9.5 mm	18 hr

2.8.1.1 Water Leach Test (ASTM 1992, D 3987-85)

The water leach test defined in ASTM D3987-85 is intended as a rapid means of obtaining an aqueous extract from a solid waste. Site-specific leaching conditions are not simulated in this test. The method is only appropriate for inorganic compounds. The material to be tested is mixed homogeneously and then a representative 70-g sample of the material is added to 1400 mL of Type IV reagent water in a sealed 2-L container. The mixture is agitated continuously for 18±0.25 hours at a temperature between 18^0C and 27^0C. The mixture is then allowed to settle for 5 min, and the aqueous phase is separated by decantation. Decant is filtered through 0.45 μm filter paper and subjected to chemical analysis (ASTM 1992).

2.8.1.2 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP test defined in EPA Method 1311 is designed to determine the mobility of both organic and inorganic compounds present in liquid, solid and multiphase wastes. Waste samples are crushed to a particle size less than 9.5 mm and extracted with an acetate buffer solution with a pH of 5 or an acetic acid solution with a pH of 3, depending on the alkalinity of the waste. The acetate buffer is added only once, at the start of the extraction. A liquid-to-solid ratio of 20:1 is used and the extraction period is 18 hr. The leachate is filtered through a 0.6 μm to 0.8μm glass fiber filter prior to conducting chemical analyses (USEPA, 1992).

2.8.1.3 Extraction Procedure Toxicity (EP Tox) Test

The Extraction Procedure Toxicity test defined in EPA Method 1310 is applicable to liquid, solid and multiphase samples. Waste samples are crushed to a particle size less than 9.5 mm, and then extracted with deionized water maintained at pH 5 with acetic acid. The liquid-to solid ratio starts at 16:1, and may increase as additional acid solution is added as needed to adjust the pH during the 24-hr test. The leachate is filtered through a 0.45 μm filter paper and then subjected to chemical analysis. Results of the EP Tox test are generally comparable to results of TCLP tests at pH 5, but may differ significantly from a TCLP test conducted at pH 3. The EP Tox test can be used for both inorganic and organic compounds (USEPA, 2007).

2.8.1.4 Multiple Extraction Procedure (MEP)

The MEP test (EPA Method 1320) is intended to simulate leaching caused by repetitive precipitation of acid rain. The repetitive extraction reveals the highest concentration of each constituent that is likely to leach in a natural environment. This test is applicable to liquid, solid and multiphase samples. Like the EP Tox test, the MEP involves an initial extraction with deionized water acidified to pH 5 with acetic acid. The liquid-to-solid ratio is 16:1. The initial extraction is followed by at least eight extractions with a synthetic acid rain solution (sulfuric/nitric acid adjusted to pH 3) with a liquid-tosolid ratio of 20:1. In every stage, the mixtures are agitated for 24 hr and then the leachate is filtered through a 0.45 μm filter paper prior to conducting chemical analyses. The MEP test can be used for both inorganic and organic compounds (USEPA, 1998).

2.8.1.5 Synthetic Precipitation Leach Procedure

The Synthetic Precipitation Leach Procedure (SPLP) defined by the EPA Method 1312, is designed to determine the mobility of both organic and inorganic compounds present in liquid, soils and wastes. This test is similar to the TCLP test, except a different leachant pH is used. Waste samples are crushed to a particle size less than 9.5 mm, and then an extraction is conducted with deionized water adjusted to a pH 4.2 to 5 using acetic acid. A liquid-to-solid ratio of 20:1 is used and the extraction period is 18 hours. The leachate is filtered through a 0.6 μm to 0.8 μm glass fiber filter paper prior to conducting chemical analyses (USEPA ,1994).

2.8.2 Batch leaching test

Batch leaching methods can be approximately described as those in which a sample is placed in a given volume of leachant solution for a set period of time. Most of the methods require some type of agitation to insure constant contact between the sample and the leachant. At the end of the leaching period, the liquid is removed and analyzed. In serial batch methods, a sample of waste is leached successively with fresh aliquots of the same leaching fluid. This method is intended to eliminate the effect of concentration on solubility and to simulate long-term exposure to the leachant solution. A leaching test should reflect the range of conditions (pH, redox potential, L/S ratio, contact time etc) that will be present in fly ash and its interaction with environment during leaching (Zandi M., 2007). Long term natural leaching of fly ash in field lysimeters was compared to batch and column leaching tests (Hjelmar, 1990). Soluble Na and K are initially leached from the ash in the lysimeters; Ca and SO_4 dominate the long term composition. The elements such as Cr, As, Mo, Se, and V which form oxyanions, are leached in the alkaline environment of the lysimeter. In the column tests, the concentration of Ca, SO_4, K, Na, Mg, As, B, BA, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se, V, Zn decreased with increased L/S. Similar results were found for the batch tests. The cumulative amount of an element leached versus the L/S ratio showed reasonable agreement for the lysimeter and laboratory tests.

Kanungo and Mohapatra (2000) conducted batch tests on two Class F fly ashes collected from India to characterize leaching from fly ash at different pH. In a series of 125-mL polyethylene bottles, 2 g of fly ash sample was added to 50 mL of deionized water (1:25 liquid-to-solid ratio). The bottles were securely stoppered to avoid contamination with CO_2 and shaken five times daily for 3 to 4 min for up to 30 d. The solid contents of the bottles were separated by centrifugation and filtration through 0.45μm membranes. Similar experiments were carried out at constant pH of 3.0, 5.5, and 8.0. The pH was adjusted using 0.1 M HNO_3 and 0.1 M NaOH. The filtrate were analyzed for trace elements and are summarized in Table 2.8. As reported by Theis et al. (1982), Kanungo and Mohapatra (2000) that for most of the trace elements, aqueous phase concentrations increase at lower pH.

Table-2.8:Release of Trace Elements in Leachate During Batch Leaching at Different pH (Kanungo and Mohapatra 2000).

Period of Leaching (d)	Trace Element Concentration (mg/L)						
	Cd	Cr	Pb	Se	Fe	Co	Ni
pH = 3.0							
1	0.10	0.40	1.00	1.30	15.00	1.00	2.50
8	0.20	0.62	2.20	1.57	26.00	1.80	4.70
14	0.35	0.84	3.80	1.95	40.00	2.60	7.20
21	0.39	0.75	4.50	1.87	62.00	3.30	10.50
30	0.42	0.85	5.00	1.73	70.00	3.50	10.00
pH = 5.5							
1	0.20	0.50	1.00	0.77	12.00	0.90	1.80
8	0.50	0.70	1.50	1.03	16.00	1.00	3.40
14	0.70	1.00	2.00	1.23	22.10	1.60	5.00
21	0.75	0.90	3.00	1.32	28.20	2.00	6.50
30	0.76	0.80	2.50	1.55	25.00	1.60	6.00
pH = 8.0							
1	0.40	0.08	0.50	ND	3.00	0.60	0.08
8	0.30	0.10	0.40	ND	0.15	0.67	1.00
14	0.50	0.10	0.30	ND	0.18	0.60	5.00
21	0.50	0.07	0.20	ND	0.10	0.45	6.00
30	0.00	0.06	0.20	ND	0.07	0.52	4.50

Querol et al., (2001) compared the extraction of water soluble major and trace elements in open and closed systems for 6 fly ash samples from Spain. They assumed that heavy metals would be more mobile in open leaching systems than in closed leaching systems due to the loss of alkalinity in open systems. At equivalent volumes, the extraction yields appear to be similar for both systems. With continued leaching in the open system, the extraction yields increase for most elements. The results were considered consistent with the dissolution of small solid particles or with coatings on particle surfaces rather than the dissolution of a homogeneous glass phase. Some of the significant batch leaching tests details are given in Table 2.9

Table-2.9 Summary of Significant Batch Leaching Protocols

S. No	Citation	Leaching Testing procedure	Metals Detected
1	Kopsick and Angino (1998)	Batch leaching, 144 hr, Leachant pH- 4, 7, 10.	Ca, Mg, Na, K, Fe, Mn, Zn, Cu and Pb
2	Praharaj. T., et al., 2002.	Batch leaching, L/ S ratio 4, 8, 12, and 16. 125 gm of ash Milli Q water pH-5.6	Al, Ca, Mg, Na, K, P, ,S, Si, As, Ba, Mo, Ti, V, Fe, Mn, Zn, Cu and Pb
3	Jankowski et al.,(2006)	Batch leaching tests have been performed on fly ashes collected from four Australian power stations.	As, B, Mo and Se

2.8.3 Sequential Leaching Test

Sequential leaching tests use a single sample that is leached by a series of different leaching fluids. The constituents extracted with a particular leachant are associated with a particular mineral phase or chemical species. Speciation is considered one of the controlling factors in the potential release of cations to the environment. Many researchers (Gang, Y. C., 2009; Polyȧk, K. et al., 2001;Sočo, E. et al.,2007 and Fernȧndez-Turiel, J. L., et al., 1994) have performed five stage sequential leaching test for metal fraction characterization. Summary of five step sequential leaching test performed (Gang, Y. C., 2009) on pulverized coal (PC) boiler ash and circulated fluidized bed (CFB) boiler ash is shown in Table 2.10.

Table-2.10: Five step sequential leaching test adapted from (Gang, Y. C., 2009)

Step no.	Fraction description	Extraction procedure
1	Extractable by water	Ultra pure H_2O, 2hr
2	Acid-soluble i.e. exchangeable ions and carbonates	0.11 M CH_3COOH, pH 2.85,16 hr
3	Reducible, iron-manganese oxides	0.1 M $CH_2OH.HCl$, pH 2, 16 hr
4	Oxidizable –Sulfides/organics	5 ml H_2O_2 85°C, 2hrs,1M CH_3COONH_4, pH 2, 16 hr
5	Residual- metals bound in lithogenic minerals	5 ml aqua regia (1:3 HNO_3:HCl), 3 ml HF, microwave digestion , 160°C 10 min, 180°C 30 min

Water extractable fraction- In PC sample, only 6.5% of total V and 3.3% Cr and others (Co,Ni, Cu, Zn, Cd, Sn and Pb) were below 1.4%, whereas in CFB sample 12.5% of total V, 0.7% of Cr and 1.1% of other elements were extracted.

Acid soluble fraction- Heavy metals in the exchangeable fraction play very important role in the evaluation of the environment and always act as pollution indicators for its environmental mobility and bioavailability. The proportion of Co, Ni, Cu, Zn and Cd was 10%,13%, 22%, 16%, and 26% respectively and other elements were below 7% for PC fly ash. For CFB sample Zn 39%, CO 15% and others were below 10% of total amount were extracted in this fraction.

Reducible fraction- 14% and 12% of V were extracted in PC and CFB sample ash respectively and other elements proportions were below 10% in both the samples.

Oxidizable fraction- Metals in this fraction always acts as a sink and reservoir for pollution. 39% and 12% of total V was detected in this fraction in CFB and PC sample respectively. No detectable Sn was present in the in both the samples.

Residual fraction- Metals in the residual fraction are safer for the environment due to their lowest mobility and bioavailability. More than 97% Sn and Pb and more than 82% Cr and Ni were observed in residual fraction in both samples. In PC sample (Zn-54%, V- 35% and Cu-85%) and CFB sample (Zn-78%, V- 58% and Cu-58%) were found in residual fraction.

2.8.4 Cascade leaching test

To simulate the recurrent flushing of ash by rainwater/groundwater and to characterization the depletion pattern of selected elements under these conditions cascade leaching test is being carried out. When water percolates through the ash pond, cumulative leaching occurs in a cascade manner (Singh, D. N. et al., 2001).This is also repetitive type of extraction test with new leachant at every step. Some of the cascades leaching tests performed by various researchers are summarized in Table 2.11. Singh, D. N et al., (2001), Baig A. A M., et al., (2008) also performed cascade leaching test for study of leaching behavior of Indian coal fly ash.

Table-2.11 Details of some of the Cascade leaching test by various authors

Sr no	Reference	Leaching Conditions	Metals detected
1	Fytianos et al., (1998)	Standard leaching test- An advantage over the column test is that, in special cases, the test may be performed on unbroken material and that high L/S ratios are reached in much shorter times.	All fly ash samples exhibited strong alkaline reaction, as indicated by pH values > 11.75 at L/S = 10 and contact time of 10 min. The percentage of leached amounts follows the trend Ca > Cd > Cr > Pb > Zn > Cu > Mn for samples.
2	Palit., A., et al., (1993)	Fly ash was leached with acidified D I water pH=4 for 23 hrs(8 hrs stirring) at various L/S ratio 10, 20, 30, 40, 60, 80 and 100.	Two fly ash samples show alkaline and remaining two shows acidic reaction at at L/S ratio = 10.For acidic fly ash the leaching trend Na,K,Pb>Fe,Cr,Ni,Zn>Mn Cu and for alkaline fly ash Na>Fe,K>MnPb,Zn>Ni>Cr,Cu
3	Prasad B., et al., (2008)	Fly ash was leached with acidified D I water pH=4 for 18rs t various L/S ratio 20, 40, 60, 80 and 100.	Both the fly ash are neutral. At L/S 100 the leaching trend as Fe>Zn>Cu>Mn>Cr>Ni>Pb>Cd for Zn>Fe>Mn>Cr>Pb>Cu>Ni>Cd.

2.8.5 Column and lysimeter leaching test

Column leaching tests are considered as simulating the flow of percolating groundwater through a porous bed of granular material. The flow of the leaching solution may be in either down-flow or up-flow direction and continuous or intermittent. The flow rate is generally accelerated when compared to natural flow conditions. However, it should be slow enough to allow leaching reactions to occur. A basic assumption in column leaching is that the distribution of the leaching solution is uniform and all particles are exposed equally to the leachant solution. Precipitation or sorption within the column may affect the results. Many researchers used column leaching test (Mudd, G. M.,et al., 2004, Benito, Y., et al.,2001, Singh, B., et al., 2004, Ram, L. C., et al., 2007, Wang, W., et al., 2008, Gitari, W. M., et al., 2008), laboratory lysimeter (Fulekar, M. H., et at.,1992, Hajarnavis, M. R., et al., 2003) and field lysimeters (Hjelmar, O., 1990) for the study of leaching behavior of coal fired power plant ash.

Hjelmar, O., (1990) concluded that laboratory column leaching tests are useful tool for prediction of concentrations of the leachate. Calcium, carbonate, sulphate, sodium, and potassium are observed in leachate of alkaline fly ash. Appreciable amount of As, Cr, Mo, Se and V are present from anionic species under alkaline conditions. Concentrations of the most of the metals decrease with increase in L/S ratio. Author also suggested controlled or reduced leaching disposal strategy for coal fly ash to minimize environmental impact. With the help of lab lysimeter mechanism of sorption/retention of heavy metal in field soil was studied and infiltration was simulated by applying ash pond effluent samples (Fulekar, M. H., et at.,1992). Result show that heavy metal content increases with increased quantity of ash pond effluent percolation.

High pH and high calcium sulfate contents were observed and these ashes should be considered as toxic as per European legislation, but not toxic according to Spanish legislation. Other heavy metals are below detection limits. At high pH the metals in the ash are precipitated (except the amphoteric elements Al, Zn, Cr etc). Compaction has reduced the permeability of fly ash but not solubility (Benito, Y., et al., 2001). Most of the metals were washed out within 140 days. Concentration of Cu, Zn and Mn in leachate exceeded the desirable limit for drinking water and while Cr and Cd concentration exceeded the permissible limit as reported by Hajarnavis, M. R., et al., (2003).

Singh G., et al., (2007) reported that significant concentrations were detected in the leachate for metals Fe, Ca, Mg, Na, K, Cu Zn, Mn and Pb. The concentrations of various trace elements in leachate vary from plant to plant and which entirely depends on inherent properties of coal. Fe, Cu Zn, and Pb do not show regular trend in leaching while Ca, Mg, Na and K found to be leached throughout the study period. Wang, W., et al., (2008), observed various leaching trends as V shaped curve, a gradually descending curve "\" and a wave like curve " ⌒ " (in decreasing order) and other 3 minor trends. Mode of occurrence of elements, time, and pH play important role in controlling the leaching behavior of ash. Maximum leached concentrations of Ni, Co, As, Cd and U from feed coal, Mo and U from fly ash and U from bottom ash exceed the permissible limit. As a result, it is likely to contaminate surface and groundwater under low pH conditions, such as acid rain. The significant column and lysimeter leaching tests carried out by some of the authors are summarized in Table 2.12.

Table 2.12 Significant column and lysimeter leaching test

S.no	Reference	Leaching Conditions	Metals detected
1	Hjelmar,O., (1990)	Field lysimeter area 8-9 m^2 ,4 acrylic columns, dia-0.2 m and 0.145 m, 17, 27 mm/hr and 44- 145 mm/hr for fourth column. Flow in one column up flow and rest of the three down flow mode.	Ca, Mg, Na, K ,As, B, Cd, Cr, Co, Cu, Mn, Mo, Se, Zn Pb, Cl, Hg, V, F, NO_3, PO_4, SO_4, etc.
2	Fulekar, M. H., et at.,(1992)	Lab lysimeter of Perspex sheet, 20 cm x 20 cm x 91 cm long. Surface soil and 1 lit/day was applied in lysimeter.	Ni, Mn, Cr, and Pb
3	Benito, Y., et al., (2001)	PVC column, 16 cm dia, 1m height, upflow mode 4cm^3/hr , sample weight 10.6-21.2 kg, L/S ratio 2:1	Ca, K, Na and SO_4
4	Hajarnavis, M. R., et al.,(2003)	2 lysimeters of RCC, 60 cm dia, 110 cm long, tap water, 2.8 lit/day, 24 weeks	Zn, Ni, Fe, Mn, Cu, Cr, Cd, and Pb
5	Ram, L. C., et al., (2007)	Glass column, 12 cm dia, 73 cm long, down flow mode, milli Q water pH-7. Flow rate 1 ml/min equivalent to L/S ratio as 0.35,2.5, 5, 10 at end of day 1, and a week interval of1,2, 3 and 4 respectively.	Ca, Mg, K , Cd, Cr, Cu, Mn, Ni, Zn, Fe, Pb, Cl, SO_4, etc.
6	Singh G., et al., (2007)	Standard open percolation column of PVC, dia 10 co and 75 cm height. DI water, gravity flow, biweekly collection of leachates.	(Al, Fe, Ti, Ca, Mg, Na, K) and trace (Ag, As, B, Ba, Cd, Co, Cr,Cu, Mn, Mo, Ni, Pb, Se, Sb, V, Zn elements.
7	Wang, W., et al., (2008)	Glass column dia-10 mm, 70 cm long, 20 gm feed coal, fly ash and bottom ash. Controlled outflow velocity 3 ml/hr. Sample frequency-4, 12, 28 and 60 hrs.	Cd, Co, Cr, Mo, Ni, Pb, Se, As, Hg, H and Th.

Ghose and Subbarao (1998) also conducted similar column leaching tests, but on Class F fly ash and Class F fly ash mixed with lime (4%, 6%, and 10%). Column leaching tests were conducted on compacted mixtures and Class F fly ash alone in rigid-wall permeameters. Tap water (pH = 7) was used as influent and a constant hydraulic gradient of approximately 10 was applied. The leachate were analyzed using atomic absorption (AA) spectrophotometry (flame) for Cd, Cr, Cu, Fe, Mg, Ni, Pb, and Zn. Goh and Tay (1993), and Ghose and Subbarao (1998) found that the concentration of trace metals generally decreases with increasing pH of the effluent.

Biliski and Alva (1995) conducted column leaching tests on agriculture soil amended with fly ash to evaluate the impact on groundwater when using fly ash for agricultural uses. Candler fine sand (pH = 5.5, sand content = 96%, organic matter = 1.3%) was sampled from a citrus grove near Lake Alfred, Polk County, FL. The soil was air-dried, ground to pass a 2-mm sieve, and packed in plexiglass columns (30-cm long, 7-cm inner diameter) to a height of 28 cm. Fly ash from Tampa Electric Company (TECO, Tampa, FL) was mixed uniformly within the top 10 cm of soil in the column at application rates of 0%, 10%, 20%, 30%, 40%, and 50%. The columns were operated with distilled water at a constant flow rate of 1 ml/min using a peristaltic pump. Leachates were collected at each half pore volume for a total of 5 pore volumes and were analyzed for metals Cu, Mn, Fe, Zn, Cr, and Se. Biliski and Alva (1995) found that the total mass leached increases significantly with increasing fly ash content. The highest concentration of most elements was observed in the leachate corresponding to 1.5 pore volumes, except for Fe and Cu. The Fe and Cu concentrations reached a maximum within one pore volume. The concentration decreased considerably for all elements beyond three pore volumes of flow.

Edil et al., (1992) conducted column leaching test on sand-fly ash mixtures to evaluate leaching from a fly ash liner material. The leachate quality was measured in terms of the chemical species that were in the feed solution and for elements of special interest that were expected to leach from the fly ash (Al, As, Cr, Se, Si, and Sr). They found that that the release pattern from fly ash follows two basic shapes namely, flush response and the lagged flush response, and most metals show the first-flush leaching pattern. The exceptions were strontium and chromium for the test specimen having low hydraulic conductivity.

2.9 MODELING STUDIES USED FOR THE FLY ASH LEACHING

Various modeling studies have been carried to address the various issues involved in fly ash disposal or utilization scenario. Some of the studies are mentioned here as, models for leaching of coal fly ash, empirical models for prediction of leachate concentrations, geochemical models, solute transport models, verification of laboratory as well as field data and assessment of groundwater impact through highway embankment. Chapelle, F. H., (1980) assumed that metals will be desorbed from fly ash surface at a rate proportional to the concentrations of metals on the fly ash surface. The constant of proportionality is a function of pH and is decaying function. Good correlation was observed between predicted with the mathematical model and measured metal concentrations.

Under saturated or near saturated conditions leaching is dominated by initial wash off and advective flow (Mudd, G. M., et al., 1997). Chemical reactions and surface phenomena are more important for coal ash, and are described on the basis of kinetic formulations for a particular species of interest or using mass transfer coefficients. For coal ash, initial wash-off of chemicals is also considered to be a significant mechanism in exchange of chemicals from surface and aqueous solutions. Lateral flow, ash dumping process, overburden stresses and reduction in permeability should be considered. For aged ash deposit unsaturated flow and non-regular infiltration should be considered.

When the natural precipitation occurs in a landfill with different age refuses, it undergoes vertical movement and becomes contaminated with inorganic substances in fly ashes (Huang, C., et al., 1998). Land filled fly ash is treated as a homogenous, non deformable, unsaturated porous medium in which moisture moves vertically downwards. The contaminant transport in liquid phase is governed by convection and longitudinal dispersion, are neglected in the solid phase. This model can be used to predict simultaneous moisture movement and contaminant transport in a real fly ash landfill with different age refuses. Trace elements leach from the coal combustion product layer as water percolates down through the profile. This water migrates downward through the subgrade soils until the groundwater table (GWT) is reached. Leaching from the Coal Combustion Products (CCP) layer is assumed to be sorption-controlled with linear and reversible partitioning or is defined empirically by the user. Transport in the vadose zone is assumed to follow the advection-dispersion-reaction equation (ADRE) with instantaneous, linear, and reversible sorption. In this study author illustrated analytical solutions to ADRE that can be used to assess impacts to groundwater (Li, L., et al., 2006), due to leaching of trace elements from coal combustion product used in subgrade, subbase and base layer.

When water percolates through a porous media it follows most probable set of path, which yields declined concentration profile in the continuously leaching water (Singh, G., et al., 2007). With this concept an empirical model for prediction of leachate concentrated was developed. Dispersion of the trace metals in the leachate of coal fly ash of various thermal power plants can be described by first order differential equation with regression coefficient 0.93 to 0.98. The decrease in the concentration of metals leachates was found to proportional to the logarithm of the time period.

The field studies (Mudd, G. M., et al., 2004) conducted over 14 months showed the leaching of As, Ba and S and Mo, Se and Sr, in which the trend suggest that adsorption and coprecipitation are important phenomena. Geochemical modeling indicated both sulfate and carbonate minerals are most likely solubility controlling mineral phase. The concentrations of Ca, Al, Fe and SiO_2 appear to be influenced by pH and presence of atmospheric CO_2. Though leachable trace elements appear to present a minor risk to groundwater quality, author advocated continued monitoring of As, Ba and S and Mo, Se and Sr in particular. Table 2.13 summarizes the some studies carried out for modeling of fly ash leaching and study of groundwater pollution.

Table-2.13: Various models used in the study of leaching of fly ash

S. No	Reference	Model	Application
1	Chapelle, F. H., (1980)	$(A_L(t)) = (A_0 - A_0 e^{-kt})\frac{M}{V}$ $K = -\ln(1 - \frac{A_L V}{M A_0})$	Each metal ion of a given species sorbed on to the fly ash surface has an equal statistical chance at any time of desorbing when that ash is leached by water.
2	Mudd, G. M., et al (1997)	$L_R = \alpha\left(\frac{S}{S_0}\right)^{\beta}(C_{\max} - C)$ $\frac{\partial c}{\partial t} = Dz\frac{\partial^2 C}{\partial z^2} - Vz\frac{\partial C}{\partial z} + L_R$	Dissolution of chemicals from mass of fly ash is surface phenomena and chemical mass is reducing. The soluble mass decays exponentially with time. The migration of solute through saturated ash incorporating leaching can be expressed with the advection-dispersion equation.
3	Huang, C., et al., (1998)	$\frac{\partial \theta}{\partial t} = \frac{\partial D}{\partial z}\frac{\partial \theta}{\partial z} + D\frac{\partial^2 \theta}{\partial z^2} - \frac{\partial K}{\partial z} \pm Q$ $\frac{\partial C}{\partial t} + \frac{q}{\theta}\frac{\partial C}{\partial z} = E\frac{\partial^2 C}{\partial z^2} + \frac{\lambda}{\theta}\frac{\partial q}{\partial z}\frac{\partial C}{\partial z} + k_n\left(\frac{M}{M_0}\right)^n (C_{\max} - C) \pm \frac{C}{\theta}Q$	A model for predicting simultaneous moisture movement and contaminant transport through a fly ash land fill with different age refuses.
4	Li, L., et al., (2006)	$R\frac{\partial C}{\partial t} = D_x\frac{\partial^2 C}{\partial x^2} + D_z\frac{\partial^2 C}{\partial z^2} - v_z\frac{\partial C}{\partial z}$	The first flush leaching pattern from coal combustion product generally corresponds to adsorption controlled release under conditions where pH and redox potential remains constant. It can be described mathematically by the advection- dispersion-reaction equation (ADRE) with instantaneous, linear and reversible sorption.
5	Singh, G., et al (2007)	$c(T_m) = C[k \ln(T_m) + c_0$	The rate of change in the dissolved contaminants can be reasonably assumed to be inversely proportional to the time "t" when water flows through the most probable set of paths.

2.10 UTILIZATION OF ASH

Lot of ash is generated from burning of coal or municipal solid waste. Both have utilization potential. Utilization of fly ash can ensure not only in reducing the magnitude of environmental problems, but also to exploit fly ash as a raw material and conserve traditional materials. Incinerator ash has very good potential for cement brick production (Cho, Gi J et al., 2008) and sidewalk blocks and subsurface materials in road construction (Lee., S. 2008). Similarly coal fly ash has also good potential for utilization. Government of India started, Fly Ash Mission (FAM) in the year 1994 for utilization of fly ash and safe management technology under Department of Science and Technology (DST). Fly ash utilization was around 10% (1998) of the total generated as against 3-5% (1994). To tackle the problem and encourage the use of fly ash for making building materials, the Government of India has imposed restriction (Gazette notification of 14th September 1999 and later amended 27th August 2003 issued by Ministry of Environment and Forest) on every construction agency engaged in the construction of buildings within a radius of 50 to 100 kilometers from a coal or lignite based thermal power plant shall use fly ash bricks or blocks or tiles or clay fly ash bricks or cement fly ash bricks or blocks or similar products or a combination or aggregate of them in such construction as per the following minimum percentage (by volume) of the total bricks, blocks and tiles as the case may be used in the construction project, namely 25% by 31st August 2004, 50% by 31st August 2005, 75% by 31st August 2006 and 100% by 31st August 2007.

In the recent years, the Ministry of Environment and Forest, Govt. of India has restricted the use of top soil for building materials and to facilitate use ash (fly ash, bottom ash or pond ash) at least 25% in manufacturing clay bricks within a radius of 50 km from coal and lignite based thermal power plant (Mathur et al., 2001). The fly ash produced form coal fired power plant in India has great potential to be utilized for various applications. Fly ash has been successfully utilized in mine filling (Prasad, B., et al., 2008), construction roads of and embankments (Murthy, A.V.S.R., et al., 2000; Khitoliya, R. K., et al., 2003), hydraulic structures (Damani, R. L., et al., 2003), raising of dykes (Mathew, M. K., et al., 2000), manufacture of several building components like bricks, blocks, tiles, agricultural applications (Samra, J. S., et al., 2003) and for vermicomposting (Bhattacharya, S. S. et al., 2003). The fly ash activity, after Fly Ash Mission Mode Project Period (i.e.31st March 2002) was named as Fly Ash Utilization Programme (FAUP). With concrete efforts and the strategies of project formulation and implementation, the Mission Mode approach that have led to increase in ash utilization and has increased from 1 million tons per year to more than 45 million tons per year during 2005. On the other hand fly ash generation in India increased up to 130 million tons per year. As per an estimate of FAUP, TIFAC (Technology Information Forecasting Assessment Center), the annual ash generation figures are expected to reach about 170 million tons by 2012 and 225 million tons by 2017 (Kumar, V. et al., 2005). About 23% of fly ash is utilized in India in the year 2003 (Kumar, V. 2003), and presently as per the Ministry of Environment & Forest figures, 30% of fly ash is being utilized in fillings, embankment, construction, blocks and tiles etc. Remaining ash is disposed in the ash pond/ash dam/lagoons in the slurry form along with bottom ash, is called as wet disposal of fly ash. Most of the ash generated from power plants is disposed off in the vicinity of the plant as a waste material covering several hectares of valuable land. In dry disposal, the fly ash is transported by truck, chute or conveyor at the site and disposed off by constructing a dry embankment (dyke). At its Dadri Power Station Uttar Pradesh, India, NTPC (National Thermal Power Corporation) has set up a unique system for dry ash collection and disposal facility with Ash Mound formation. This has been conceived for the first time in Asia which has resulted in progressive development of green belt besides far less requirement of land and less water requirement as compared to the wet ash disposal scheme.

2.11 ENVIRONMENTAL EFFECTS OF FLY ASH DISPOSAL

Fly ash is an undesirable by-product of coal combustion whose interaction with soils, surface water, groundwater and the environment has created health hazards to human population, disturbed agriculture and natural ecosystems. Utilization of fly ash is the one way to solve the disposal problems, but utilization of fly ash is less in India compared to global utilization and major portion of fly ash is disposed in the slurry form covering several hectares of valuable land. In India, less attention has been paid to the selection of area, operational cost, health hazard, and air, water and land pollution due to the fly ash disposal. Environmental pollution due to non-degradable inorganic fractions of fly ash and its interaction with soils, including their solubility, mobility and bioavailability has become alarmed in recent years due to potential effects on human health, agricultural and ecosystem (Khandekar, M P., et al., 1999). Due to minute particle size it gets airborne easily and causes air pollution. The size fraction less than 1 μm have longer residence time in atmosphere and pose a possible health effects (Meserole, F. B., et al., 1979). For this more emphasis is required on the physical containment of ash, in order to prevent surface water and air pollution (Tare, V., et al., 2005). Presence of potentially toxic elements like, Arsenic, chromium, boron, vanadium, cadmium, antimony, and fly ash has been considered as hazardous material for living organism. Some heavy metals leach out in ash pond and contaminate soil, subsurface and groundwater. These heavy metals have been known to limit the growth of plants and microbial population. When coal combustion waste is discharged into aquatic system, some potentially toxic trace elements in water, sediments and suspended solids are accumulated by biota and further transferred through the food chain (Rowe C. L. et al., 2002). Baba, A., et al., (2006), also reviewed the effects of fly ash on ecosystems and utilization schemes of fly ash. Apart from various utilization avenues various deleterious effects of fly ash disposal on soil and water environment, aquatic ecosystem are shown through flow chart in Figure 2.2

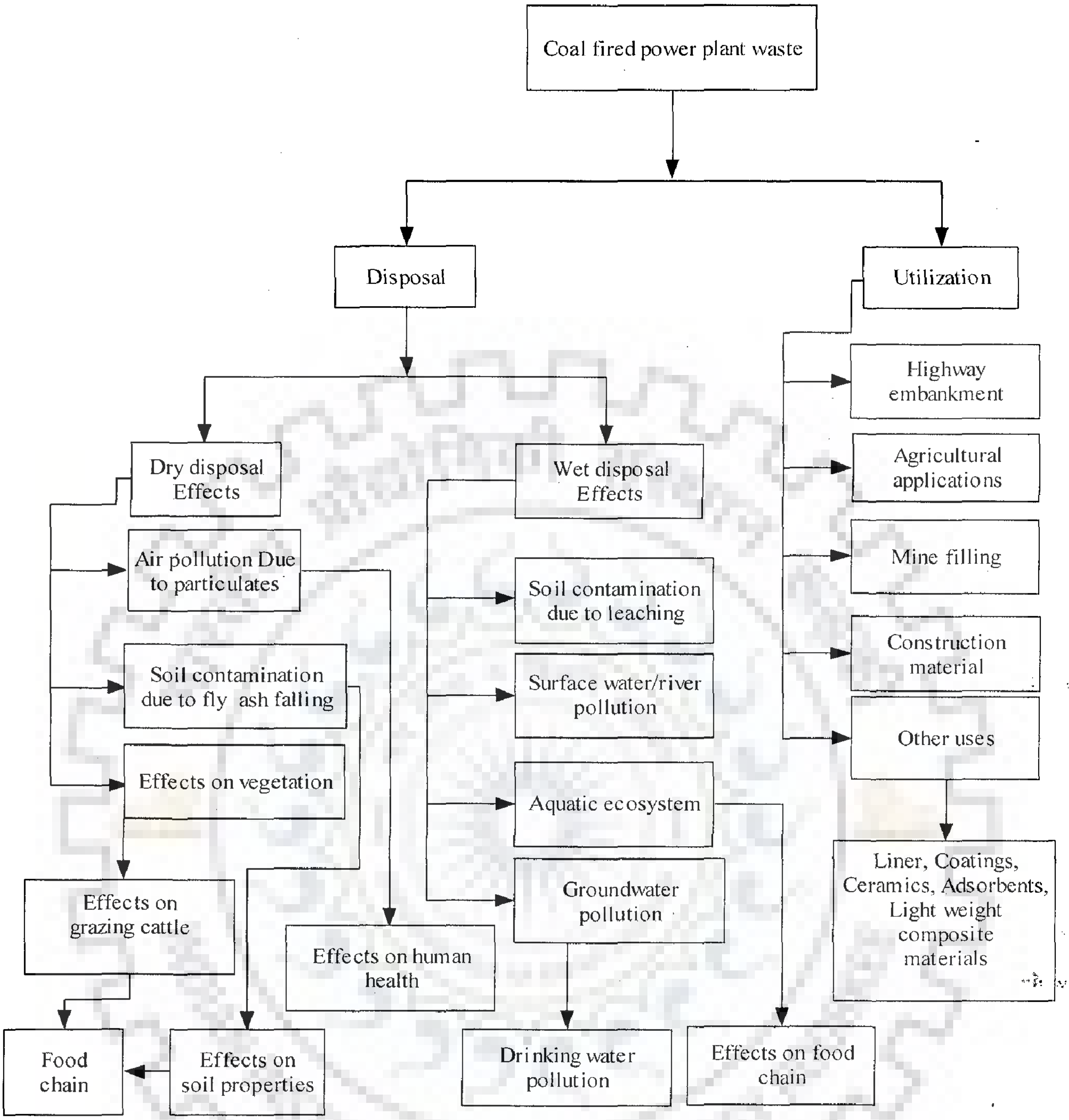


Figure 2.2 Utilization and environmental effects of fly ash disposal

Major environmental problem have been created in Singrauli region (also known as power capital of India) by coal ash disposal ponds. It is estimated that thousands of hectares of land will be required for coal ash slurry pond construction every 25 year. Fulfilling this requirement will only aggravate existing environmental and social problems in the region. (Michalski, S. R., et al., 2001).

2.11.1 Soil environment

Soil pollution is caused by two ways namely atmospheric fallout of fly ash and leaching of surface associated toxic trace metals and soluble salts. Top soil around the power plant (Singh, J., et al., 1994) and ash pond (Praharaj , T., et al., 2003, Gulec, N., et al., 2000, Mandal, A., et al., 2006) is contaminated due to fly ash dispersal/fallout and slurry disposal. Many forest ecosystems in Germany are strongly influenced by emissions of pollutants like SO2 and alkaline dust from coal fired power plant (Klose, S. et al., 2000). Major dust pollution were observed in Delhi, India around the Indraprastha Power Station (IPP Station) and Rajghat Power house (RPH) from fly ash dispersal (Mehra, A., et al., 1998). The accumulation of B, Mo, Se and other heavy metals and soluble salts in fly ash poses serious constraints for land disposal of fly ash (Adriano, D.C., 1980). After extensive study of soil contamination around Kolaghat thermal power plants of India located in, West Bengal India, it was found that the top soil and the soils collected from the different depth profiles surrounding the ash ponds, are enriched in the trace elements Mo, As, Cr, Mn, Cu, Ni, Co, Pb, Be, V, Zn (Mandal, A., et al., 2006). The physicochemical and mineralogical properties of the profile soil in the predominant wind direction are found to be modified compared to the background and other soil profile. pH of fly ash is lowered by addition of fly ash which affects the agricultural qualities of soil (Mandal, A., et al., 2006).

Patel C. B., et al., (1987) observed through fly ash fallout measurement that Cu, Co, Ni, Pb, Zn,Bi, & Sb carried in fly ash fallout from a Korba thermal power plant Madhya Pradesh, India, had permeated soil horizons up to a depth of 0.9 m. The concentration in top 0-30 cm thickness of soil layer are as follows: Cu-68.18%, 47.72%; Co-66.16%, 41.35%; Ni- 73.82%, 41.09%; Pb- 65.55%-36.11%; Zn- 77.94%, 51.47%; Bi- 0%-0%; Sb- 30.67%, 0%. The permeability rates of the elements have been found to be in the following order: Zn>Ni>Cu>Pb>Co>Sb>Bi. After measurement of fly ash fallout from a Korba thermal power plant Madhya Pradesh, India, from an area of 64 km^2 in the vicinity of power plant, it was observed that predominant wind direction fall rates are more (Patel C. B., et al., 1985).

Fly-ash deposition significantly increased the pH values in the three horizons and mineral topsoil (0–10 cm) in Eastern Germany (Klose, S. et al., 2004). Increased amounts of fly ash put on land will however cause enrichment of soil with salts due to solid phase dissolution reactions. With the decrease of pH, trace metals like Fe, Cu, Zn, Ni, Pb, Cr and As will be released from soil into groundwater or surface water. Excessive sulphur and other trace metals loading will give infertile land, as was demonstrated by the deposition of fly ash at the Khaperkheda Thermal Power Plant disposal site (Fulekar, 1993; Khandekar et al., 1999).

Increase in soil natural radioactivity in the close vicinity of several thermal power plants in India was observed by Ramachandarn, T. V., et al., (1990). After assessment of radioactive contamination around Yatagan (Mugla,Turkey) coal fired power plant waste disposal site was found to enriched with radium (Baba, A., 2002). Studies of Kolaghat Thermal power station reveals that Radionuclides (U, Th) show enrichment of 3-5 times in coal ash compared to their crustal average and are much higher than in the pond ashes of other thermal power plants of India (Mandal, A., 2005).

The ash from the ash ponds of power plants of Kolaghat, Durgapur and Bandel, West Bengal, India contains 2 to 3 times more natural radionuclides than that in feed coal. Thus there is significant amount of health risk to the population living in the surrounding areas. Ash samples have radium equivalent activity (Ra_{eq}) and external hazards index (H_{ex}) values closest to 370 Bq/kg and unity respectively, which have implications in terms of radiation hazard arising due to the use of these ash samples in building and construction (Mandal, T., 2006).

Liljana Mljač, L., et al., (1996) recorded from study of the coal-fired SoStanj thermal power plant, Slovenia, that the fly ash deposit has enhanced concentrations of uranium chain radionuclides in water and in sediments. The strongest influence was found in contamination with ^{226}Ra, namely in water, in sediments, and in periphyton.

The radioactive evaluation of the pulverized coal and ashes of the Figueira plant showed concentrations above the world average for the uranium series, mainly for ^{210}Pb. Radioactive equilibrium within the uranium series is disturbed due to the various enrichment factors for ^{238}U, ^{226}Ra and ^{210}Pb in the fly-ash samples collected along the emission control system from Brazilian Power Plant. While utilizing such ash for commercial applications, like bricks, road pavement, agriculture, etc careful consideration are required (Flues, M., et al., 2006) and also proper dosimetric calculations are necessary. Radiological impact of the Kolaghat thermal power plant in West Bengal, India has been assessed by Mandal, A., et al., (2003). They observed that the enhanced concentration of most radionuclides ^{238}U, ^{232}Th and ^{40}K in ash. The total gamma dose rate of the Kolaghat ash pond is quite high compared to that of other thermal power plants in India.

2.11.2 Groundwater

Groundwater gets polluted due to industrialization and agricultural activities (Ray, C., et al., 1996). Numerous researchers have documented adverse environmental impacts caused by disposal of coal combustion wastes to groundwater and surface waters, plants aquatic life and other organism. The groundwater environment is more vulnerable than surface water due to lower velocity under low permeability and possible accumulation of leached elements in the groundwater (Spencer, L. L. S., et al., 1987). Carlson C. L. et al., (1993) maintain that the major environmental impacts of coal combustion waste include: leaching potentially of toxic trace metals into soils, groundwater and surface waters; hindering the effects on the plant communities; and the accumulation of toxic metals/elements in the food chain. Sandhu, S. S., et al., (1993) specifically studied the leaching of Ni, Cd, Cr and As from coal ash impoundments of different ages. They concluded that the measurable amounts of metals are leached through old and new ash deposit. Ash disposal basin may be potential sources of groundwater contamination for many years after ash deposition has ceased (Sandhu, S. S., et al., 1993). Theis et al., (1978) observed a substantial increase in the concentration of Fe, Ni, Pb, Cu, Zn, and As in local groundwater when fly ash was disposed in ash pond at a power plant in Indiana following a shutdown of the plant. Groundwater quality near the ash pond is changed due to leaching of soluble ions present in fly ash (Suresh, I. V., et al., 1998). After analysis of (R Sinha et al ., 2000) groundwater samples from tube wells for contamination due to Feroze Gandhi Unchchar Thermal Power Plant, near Ganges river, the concentrations of Mn and Cd was observed to be slightly higher than WHO limits and contamination may be due to long term operation of ash disposal. Groundwater samples from monitoring well installed near a fly ash lagoon in Korea, showed similar concentration patterns to the fly ash slurry and water samples. This confirms that the groundwater is influenced by ash leachate via leakage from the ash pond (Choi, S. K., et al., 2002).

Study was carried out around a coal ash disposal pond near Angul Orissa, India for delineation of contamination of groundwater by applying geochemical and geographical information system approach (Praharaj, T., et al 2002). Both open wells and tube wells are contaminated with Fe, Ba, Cu, Mn, S, Pb, V, and Zn at various degrees. Contamination in tubewells is attributed to ash pond leachate. Open wells are contaminated due to fly ash fallout. Concentration of Mn, Fe, and Pb are above USEPA-specified maximum permissible contaminant level, and which may cause potential health hazards in the area from consumption of this water. Metals such as Cu, Zn, and Ba are found in groundwater under permissible limit, but their cumulative build up in longer run may pollute the groundwater.

Geochemical studies (Mandal, A., et al., 2005) of water samples show that tube wells near ash pond (Kolaghat Thermal Power Sation, West Bengal, India) and in the surrounding villages are contaminated by toxins released from the ash pile. The concentrations of tube well water denote significant contributions from ash pond in the form of metals as Al, Ni, Fe, As, Zn, Mo, Mn, Ba, and Pb. Metals such as Mn and Pb exceeds the WHO guidelines, also Al and As show enrichment above WHO guidelines in some places. Excess amount of arsenic and manganese affects the cardiovascular system, gastrointestinal tract, kidney, liver, skin and blood and prostrate. Excess amount of lead is responsible for dysfunction of the kidney, gastrointestinal tract and respiratory system due to inhalation of fine ash particles rich in lead. Guima Sasi (2005), analyzed 40 groundwater wells near Soma power plant, Turkey for various metals, and found that Fe concentrations in 12 wells were higher than the WHO, the Turkish and European

Countries (EC) guidelines and Zn concentrations in 5 wells were higher than the EC guidelines also in some wells Pb concentrations were high but within limits. Remaining metals are within the guidelines. But metal tends to accumulate in groundwater and if no action is taken, after some time the concentrations of these metals will exceed the guidelines. These are originated from ash pile. Anthropogenic metal concentration decreases away from ash pile.

Dry ash has been placed directly in contact with a shallow sand and gravel aquifer at a Southeastern fly ash land fill in USA. Substantial modification of groundwater quality has been occurred due to sulfates, calcium and magnesium. Thus the placement of fly ash in unlined abandoned sand and gravel pit, due contact with water will be favourable situation for groundwater contamination (Cherkauer, D. S., 1981). Groundwater impacts from coal ash used in highways has been investigated (Li, L., et al., 2006) with the help analytical solution of advection dispersion- reaction equation combined with computer program (WiscLEACH). The studies indicate that the maximum groundwater concentration typically occurs close to the groundwater table and near the centerline of the pavement structure. The peak concentrations decreases as the depth to groundwater increases, thickness of coal combustion waste layer decreases, seepage velocity in the vadose zone decrease or the seepage velocity in groundwater increases. After assessment of groundwater data (monthly basis for 1 year) for the impact of filling of open cast mine of Damoda, India, with fly ash, it was found that initial stage fluoride concentrations are high and later stage it drops down. Concentration of Mn were exceeded the drinking water limits throughout the investigation period. Overall groundwater quality at the periphery of ash filled zone was slightly affected and no apparent effect on groundwater quality 0.5 km away from ash filled area, where the groundwater is used for drinking water (Prasad, B., et al., 2008).

Gurunadha Rao, V. V. S., et al., (2009), reported the assessment of groundwater conditions and predicted future scenario of groundwater contamination, with the environmental impact assessment study of ash pond of a thermal power plant in Jharsuguda district of Orissa, India. The hydrogeological, geophysical, remote sensing, water level, and water quality-monitoring database, prima facie does not predict groundwater contamination from ash pond. Detailed investigations of coal, ash, water, flora and fauna of six thermal power plants of India, it was found that leaching of fly ash expected, but there is less possibility of pollution of groundwater (Tare, V., et al., 2003). More emphasis should be given to avoid toxicity of heavy metals through the direct intake of water with suspended particles and through breathing, and for this precautionary measures are required.

2.11.3 River and aquatic environment

Industrialization, urbanization and modern agriculture practices have direct impact on the water resources (Parashar, C. et al., 2008). Power plants are mega project which requires lot of water for ash slurry disposal. In India most of the power plants are located near the river and effluent from ash pond overflows due to inadequate design of ash pond (Prasad, B., 2004) or diverted to the river (Mehra, A., et al.,1998) near to the power plant. River water and sediments get enriched due to soluble salts and metals due to wet disposal of fly ash. This directly affects the aquatic ecosystem, which has long lasting effect on food chain as well.

Assessment has been done (Khan R., et al., 2005) in and around the Neyveli mine- industrial complex for the level of heavy metal contamination in the surface water bodies, its distribution and sources and possible risk connected with the use of water for agricultural irrigation. It was found that heavy metal contamination in surface water bodies are contaminated and the mean values of Cu, Zn, Mn, Fe, Ni, Cd, Cr, Co, Pb and Hg in the investigated area are respectively 2,6,17,75.5, 200, 260, 275, 350, 484, and 1200 times higher than the average levels in the worlds rivers. The Fe, Cr, Co, Ni, Pb, Mn, and Hg, in all of the surface water bodies exceeded the average levels in the world's rivers. Untreated waste water from fly ash pond drains into natural reservoirs (Kolakudi, Walaza and Perumal ponds) and Paravannar river resulting in concentrations of metals higher than the average world river water values. Waste water discharged from ash pond and natural reservoir is being used for irrigation in surrounding area nearly four decades. This toxic water enriched with metals such as Hg, Cr and Co was used for irrigation purpose. This toxic water has exceeded the limit for irrigation of water metals such as

Hg, Cr and Co. Irrigation using this metal loaded waste water pollute soil as well as allows toxic metals to enter into the food chain, posing serious health hazard.

Talcher Thermal power plant in Orissa, which generates 3000 tonne of coal ash every day, found that, 15% of the toxic metals are leached out and the adjacent Nandira river was receiving 208 kg of iron, 56 kg of zinc, 45 kg of copper, 5 kg of calcium, 56 kg of nickel, 4.6 kg of uranium, 16.5 kg of thorium, 60.6 kg of chromium and 11.2 kg of cobalt per day, all in a mobile state (Sahu, 1994). In Jharkhand Damodar Valley Corporation has two major power plants viz. Bokaro Thermal Power Plants (BTPS) and Chandrapura Thermal Power Plant (CTPS) are located at the bank of Konar and Damodar rivers respectively. In BTPS frequent overflow of ash slurry from ash pond to Konar river is there. In CTPS some times ash slurry goes directly to Damodar river, without going to the ash pond. Recommendations have been made to take immediate step to stop disposal of ash into Damodar River and find out ways to safely manage and reuse the generated coal ash (Prasad, B., 2004).

There are major instances of major dust pollution around the Indraprastha Power Station (IPP Station) and Rajghat Power house (RPH) from fly ash dispersal. The supernatant from these ponds is discharged into river Yamuna. It was found that fly ash dispersal from stacks are a source of alkali, alkaline-earth and to some extent heavy metals in soils in the vicinity of power stations, and enrichment of elements in river overbank soils are a result of discharge of fly ash leachates from ash disposal ponds (Mehra, A., et al.,1998). Fly ash effluents from ash ponds significantly increased the concentration of some elements, viz., Al, Sb, Bi, Cd, Cr, Co, Li, Mn, Mo, K, Si, and Zn inYamuna river water due to slurry disposal of Indraprastha thermal power plant in Delhi India, (Walia, A., et al., 1998). Fly ashes from Chandrapura Thermal power plant, Bihar, Jamadoba Thermal power plant, Bihar, Durgapur Thermal power Plant, West Bengal and Ramagundam Thermal Power plant, Andhra Pradesh have studied for leachate analysis. Laboratory experiment reveals that after immediate release of heavy metals from these fly ashes may not be alarming but the disposed coal ashes in field are always in contact with soil and weathering takes place. All these factors may enhance the possibility of long term leaching of heavy metal ions to soil and ultimately to groundwater. So, systematic and proper disposals of fly ashes are required to prevent environmental contamination. A comprehensive utilization of fly ashes would be a proper alternative way to manage the disposal of huge quantity of fly ashes from thermal power plants (Prasad, B. et al., 1999).

The river Pandu, a tributary of the Ganga, which flows for 120 km after originating at Farrukhabad, is heavily polluted with industrial and human waste. Villagers lay a major share of the blame on the Panki Thermal Power Plant near Kanpur. The plant uses 3,000 tons of coal and churns out 40 tons of fly ash every day. This ash is deposited in a fly ash pond in the vicinity, but it invariably overflows and finds its way into the Pandu river, giving it a silver grayish colour. Further downstream, sewage and effluents from other industries, including an ordnance factory, has turned the water black. When the monsoons are over, and the water in the river recedes, creates difficult situations for the villagers. The water leaves behind a blanket of fly ash on a vast tract of agricultural land. In the dry season, farmers have to depend on the mercury-rich ash-laden water to irrigate their fields. This once 'highly fertile' land has become almost uncultivable.

Tripathy, S., et al., (2006) delineated water and sediment contamination in river near coal ash pond in Orissa, India. They reported that Al, Mn, Fe and Pb are major contributor to river water from ash pond effluent, and due to those metals river water is not suitable for drinking purpose. Most of the elements are found to be enriched in sediments and water samples of down stream of effluent discharge. Thus changes in physicochemical properties of sediments have altered their natural ability to scavenge heavy metals. The mineralogical–morphological characteristics of downstream station of Nandira and Brahmani rivers, Angul Orissa, India confirm the contamination of metal content coal fly ash samples generated from the thermal plants (Rath, P., et al., 2009)

The ecological impacts of thermal power stations on the aquatic ecosystems are reported by (Khapekar, R R., 2008). All chemicals used for the treatment of waste water and heated water from thermal power stations are allowed to enter into the nearby water bodies. Due to higher temperature of released water the solubility of dissolved oxygen decreases.Due to entrapment and impingement fish kills occur, which in turn result modification of food chain. The fly ash particles (particularly cenospheres/floaters) decrease the visibility of receiving water body causing less penetration of sunlight which ultimately effects the photo synthetic production of green plants leading to disturbance in food chain.

Rowe C. L., et al., (2002) reviewed in detail the adverse effects of coal combustion residues in United States, on aquatic organisms and health of aquatic ecosystem and they noted variety of biological responses in organisms. In some vertebrates and invertebrates exposure of coal combustion residues has led to numerous histopathological, behavioral, and physiological (reproductive, energetic, and endocrinological) effects. Fish kills and extirpation of some species have occurred due coal combustion residue release, which have indirect effect on survival and growth of aquatic animals. Authors recommended that factors influencing the leaching of soluble salt and trace elements will be important in identifying the adverse impacts of groundwater contamination on wild life and human health.

The major potential harmful impacts of ash disposal on terrestrial ecosystems are reported by (Carlson C L., et al., 1993). Leaching of toxic substances from ash into soils and groundwater, reductions in plant establishment and growth, changes in plant elemental composition; and increased cycling of potentially toxic metals through food chain are the hazardous effects of fly ash disposal. Detrimental effects on plants are caused by excessive Boron (B), increasing salinity and alkalinity from the application of unleached ash. B, Mo, S and Se are readily soluble and available to plants and they are accumulated in plant tissues in sufficient quantities. High Boron concentrations in soil can be toxic to growing plants, whereas high Mo and Se uptake by plants are potentially hazardous to grazing animals. Adverse physical and chemical characteristics of fly ash deposits limit colonization by microorganisms. Ash basin effluent and surface runoff affect both water quality and the biota that inhabit receiving lakes and streams. Fish kills have been observed due to ash pond effluent. Ash basin discharges have also resulted in reduced densities and diversity of aquatic macro invertebrates.

Milk samples collected around Koradi Thermal power plant, India were analyzed (Fendar, B. S., et al., 1992) for metals Cu, Pb, Zn, Ni, Co, Cd, and Mn. It was observed that the fly ash of thermal power plant leads to increase in concentrations of toxic trace metals Cu, Pb, Zn, Ni, Co, Cd, and Mn in milk samples collected from the other areas exposed to the thermal power plant. Plants and soils downwards of a power plant in Nevada burning a high arsenic coal (> 500 µgm/gm) were markedly enriched in arsenic (Berry and Wallace, 1974). Authors stressed the hazard of arsenic transfer to humans from the milk of those cows feeding in the area. The arsenic coal burned at a Czechoslovakian plant resulted not only in the contamination of adjacent pasture, but also the poisoning of livestock feeding in the area (Kuhnert, 1973).

Changes in water chemistry characteristics, macroinvertebrate communities and fish assemblages in a low order Southern Ohio stream (Stingy Run) is a result of from acid mine drainage stream to a fly ash receiving stream (Reash, R. J., et al., 1988).

2.11. 4 Effects of fly ash spill due to ash pond failure

A breach in the embankment of a fly ash slurry pond at the Kolaghat Thermal Power Station West Bengal, India, forced over a thousand residents of adjoining Bon Mecheda, Andulia and Ruxa Chowk villages to leave their residence as the hazardous slush invaded their homes and led to an emergency shut-down of the Kolaghat plant. In the clean up process brackish water is pumped out of villages through the Bankur canal and finally disposed to Rupnarayan River leading to ecological disturbance.

On December 22, 2008, the retaining wall broke on a waste retention pond at the Tennessee Valley Authority (TVA) Kingston Fossil Plant, Tennessee, and an estimated 4.1 million m^3 of coal ash slurry was spilled onto the land surface and into the adjacent Emory and Clinch Rivers (TVA, 2009). This was the largest coal ash spill in US history. The coal ash sludge spilled into tributaries that flow to the Emory River and directly into the Emory river itself, which joins to the Clinch River and flows to the Tennessee river, a major drinking water source for downstream users. Ruhl, L ., et al., (2009) investigated the potential environmental and health impacts and found that due to this TVA coal ash spill, which caused leaching of coal ash contamination of surface water occurred and to some extent it gets diluted in the river Emory and Clinch rivers. They also reported that accumulation of Hg and As- rich coal ash in river sediments has the potential to disturb the ecological balance in the downstream rivers by fish poisoning and methylmercury formation an anaerobic river sediments. The surface release of coal ash with high levels of toxic elements (As = 75 mg/kg; Hg = 150 µg/kg) and radioactivity (226Ra + 228Ra = 8 pCi/g) to the environment has the potential to generate resuspended ambient fine particles (<10 µm) containing these toxics into the atmosphere that may pose a health risk to local communities.

2.12 HEALTH ASPECTS OF FLY ASH DISPOSAL

The concentrations of trace elements in fly ash and bottom ash are typically higher than those found in the earth is crust, coal, and soil indicating at the coal combustion process tends to enrich these by-products in trace elements. Therefore, an unavoidable consequence of utilizing coal combustion waste is the release of these concentrated metals and metalloids into the surrounding environments. From a regulatory perspective, coal combustion waste are not considered to pose sufficient danger to the environment, however, the impact of land application and disposal of coal combustion waste on human health and environment is still a concern.

The primary routes of fly ash entry to human body are through the respiratory system (inhalation), eyes and skin. Short term exposure may result in irritation of eyes, skin or the mucous membrane of the respiratory tract. Persistent exposure to airborne dust may cause chronic bronchitis and pulmonary fibrosis (Cho, K., et al., 1994). Any adverse effect of fly ash is more likely to occur in the respiratory tract than in the alimentary canal, simply because the mechanism in the respiratory tract is less effective for expelling fine particles. After inhalation fine particles (<10 µm) are efficiently deposited in deep lung and least efficiently removed by mucociliary transport. Coal ash contains toxic substances that can irritate an inflammatory response. Irritation can result in scarring of the lung tissues or silicosis. If these scars become widespread in the lungs, they can hamper breathing (EPRI Environmental Focus report, 1998). Fergusson J. E., (1990) estimated the metal deposition in lungs and absorption into blood stem. Lead is reported to deposit in lungs in the proportion of 30-85% and adsorption into blood stream fell into the range of 40-100% and the small particles would be 100% absorbed. The submicron ash particles are more enriched with heavy metals are more dangerous to health. Fine particles can penetrate extensively to the bronchiole and alveoli; undergo deposition through Brownian motion in human lungs (Lee, P. H., et al., 1998).

The possible risks to workers from Afsin-Elbistan-A power plant were investigated (Celik, M., et al., 2007) by analyzing the frequency of chromosomal aberrations, polyploidy, sisterchromatid exchanges and micronuclei in peripheral blood lymphocytes in 48 male workers without history of smoking, tobacco chewing or alcohol consumption. The levels of all four markers were significantly higher in exposed workers than in controlled environment. These cytogenitic changes might originate from the cumulative effect of the many chemical compounds that are present in coal ash and gaseous emissions rather than a specific substance.

An extensive research (Meij, R., 2001) was carried out in order to map exposure and its effect on employees and people living nearby/involved in processing of coal fly ash (pulverized fuel ash). Under normal operating conditions, concentrations of inhalable pulverized fuel ash associated with occupational exposure in power stations vary between 0.1 and 7 mg/m^3, while concentrations of respirable pulverized fuel ash associated with such exposure in power stations are between 0.1 and 2.3 mg/m^3.

Studies by health authorities at Santhaldih, in Purulia district of West Bengal, reveals that a large number of people in the area are victims of lung infections and skin disease, caused by fly ash contamination of air and water. The power plant, first commissioned in 1973, with a total of 480 MW capacity, produces 0.6 MT of fly ash every year. The authorities had built two ash tanks at Santhaldih, which have now been filled up. And the fly ash, now that it cannot be stored in these ash ponds, is getting scattered over 25 villages in the neighborhood. The effect of the ash is found on local animals and vegetation, too. The cattle feeding on contaminated vegetation are victims of skin diseases and dental disorders. The population of birds and water animals is also decreasing (TERI, 2000).

All substances emitting radiation have been considered as carcinogenic and at higher doses, ionizing radiation may cause developmental defects leading to impaired brain functions, for example severe mental retardation. The target organ of the radionuclides U and Th are bones and lungs. Increased incidence of leukaemia, bone sarcomas and chromosomal aberrations are due to the radiotoxicity of thorium. Exposure to high dose rates has shown cases of lung and bone cancer in the population within an 88 km radius of the power plants of Indraprastha, Bandel and Badarpur (Lalit et al., 1986). Although the cases of radiation hazards to the local population of Kolaghat have not been studied in detail, considering the high dose rates it can be said that there are sufficient chances of a danger of lung and bone cancer to the population of the neighbouring villages of the Kolaghat power plant. Therefore, proper disposal methods of the fly ash, for example, an increase in the stack height of the chimneys, covering of the ash pond with a concrete layer and lead bricks to attenuate the gamma radiation are recommended to reduce the possible hazards to the local residents of the Kolaghat thermal power plant.

2.13 NEED OF LINERS FOR ASH POND

One of the major concerns about the disposal of coal combustion byproducts is leaching of heavy metals into surface and groundwater, which may contaminate the water quality near ash disposal area (Asokan P., et al., 2004). Wet disposal technique of ash disposal without lining makes, the surrounding prone to the heavy metal contamination (Sushil, S., et al., 2006). Water is becoming scarce and needs to be preserved against the losses due to seepage and evaporation. The lining arrests the seepage and does not allow the leachates to migrate into the groundwater. The environmental clearance for most of the newer power plants in the recent past, irrespective of disposal method (dry or wet), stipulates requirement for installation of impervious liners for ash dump areas and for coal stock yard to prevent leaching of pollutants such as heavy metals and suspended particulate matter from coal thermal ash dump areas leading to contamination of groundwater. As per Pollution Control Board of India norms, an impervious membrane has to be provided to prevent pollution of the ground water (Gandhi, S. R., 2005). World Bank (1998) has given guideline to monitor and treat leachates and overflows from settling ponds in addition to disposing of them in lined places to avoid contamination of water bodies. Bailey et al., 1999 reviewed low cost sorbents (bark, lignin, dead biomass, peat moss,leaf mould, clay etc) for removal of heavy metal from wastewater. Chakraborty, s., et al., (2006) used agro based xanthates for removal of copper from wastewater. Tare, V. et al., used insoluble xanthate for remocal of metallic cations.

For the first time in India, Spectrum power station at Kakinada, has adopted Fabriform concrete bags over LDPE film in the raw water storage reservoir for preventing the seepage from the pond (Rengaswamy, A., et al., 2000). The primary purpose of the liner system is to isolate the leachate from the environment and, therefore, to protect the soil and ground water from pollution originating in the landfill. Provision of low permeable liner can reduce the concentration of heavy metals.

A typical 1000 MW coal based thermal power plant with 100 to 150 hectares for ash pond and 20 hectares of coal yard area would require an additional capacital expenditure of Rs 400-600 million in order to provide such impervious layer inaccordance with MOEF guidelines which is approximately 1% of the total capital cost. However this cost would vary depending upon the disposal method, terrain, calorific value of coal and its ash content etc.

Low permeability liners (low permeability soil liner, low permeability compacted clay liners, low permeability soil admixed liner), geomembrane liners (Chahar, B. R., 2009), (thermoplastic polymers, thermoset polymers and combination of both), geotextiles, geosynthetic clay liners, geogrids, geonets and geocomposite drains are the various types of liners and used according to the requirement. Geomembrane developed by Deopura B. L., et al., (2006) at IIT Delhi India of thickness around 0.5 mm have significant effect to control the seepage. Geomembrane either alone or in conjunction with concrete/ brick cover can greatly increase the effectiveness of lining system. Low permeability clay liners are easily available and economically viable and they are also known to retain the heavy metals due to their surface characteristics (Cherry 1987; Fetter, 1990).

General requirement of clay liners are given as below (Sarsby, R., 2000)

1. Hydraulic conductivity of liner must be 10^{-9} m/sec or less.
2. The clay layer must be free of natural or compaction induced fractures.
3. The minimum thickness of a compacted clay liner for a domestic or commercial waste facility should be 1 m.
4. Minimum clay content (particle size smaller than 2 μm) of 10-20%.

Compacted clay of appropriate quality has very low/negligible hydraulic conductivity in the order of 10^{-7} cm/sec or even lower has been successfully used as liners in some countries. Based on the service conditions and the property of compacted clay being considered a layer of compacted clay of thickness in the range of 200 to 600 mm could be sufficient for the use as impervious liners in coal/ash dump areas. This could reduce the cost of impervious liners. Thus to reduce seepage losses from ash ponds or waste impoundments for water conservation and environmental protection, the provision of liner is necessary. Of course the decision of liner should be backed by proper investigation of local hydro-geological conditions.

2.14 INFILTRATION OF WATER AND ASH SLURRY IN TO ASH POND

Before setting up any monitoring plan for contaminated site useful information about site such as geological and hydro-geological information, pedological and historical data about land use in the area should be collected and analyzed properly. Incase of ash pond physical and chemical properties of fly ash along with leaching pattern, hydro-geological condition, prevailing climate conditions as well as leachate travel time through unsaturated zone at the groundwater table will be greatly helpful for monitoring of groundwater contamination and remediation of contaminated site. Toxic metals present in the leachate, infiltrating the soil may be transported or absorbed on the grain surfaces in the unsaturated zone where they are further transported and spread on a wide scale. Study of the dynamic properties of the groundwater and the mechanisms of flow may be very important in planning and designing of remediation projects. A monitoring of the groundwater velocities and directions of flow is thus an essential part of the whole monitoring plan (Mirsal, I. A., 2004). Leaching of a large combustion residue disposal site may continue for hundreds of years, especially if measures are not taken to reduce infiltration (Hjelmar, O., 1990). When ash is disposed in the ash pond (in successive layer deposition), once first layer is disposed, in the second disposed layer hydraulic conductivity decreases rapidly which delay the travel time of the leachate to the groundwater table.

2.15 RECLAMATION OF ASH POND

Many disposal ponds are now or will soon be filled to their design capacity. For many power plants authorities, an attractive possible reclamation plan is to use the closed ash pond as a foundation of a new disposal facility (Tu, Wei., 2007). Another option for abandoned ash pond is to eco-friendly revegetation (Haynes, R. J., 2009) and biological intervention (Juwarkar, A. A., 2007). Revegetation of abandoned ash disposal sites is desirable since it stabilizes the surface against wind and water erosion and also provides a more aesthetically pleasing landscape around thermal power plant (Haynes R. J., 2009). Phytoremediation offers an effective way to prevent cycling of toxic metals from fly ash and growing of multipurpose tree species on the problem soils is an environmentally safe strategy for gainful utilization of fly ash (Jala, S., 2006). Fly ash disposal site of Khaperkheda thermal power station, Khaperkheda in Maharashtra state, India was amendmended with farmyard manure. After the amendment of farmyard manure and biofertilizer inoculation, the concentration of different metals such as cadimium, copper, zinc, nickel, chromium, iron, manganese and lead are reduced by 25%, 46%, 25%, 48%, 31%, 65%, 23% and 47% respectively, because organic amendments such as mature compost and manure, which contain a high proportion of organic matter helps in decreasing the bioavailability of heavy metals in soil, thus permitting the reestablishment of vegetation on contaminated site (Juwarkar et al., 2007). Mycorrhizae also play a crucial role in protecting plant roots from heavy metals (Galli et al.,1994). Mycorrhizae through their mycelia network accumulate heavy metals from the fly ash and retain them within their cell, thereby reducing the toxicity of the metals to the plant.

Renschler, C. S., (2007) suggested that there is need for interdisciplinary approach to problem identification, research in geomorphology, ecosystem ecology. It will be useful for gradual reclamation of ash ponds which in general is the ultimate aim, once capacity of ash pond is filled.

2.16 CONCLUDING REMARKS

Utilization of fly ash is less in India even with concrete efforts of Government of India and other agencies, resulting wet disposal of fly ash in almost all the power plants. Coal is an inherently heterogeneous raw material, so is its combustion by-product, fly ash. A typical fly ash aggregate is composed of spherical particles embedded in an amorphous matrix and it is Ferroaluminosilicate mineral. The physical and chemical properties of coal ashes are dependent on coals geological origin, combustion conditions, efficiency of particulate removal and degree of weathering before final disposal. The chemical properties of the coal ashes strongly influence the environmental impacts that may arise due to utilization or disposal. As such there is no leaching protocol available in India. Different elements have different leaching behaviour. The pH is a master variable which controls the leaching of fly ash. A leaching test would be such that it should simulate field conditions. Very few studies have been done in India to address the issues of leachability, field investigation and modelling of leaching of fly ash.

Wet disposal of fly ash is considered as a potential source of contamination due to enrichment and surface association of trace element in the ash particles. The adverse impact includes contamination of surface, subsurface water and groundwater with toxic heavy metals present in the coal ashes, loss of soil fertility around the plant sites. This is also related to recycling of potentially toxic elements through food chain. Hence a detailed study of their chemical composition, morphological studies, mineralogy and leaching behavior are essential for study of evaluation of environmental effect of wet disposal of fly ash. Provision of liner is necessary in order to prevent the contamination of groundwater from ash pond seepage and decision of chioce of liner should be backed by proper hydrogeological investigation. Gradual reclamation of ash ponds should be encouraged.

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROGRAMME

3.1 PREAMBLE

The disposal of fly ash in the wet form has caused a variety of environmental problems particularly to soils and water environment due to an extreme pH and high concentrations of soluble salts, trace metals and other pollutant that leach from fly ash. Physical and chemical properties as well as morphology and mineralogy of fly ash gives an important index, which can be useful for utilization of fly ash or for the assessment of effect of wet disposal of fly ash. Various instruments were used for characterization of fly ash in the present study are XRD (X-ray Diffraction), SEM (Scanning Electron Micrography), SEM-EDAX (Scanning Electron Micrography- Energy Dispersive X-ray Diffraction), AFM (Atomic Force Micrography) and laser particle size analyzer. The laboratory testing programs have been designed to address issues of leachability. The instruments used for leachate analysis and characterization of fly ash are briefly discussed in this chapter. Cascade leaching test was conducted on collected fresh fly ash samples. A soil column study with fly ash slurry has also been conducted in order to check the mobility of metals through soil column.

3.2 STUDY AREA

The fly ash samples were collected from Guru Hargobind Thermal power plant (Lehra Mohabat) Bhatinda Punjab, Dadri Thermal Power Plant Uttarpradesh, Nashik Thermal Power Plant Eklahara, Maharashtra and Suratgarh Super Power Plant, Rajasthan India in the dry form and their locations of these power plants are shown in Figure 3.1 in the map of India. This ash was not subjected to any pretreatment procedure and obtained directly from the hopper and stored in moisture-proof bags and plastic containers to avoid deterioration with time. Soil samples have been collected in moisture proof bags from Bhatinda and Nashik thermal power plant, and those samples were used in soil column studies.

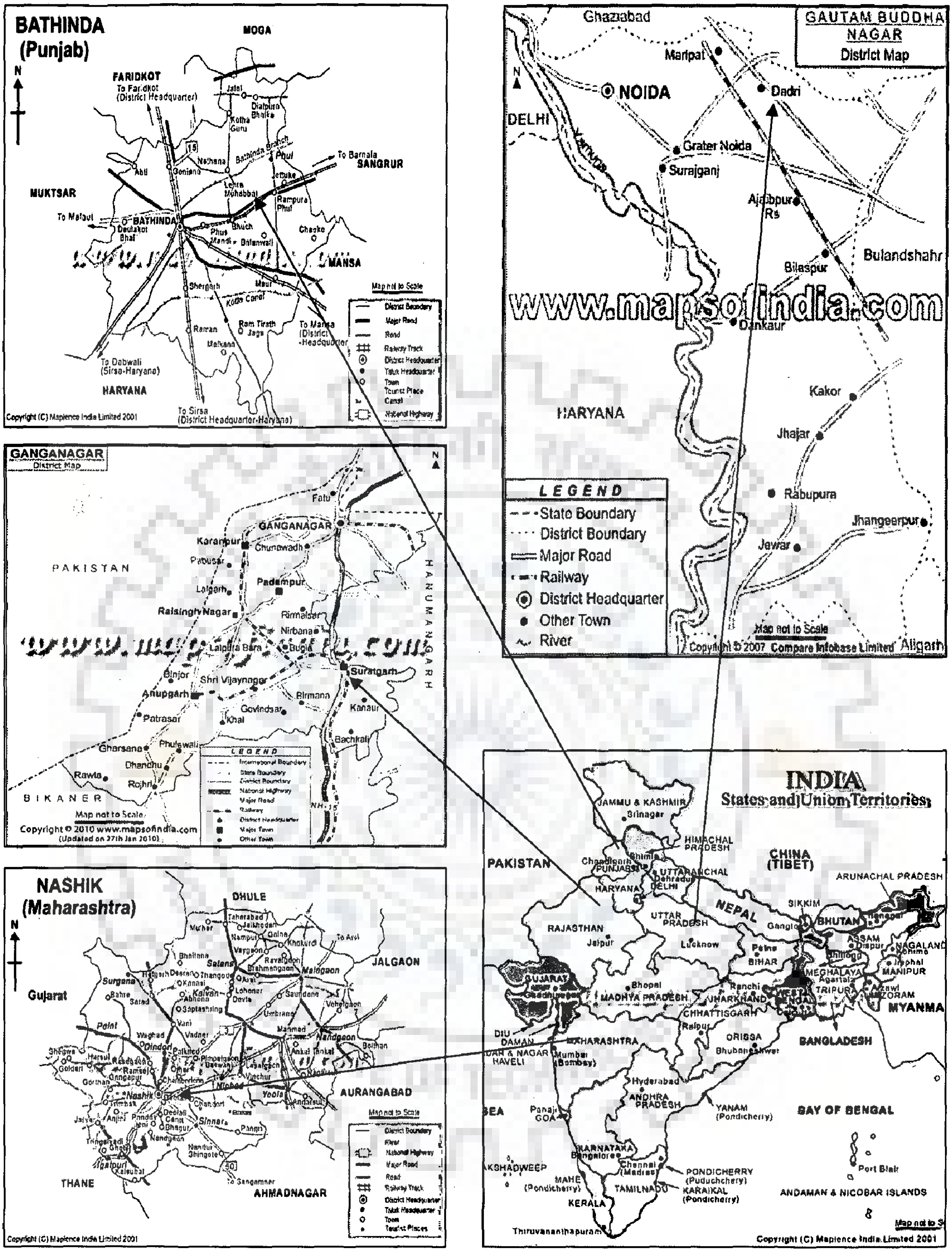


Figure 3.1 Map of India showing locations of power plants.

3.2.1 Fly ash utilization Status in Study area

In the Guru Hargobind Thermal Plant Lehara Mohabat, Bhatinda 49.58% of fly ash was used in the year 2003-2004 and mostly used for cement production. At Nashik Thermal Power Station 25% in 2003-2004, 7.55% in 2004-2005 and 22.2% in 2005-2006 respectively were used for cement production, brick manufacturing, landfill, agricultural and other ash based projects. At Dadri power plant, National Thermal Power Corporation (NTPC) has established for first time in Asia a 100% dry ash extraction-cum-disposal system in the form of ash mound. It resulted in progressive development of green belt besides reduction of land and water requirement as compared to the wet ash disposal system. Dadri fly ash is being used for cement production, construction for Delhi metro rail, embankment and other ash based products. Similarly ash utilization at Suratgarh Thermal Power Station is also encouraging, 22.85% utilization of generated ash have achieved during the year 2003-04. To increase the utilization of ash from this plant cement factories and brick manufacturing units are being encouraged. A cement manufacturing company M/s Shree Cement has started lifting ash and two small brick manufacturing units have come up near the plant. It is expected that the ash utilization will gain momentum. Due to location of this plant at remote desert place, it may take relatively longer time to increase ash utilization. An action plan has been formulated and efforts in this direction are being made. Ash pond surface water, freshly disposed slurry water, effluent samples and groundwater samples at Kotamgaon and Hinganvedhe villages near to Nashik thermal power plant ash pond were also collected.

3.2.2 Installed Capacity of Power Plants

In the present study data pertaining to installed capacity, annual ash generation, type of coal used, area of ash pond etc from the four plants were collected. The installed capacities of the power plants are given in Table 3.1

Table 3.1 Installed capacity of power plants

Sr No	Power plant	No & Capacity MW	Total capacity MW
1	Guru Hargovind Thermal Power Plant, Lehra Mohabat, Bhatinda, Punjab	2 x 210 MW	420 MW
2	National Thermal Power Corporation Dadri, Uttarpradesh.	4 x 210 MW	840 MW
3	Nahsik Thermal Power Plant, Eklahra Maharashtra.	2 x 140 MW 3 x 210 MW	910 MW
4	Suratgarh Super Thermal Power Station, Rajasthan.	5 x 250 MW	1250 MW

3.2.3 Field investigation Area

Fly ash, soil, ash pond effluent, immediately disposed slurry, ash pond surface water and groundwater samples from open dug wells were collected particularly for Nashik pond which is shown in Figure 3.2. Ash pond consists of two effluent channels, namely Eastern and Southern channel which later joins to Darna river which is a tributary of Godavari river. The length of those channels are approximately 7-8 km. Groundwater samples from open dugwells of two villages i. e. Kotamgaon and Hinganvedhe were colleted, in the present study. Physical observations are also made through actual site visit at Nashik ash pond and surrounding of the ash pond.

Figure 3.2 Plan of Nashik ash pond and adjoining Darna river

3.3 PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF FLY ASH

Physical properties help in classifying the coal ash for engineering purposes and same can also be useful in utilization of fly ash. The chemical properties of coal ash greatly influence the environmental impact due to utilization/disposal as well as their engineering properties. The adverse impacts include contamination of surface and subsurface water due to leaching of toxic metals present in coal ashes, loss of soil fertility and aquatic ecosystem. To check environmental implications of fly ash disposal, it is necessary to study leaching behavior of fly ash with experimental studies. A leaching test should reflect the range of conditions (pH, redox potential, L/S ratio, contact time etc) that will be present in fly ash and its interaction with environment during leaching (Zandi M., 2007). Knowledge of physical, chemical, mineralogical, and morphological properties of ash along with leaching behavior is an important index for decision making for environmental assessment as well as for utilization of ash and to monitor the post disposal conditions.

3.3.1 Physical properties of fly ash

Physical properties such as color, specific gravity, specific surface area by using Blain's air permeability apparatus, falling head permeability of fly ashes are determined in Geotechnical section of Civil engineering Department of I I T Roorkee. The specific gravity of the fly ash was determined according to IS 2720-1980 guidelines. The specific surface area of fly ash was determined by Blain's air permeability method as per IS: 1727-1967 guidelines. Permeability was determined as per falling head apparatus method. All the samples for permeability were prepared at Maximum Dry Density (MDD) and Optimum Moisture Content (OMC) of fly ash.

3.3.2 Chemical properties of fly ash

Major oxides are determined with help of X Ray Fluorescence (XRF) apparatus. Collected fly ash samples were given for XRF analysis at Wadia Institute of Himalayan

Geology Deharadun, India. Total heavy metal compositions were determined by Aqua regia digestion method.

3.4 INSTRUMENTS USED FOR CHARACTERIZATION OF FLY ASH

Modern instruments give quick and accurate result and data obtained can be sufficiently useful for field evaluation or field application. The ash characterization was performed primarily with the help various instruments such as X-Ray Diffraction (XRD), Scanning Electron Microscope along with Energy Dispersive X-Ray Analysis (SEM EDAX) and Atomic Force Microscopy (AFM). For the study of the particle size analysis, laser particle size analyzer was used. For the identification of minerals XRD was used. Morphological features were recorded with the help of SEM (microscale) and AFM (nano scale). SEM-EDAX gives chemical composition as well as morphological features. So it is more useful compared to SEM.

3.4.1 Scanning Electron Microscope (SEM)

The application of scanning electron microscope (SEM) technique has made it possible to resolve the structure of materials to a fraction of a micrometer. When a beam of electrons strikes the surface of specimen at ground potential, back scattered electron, X-rays and secondary electrons are radiated. Appropriate collection and processing of these radiations give lot of information about the surface characteristics of specimen. The Scanning Electron Microscope (SEM) is a type of electron microscope capable of producing images of a sample at high resolution. Due to the manner in which the image is produced, SEM images have a distinctive three-dimensional appearance and are useful for judging the surface structure of the sample (Mattigod, 1982).

The ash samples were oven dried and mixed to attain a homogenous mixture. To study morphology of fly ash particles in the present investigation Scanning Electron Microscope (LEO 435 VP) has been used and it is shown in the Figure 3.3. The carbon tape was used to attach the samples to the holder. Oven dried fly ash particles were mounted on both side adhesive carbon tape affixed to aluminium stub. Fly ash sample was coated with pure gold in high vacuum evaporator for 60 seconds. The coated sample of fly ash was subjected to Scanning Electron Microscopy. Sharp images were obtained from the SEM and this was achieved by adjusting the focus, the brightness and contrast.

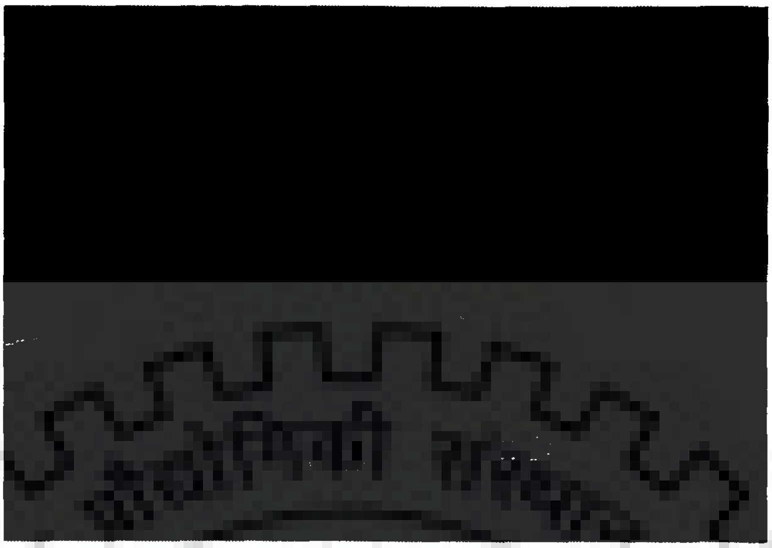


Figure 3.3 Scanning Electron Microscope (LEO 435 VP)

3.4.2 Field Emission Scanning Electron Microscopy (FESEM)

Scanning electron microscopy (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages, using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas. It detects the secondary and back-scattered electrons from a sample surface bombarded by an electron beam scanning its surface. Figure 3.4 shows a schematic diagram of the field emission scanning electron microscope.

The source of the electrons is electron gun. The beam is emitted with in a small specials volume with a small angular spread and selectable energy. The electrons are accelerated to high kinetic energies by using an anode at high positive potential. The first

Field Emission Electron Microscope (FEI Quanta 200F model) which is used in the present study, for surface morphological studies of the fly ash is shown in Figure 3.5. FESEM uses field emission electron gun which provides improved special resolution down to 1.5 nm that is 3 to 6 times better than conventional SEM and minimized sample charging and damage. In conventional SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride (LaB_6) cathode and are accelerated towards an anode; alternatively electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 50 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot size (1 to 5 nm). The basic mechanism of field emission is that a high voltage applied between a pointed cathode and a plate anode caused a current to flow. The field emission tip is generally made of a single crystal tungsten wire sharpened by electrolytic etching. A tip diameter of 100 to 1000 Å is used, with the apparent source size much less than that. The field emission process itself depends on the work function of the metal, which can be affected by adsorbed gases. This is the reason a very high vacuum is required.

The SEM EDAX analysis was conducted on the oven dried sample. Oven dried fly ash particles were mounted on both side adhesive paper tape affixed to aluminium stub. Fly ash sample was coated with pure gold in high vacuum evaporator for 60 seconds. The coated sample of fly ash was subjected to Field Emission Scanning Electron Microscope (FESEM, Quanta 200 F, FEI Netherlands) with EDAX Genesis software attachment made in Czech Republic has been used for microanalysis. Using the energy dispersive x-ray analysis (EDAX) attachment with the SEM, elemental composition analysis can also be done. An EDAX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen.

condenser lens that works in conjunction with the condenser aperture helps to narrow the beam and also limit its current. The second condenser lens then forms the electrons into a very thin, coherent beam. The beam is scanned, point by point over the sample (like in a television) by using a set of scanning coils. The objective lens does the final focusing of the beam onto the sample. At each point the numbers of secondary and back-scattered electrons reaching the detector are counted to be used for determining the relative intensity of the pixel representing that point in the final image. The higher the atomic number of the specimen material, the greater is the number of secondary electrons that reach the detector, giving rise to a higher intensity in the image. A sample needed to be analyzed in SEM need to be conducting. Since all metals are conductive, so no special sample preparation requires for them but all non-metals need to be made conducting by covering the sample with a thin layer of conductive material like gold. SEM is a destructive technique in the case of non-metals since during coating the gold atoms fall and settle onto the surface of the sample producing a thin gold coating.

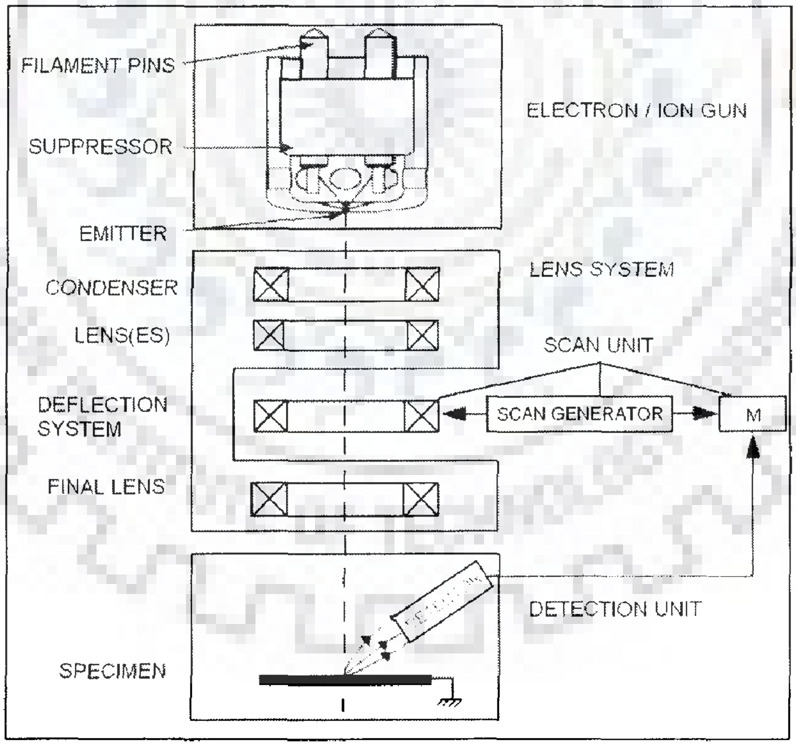


Figure 3.4: Schematic diagram of FESEM

Figure 3.5 Field Emission Scanning Electron Microscopy (FEI Quanta 200F)

3.4.3 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) maps out the topography of a surface by sensing the forces of interaction between the atoms belonging to the sample surface and the ones on the tip of the probe. Figure 3.6 shows the basic components of an AFM. To image the surface features, the sample is scanned by an atomically sharp tip, usually made of Si or Si_3N_4, attached to the lower side of a reflective cantilever. Light from a diode laser is focused on the cantilever and is reflected on to a segmented photodiode. As the sample is scanned below the tip, the cantilever moves up and down which changes the ratio of light falling on the four elements of the photodiode. The difference in the intensity falling on the four elements is converted into a proportional voltage by the photodiode. This voltage serves as a feedback signal enabling the tip to maintain either a constant force or a constant height above the sample.

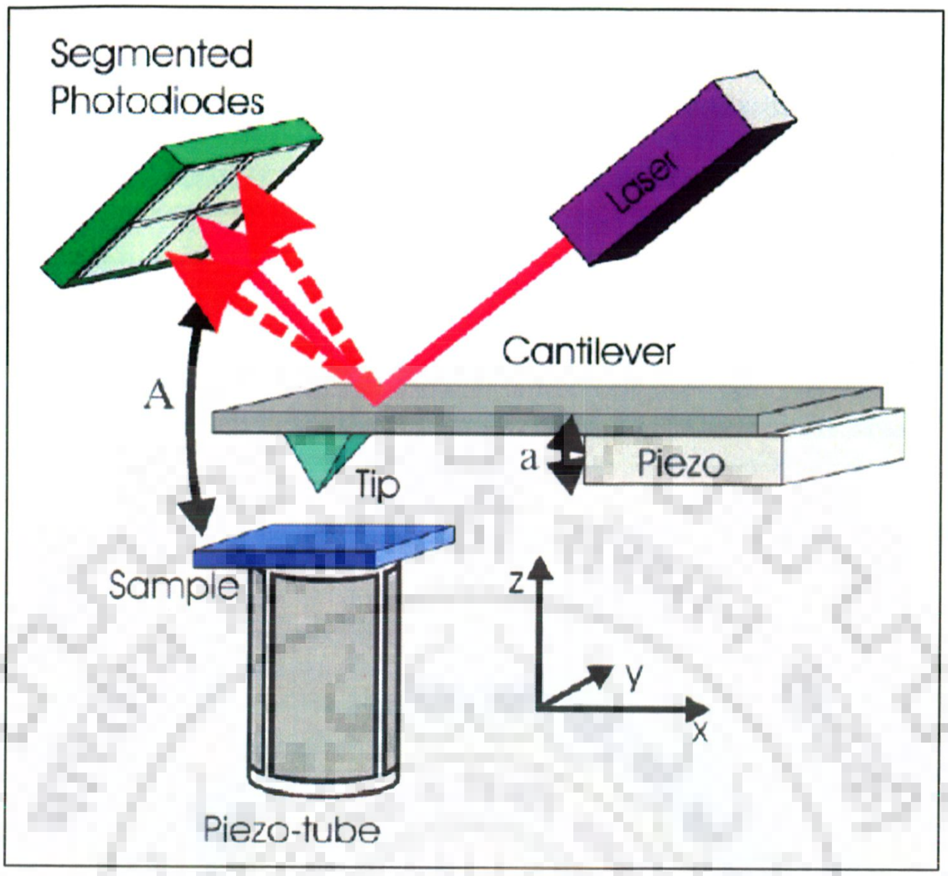


Figure 3.6: Schematic diagram of AFM

For most applications the instrument is operated in one of the following three modes:

(i) **Contact Mode:** The contact mode where the tip scans the sample in close contact with the surface is the common mode used in the force microscope. The force on the tip is repulsive with a mean value of 10^{-9} N. This force is set by pushing the cantilever against the sample surface with a piezoelectric positioning element. In contact mode AFM the deflection of the cantilever is sensed and compared in a DC feedback amplifier to some desired value of deflection. If the measured deflection is different from the desired value the feedback amplifier applies a voltage to the piezo to raise or lower the sample relative to the cantilever to restore the desired value of deflection. The voltage that the feedback amplifier applies to the piezo is a measure of the height of features on the sample surface. The typical problem with the contact mode is that the tip may scratch the surface and change its intrinsic features.

(ii) **Non-Contact Mode:** In this mode the tip is held at 50 - 150 Å above the sample surface. Attractive Van der Waals forces acting between the tip and the sample are detected, and topographic images are constructed by scanning the tip above the surface. Since the attractive forces from the sample are substantially weaker than the forces used by contact mode therefore the tip is given a small oscillation so that AC detection methods can be used to detect the small forces between the tip and the sample, by measuring the change in amplitude, phase, or frequency of the oscillating cantilever in response to force gradients from the sample. For highest resolution, it is necessary to measure force gradients from Vander Waals forces which may extend only a nanometer from the sample surface.

(iii) **Semi-Contact Mode:** Semicontact mode was developed as a method to achieve high resolution without including destructive frictional forces both in air and liquid. In this mode, the cantilever is made to oscillate at its natural frequency by using a piezo-electric crystal. The oscillating tip is moved close to the sample surface till it begins to just tap it and is then immediately lifted off again, while the sample is continuously scanned below the tip. The change in oscillation amplitude during the tapping period is used as a feedback to maintain constant height or force between the tip and the sample. The feedback voltage serves as a measure of the surface features. The advantages of the semi-contact mode are that as the tip is not dragged over the sample there is no damage caused to the sample and also the tip is prevented from sticking to the sample surface due to adhesion.

The AFM setup used in the present study is shown in Figure 3.7. A special table to isolate mechanical and acoustical vibrations is necessary to perform high resolution (atomic scale) work.

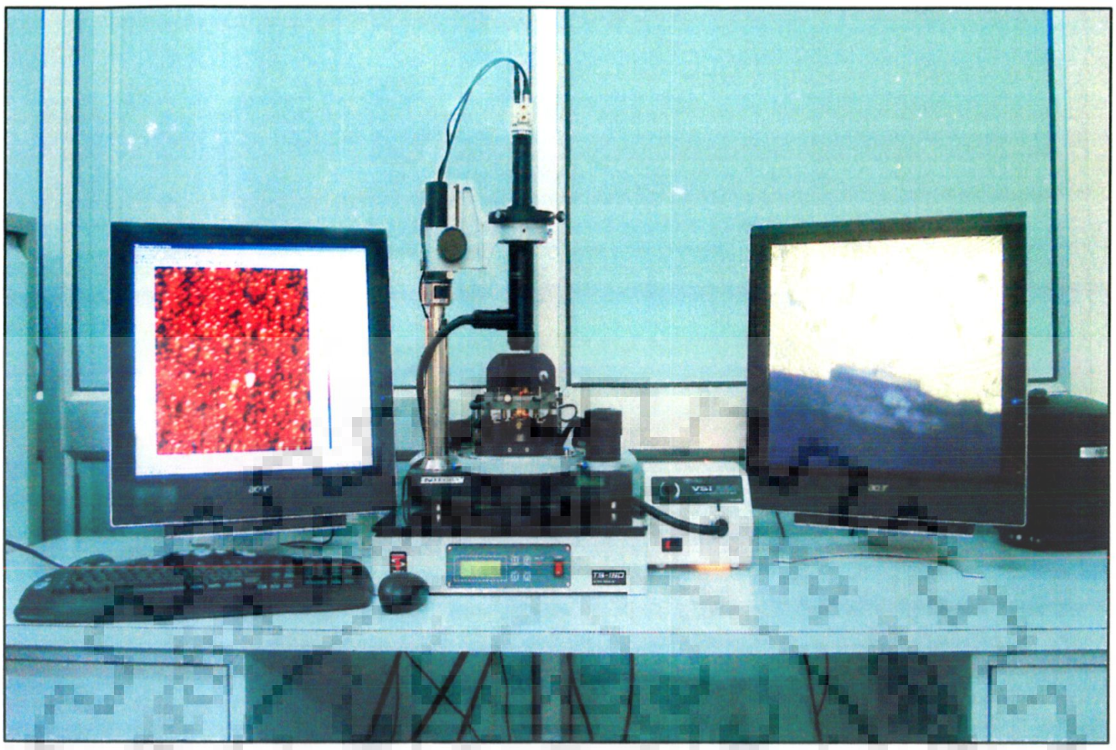


Figure 3.7 Atomic force Microscope AFM (NT-MDT: NTEGRA)

3.4.4 X-Ray Diffraction (XRD)

The most common analytical method to characterize the ash is the X-ray powder diffractometer (XRD) (Ward and French, 2005). The XRD is an instrument that is used to identify minerals, as well as other crystalline materials. Previous research has shown that the XRD complements other mineralogical methods, including optical light microscopy, electron microprobe microscopy, and scanning electron microscopy. XRD provides the researcher with a quick and dependable tool for routine mineral identification. XRD is mainly useful for identifying fine-grained minerals and mixtures or intergrowths of minerals (Ward and French, 2005). However XRD does not provide the quantitative compositional data obtained by the electron microprobe or the textural and qualitative compositional data obtained by the scanning electron microscope (Irgolic et al., 1998).

X-ray diffraction is a non-destructive technique. The basic principle of the XRD is based on the Bragg's law which describes the condition for constructive interference for X-rays scattered from atomic planes of a crystal. The angle between the diffracted beam and the incident beam is always 2θ, and it is this angle, rather than θ, which is usually measured experimentally

$$2d\sin\theta = n\lambda$$

where λ is the wavelength of incident radiation and d is the interplanar distance between the lattice planes which is given by

$$d = \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right]^{1/2}$$

Where *h*, *k* and *l* are the indices of the lattice planes and *a*, *b*, *c* are the dimensions of the unit cell. From the above relations one can easily evaluate the lattice parameters when the values of d and corresponding values of θ (for fixed value of λ) are known. In the present study X-ray diffractometer (Bruker D8 Advance diffractometer) has been used. The radiation (Cu Kα) emanating from the X-ray tube is diffracted at the specimen and recorded by a detector.

The specimen is rotated at constant angular speed in such a way so that angle of incidence of primary beam changes, while detector moves about the specimen at twice the angular speed. The diffraction angle (2θ) is thus always equal to double the glancing angle (θ). The beam path is shown in the Figure 3.8. Whenever the Bragg condition, $2d\sin\theta = n\lambda$, is satisfied, the incident X-ray beam is diffracted at the specimen and reaches the detector. The detector converts the X-ray quanta into electron pulses, which are recorded by recorder. Bruker D8 Advance diffractometer uses NaI scintillation counter as a detector. It can detect the diffracted radiations in the wavelength ranging from 0.5 to 3 Å. Monochromators are used to suppress the undesired portions of radiation. To restrict the irradiated specimen area, aperture diaphragm is arranged between the tube and the specimen as shown in Figure 3.8. The second aperture diaphragm shields the strong scattered radiation of the first aperture diaphragm. The resolution depends upon the detector diaphragm. The scattered radiation diaphragm is used to suppress undesired scattered radiation.

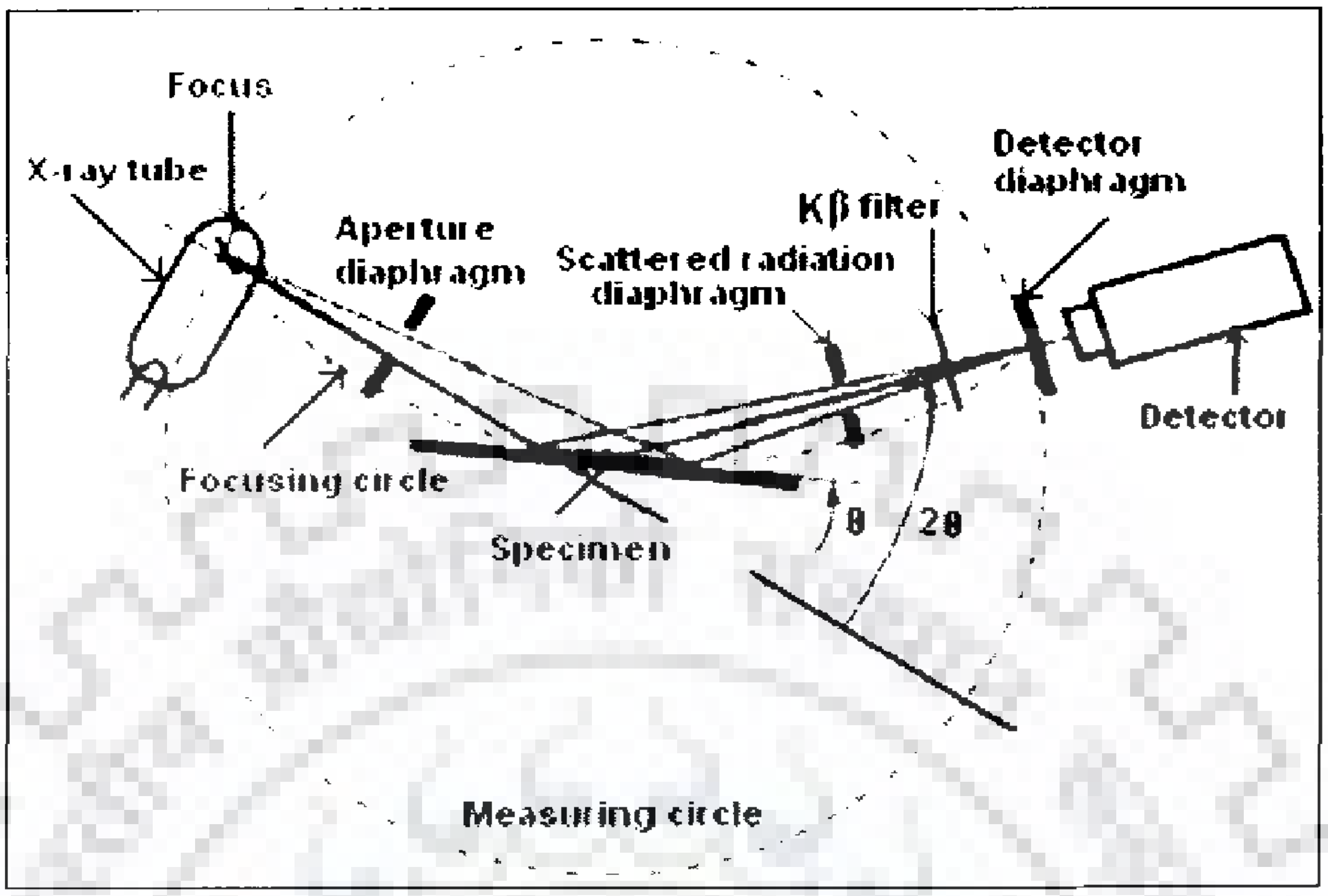


Figure 3.8 Schematic diagram of beam path

The crystallographic information is obtained by evaluating 'd' values and indexing of reflections. The characteristics diffraction pattern of a given substance can always be obtained whether the substance is present in pure state or as one constituent in a mixture of several substances. This fact is the basis of the diffraction method of chemical analysis. X-ray diffraction pattern is characterized by a set of line positions (2θ) and a set of relative intensities (I). The angular position of lines depends on the wavelength of the incident ray and spacing (d) of the lattice planes. The technique can be used for quantitative analysis in which the concentration of phases are calculated by determining the area of the peak, since the intensity of diffraction lines due to one constituent of a sample depend upon the concentration of that constituent in the sample specimen. The qualitative analysis for a particular substance is accomplished by identification of the pattern of that substance. X ray diffractometer (shown in Figure 3.9) analysis was carried out using Burker AXS D8 ADVANCE diffractometer from Germany Cu K-α radiation with Goniometer speed 1°/min in scanning range (2θ) 5°- 70 ° and corresponding peaks are identified by JCPDF software. For the analysis the samples were air dried and mixed homogenously, and then they were placed on the holder. The ash was then flattened with a glass slide. The next step was to further compact the sample within the holder itself and this was achieved by a screw and clamp mechanism. Once the sample is prepared, the machine is switched on and the sliding door is opened and the compacted sample is placed on a magnetic stand. The sliding door is closed and the x-rays are started. For this machine, it takes about 6 seconds for the x-ray to start beaming on the specimen and as can be identified when a red light turns is on the machine itself. The instrument is run for 45 minutes, during this period the magnetic stand with the sample is rotated about its axis. The diffracted results are then obtained and the noise is filtered using the manufacturer developed software.

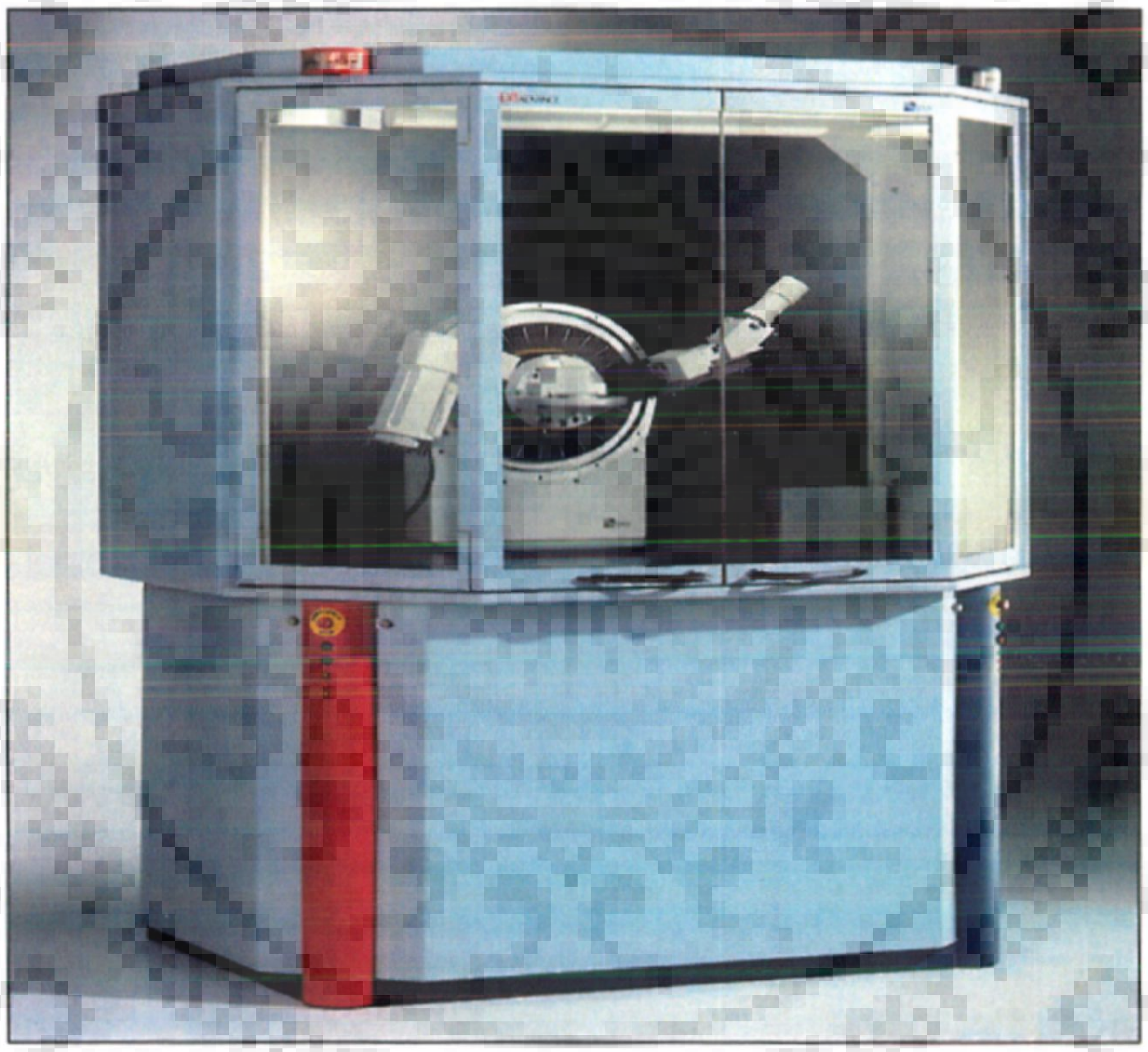


Figure 3.9 X-ray Diffractometer Bruker D8 Advance

3.4.5 Particle size analysis

In this method, a laser beam passes through a sample of particles, and light intensity data is collected at different scattering angles away from the axis of the laser beam. The method gained immense popularity in recent years because it is versatile, fast, highly reproducible and relatively simple to use. Laser Particle Size Analyzer (CIS 100 ANKERSMID) has been used to study the particle size distribution of fresh fly ash is shown in Fig.3.10. The Ankersmid CIS-100 is a Computerized Inspection System for Particle Size Analysis (PSA) in the range of 0.5-3600 micron and Dynamic Shape Characterization (DSC) employing laser and video measurement channels respectively. Together, both channels provide all necessary information to analyze and characterize spherical, non spherical and elongated particles, with high resolution accuracy and reproducibility. The CIS-100 provides the best particle sizing solution for a diversified, dry and wet spectrum of application. In the present study video measurements are not taken.

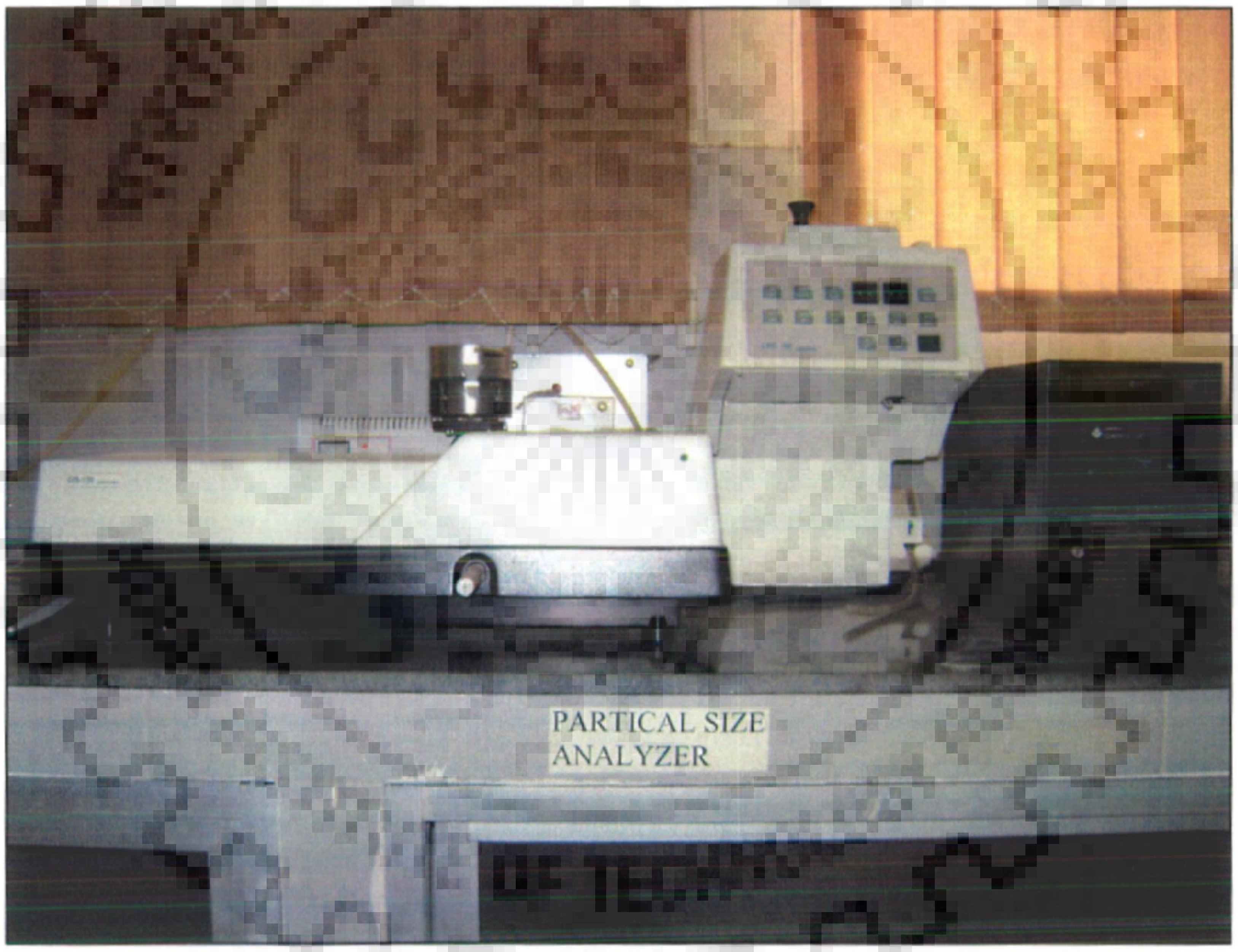


Figure 3.10 Laser Particle size analyzer for fly ash

3.5 EXPERIMENTAL PROGRAMME

The United States Environmental Protection Agency (USEPA) Science Advisory Board (SAB) has recommended that development of a leaching method to characterize the leachability/mobility of wastes involve the following: (1) a better understanding of the controlling mechanisms of leaching, (2) multiple tests to address different disposal scenario, (3) improved models to complement the leaching tests and (4) field validation of leaching tests and predictive models (U. S. EPA SAB, 1991). The ash used in the present research for leaching test was completely free from moisture. Leaching tests consisted of Toxicity Characteristics Leaching Procedure (TCLP) and cascade leaching test.

The TCLP test simulates the type of process a waste might be exposed to under natural conditions in a landfill. If a TCLP determination indicates that these elements are present at the concentrations that exceeds maximum contaminant levels (MCLs) then the original waste is considered to be toxic and is subject to stringent disposal regulations. There are a variety of leaching tests available for application to waste materials. A leaching test involves contacting the waste material with a liquid to determine which constituents will be leached by the liquid and released to the environment. Leaching method vary in test type, leaching aspects addressed, and the particular use for which the test is designed.

3.5.1 Toxicity Characteristics Leaching Test Protocol for fly ash

The TCLP test defined in EPA Method 1311 is designed to determine the mobility of both organic and inorganic compounds present in liquid, solid, and multi-phase wastes. Waste samples are crushed to particle size less than 9.5 mm and extracted with an acetate buffer solution with a pH of 5 or an acetic acid solution with a pH of 3, depending on the alkalinity of the waste. The acetate buffer is added only once, at the start of the extraction. A liquid-to-solid ratio of 20:1(Acidified water: Fly ash) is used and the extraction period is 18 hr. The leachates were filtered through a 0.45 μm filter paper and subjected to chemical analyses.

3.5.2 Cascade Leaching Test Protocol

Leaching tests are designed to provide some indication of the potential environmental effects of fly ash disposal on the groundwater compositions. Since many of trace elements are extracted in much higher percentages by acid than by water extractions it is aimed to provide an estimate of total quantity of an element that could eventually be leached from fly ash. Usually leaching occurs in cascade manner when fly ash was disposed in the ash pond. To simulate this field leaching of fly ash cascade leaching test was used in the present research work. Usually some kind of agitation is required in order to keep fly ash in contact with water. It was found that period required to complete leachability was around 18 hours. With buffer period of another 8 hours the extraction time was kept at about 24 hours (Baig M., et al., 2008). Agitation device used in the present investigation for cascade leaching test is shown Fig. 3.11

Figure 3.11 End to end agitation device used for cascade leaching test

3.5.3 Release as a Function of L/S Ratio

This protocol consists of cascade leaching test over a range of L/S ratios 2, 4, 6, 8, and 10 using De Ionized (D.I.) water as a leachant. The mass of material used for the test was 100 g of dry sample. For the first extraction 100 gm of ash mixed with 200 ml D.I water giving L/S ratio 2. After 24 hours it was filtered with 0.45- µm-pore size Whatman's filter paper and again fresh leachant was added to give rise to cumulative L/S ratio as 4 and again it is agitated. Cascade leaching tests at pH = 4 (50 gm of sample) was also conducted to simulate long term leaching behavior for L/S ratio 5,10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100. The bottles were sealed with leak-proof lids and then tumbled on a rotary shaker at 30 rpm at a room temperature (20 ± 5°C) for 24 hrs. At the end of the agitation period, the extraction vessels were removed from the tumbler and the leachates were clarified by allowing the bottles to stand for 15 min. A volume of clear supernatant from each extraction bottle was decanted to measure and record the solution for pH. Total Dissolved Solids and Electrical Conductivity. For each extraction, the solid was separated from the liquid by 0.45- µm-pore size Whatman's filter paper. The samples then were collected and preserved with 2% nitric acid for metal analysis. Samples were stored in a refrigerator at 4°C until their analysis.

3.5.4 Soil Column Leaching Study

Metals have substantial mobility in the subsurface environment which are easily leached and transported in groundwater. If these metals leached, they may create adverse impact on groundwater quality. With this view it was necessary to study the mobility of selected metals through soil column. For this purpose, soil samples were collected from power plant of Bhatinda and Nashik. Same soil was filled in two acrylic column having diameter of 5 cm and height of 30 cm. Then fly ash slurry was prepared at L/S ratio 10 with acidified water to pH = 4 with Bhatinda Fly ash and Nashik Fly ash and same slurry was poured in open column and leachates were collected at the bottom of the column.

After collection, samples were measured for pH, TDS, EC and then acidified to a pH less than 2 and refrigerated until analysis using an Atomic Absorption Spectrophotometer (AAS). The operation of the AAS and results of metal analysis is explained in following sections. The experimental set up of the present study is shown in Figure 3.12 for soil column study.

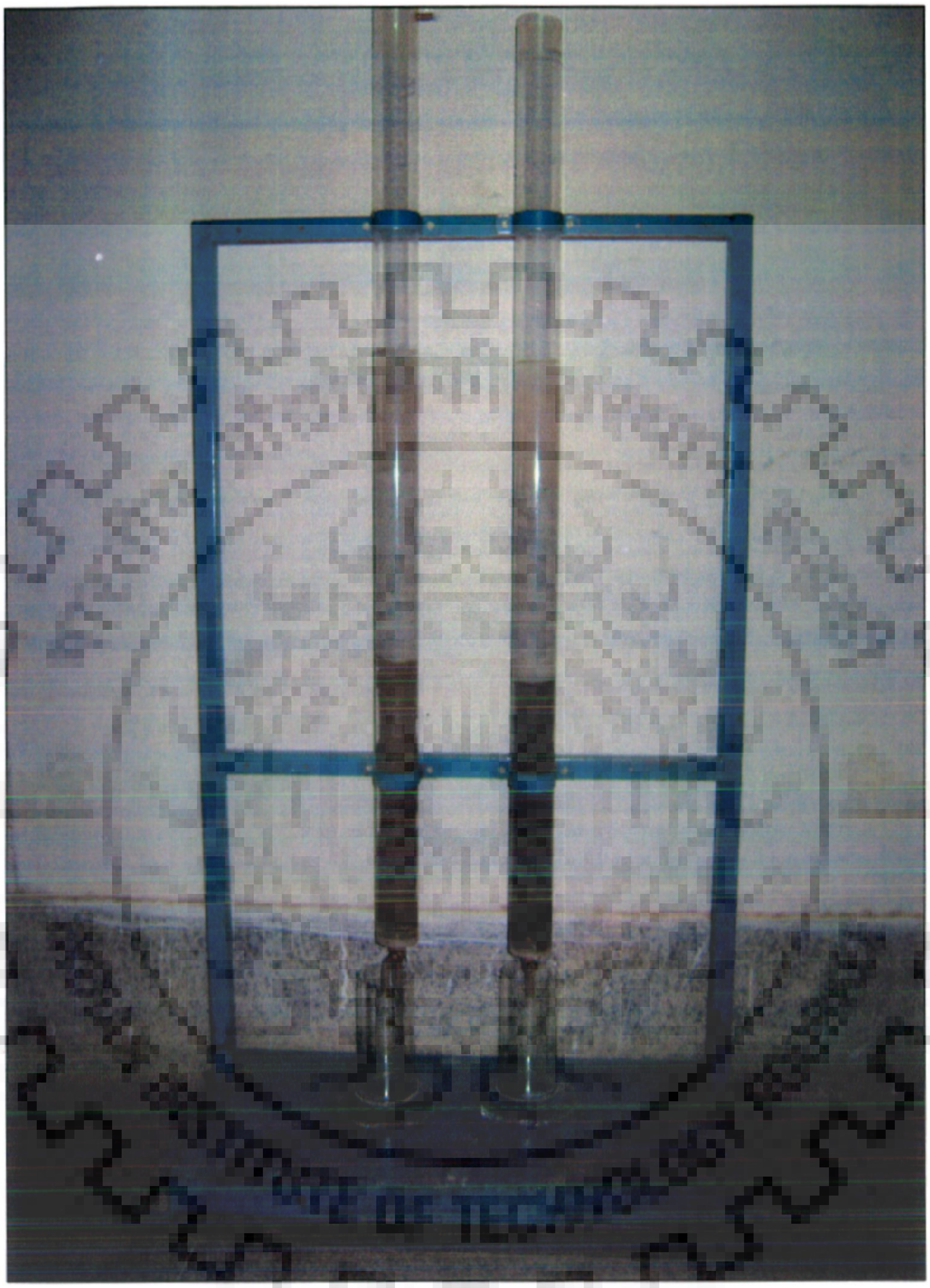


Figure 3.12 Experimental set up soil column study.

3.5.5 Summary of Method for Analysis of Metals

As already mentioned fly ash samples from power plants have been collected in the present study. The details of collection, filtration and preservation are presented in subsequent paragraphs. In addition to that analysis of metals, properties analyzed etc. are presented in this section.

3.5.5.1 Sample Collection, Filtration, and Preservation

In the present study the standard methods given in APHA (1996) has been followed for sample collection, filtration, preservation and analysis. To avoid contamination and interferences, several measures were taken such as minimizing exposure, wearing gloves, using metal-free apparatus, and ensuring a clean environment. Immediately after leachate collection, samples were filtered through a 0.45 μm filter paper and acidified with concentrated 0.5% HNO_3 so that pH of the sample becomes less than 2. Samples were collected in new 500 ml high-density polyethylene bottles that were washed with acid solution (2% HNO_3) before use. The sampling bottles were sealed to prevent volume change and evaporation. All samples were preserved at 4°C before chemical analysis.

3.5.5.2 Preparation of Standard Solution

In the present study stock solutions obtained from Merck were used for all calibrations. The stock solution was diluted using deionized water. Calibration standards were prepared fresh each time. A blank and at least three standards were prepared within the appropriate range.

3.5.5.3 Flame Atomic Absorption Spectrometry

In flame atomic absorption spectrometry, either an air/acetylene or a nitrous oxide/acetylene flame is used to evaporate the solvent and dissociate the sample into its component atoms. When light from a hollow cathode lamp (selected based on the element to be determined) passes through the cloud of atoms, the atoms of interest absorb the light from the lamp. This is measured by a detector, and used to calculate the concentration of that element in the original sample. The electrons of the atoms in the atomizer can be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy (i.e. light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity. As the quantity of energy (the power) put into the flame is known, and the quantity remaining at the other side (at the detector) can be measured, it is possible, from Beer-Lambert law, to calculate how many of these transitions took place, and thus get a signal that is proportional to the concentration of the element being measured. The basic structure of an Atomic Absorption Spectrometer is shown in Figure 3.13.

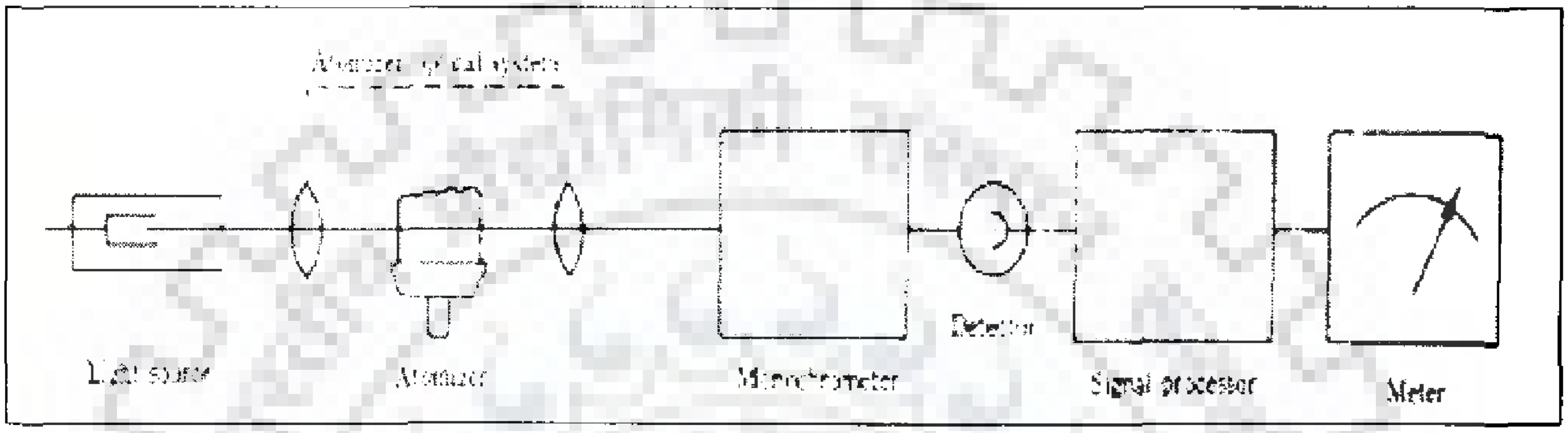


Figure 3.13 Basic structure of an Atomic Absorption Spectrometer

The use of a flame limits the excitation temperature reached by a sample to a maximum of approximately 2600°C (with the N_2O/acetylene flame). For many elements this is not a problem. Compounds of the alkali metals, for example and many of the heavy metals such as lead or cadmium and transition metals like manganese or nickel are all atomized with good efficiency with either flame type, with typical FAAS detection limits in the sub-ppm range. Instrument parameters such as drying time, washing time, and wavelength were adapted from the standard method for each element as described in the operation manual. Other operating parameters, such as atomizing time and temperature and purge gas atmosphere, were chosen as suggested by the instrument manufacturer (G B C Avanta). Atomic absorption Spectrometer used for the analysis of metals is shown in the Figure 3.14

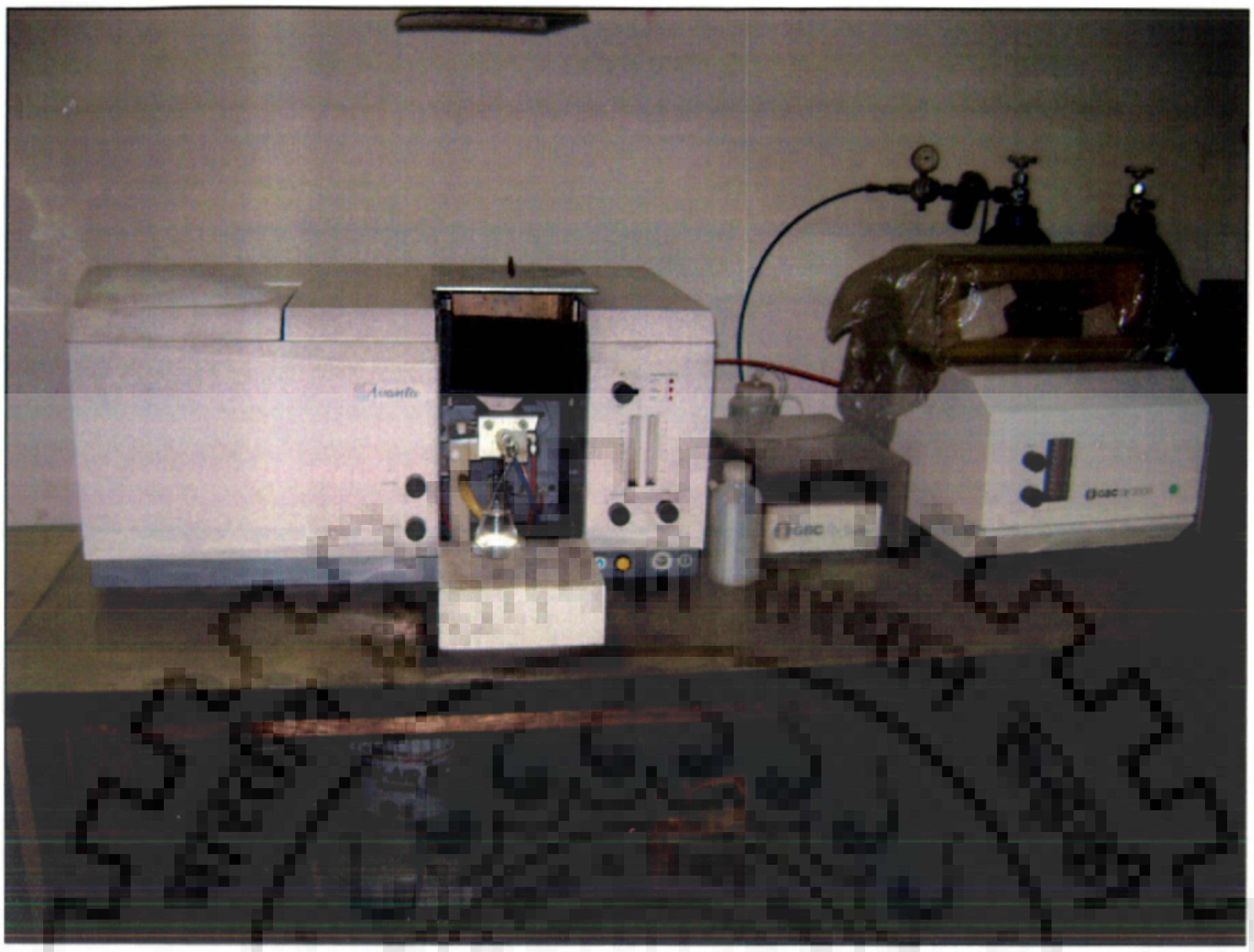


Figure 3.14 Atomic Absorption Spectrometer (G B C Avanta)

3.5.5.4 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS (Figure 3.15) is a multi-element technique that also uses an ICP plasma source to dissociate the sample into its constituent atoms or ions. However, in this case, the ions themselves are detected, rather than the light that they emit. The ions are extracted from the plasma and passed into the mass spectrometer, where they are separated based on their atomic mass-to-charge ratio by a quadrupole or magnetic sector analyzer. The high number of ions produced, combined with very low backgrounds, provides the best detection limits available for most elements, normally in the parts-per trillion ranges.

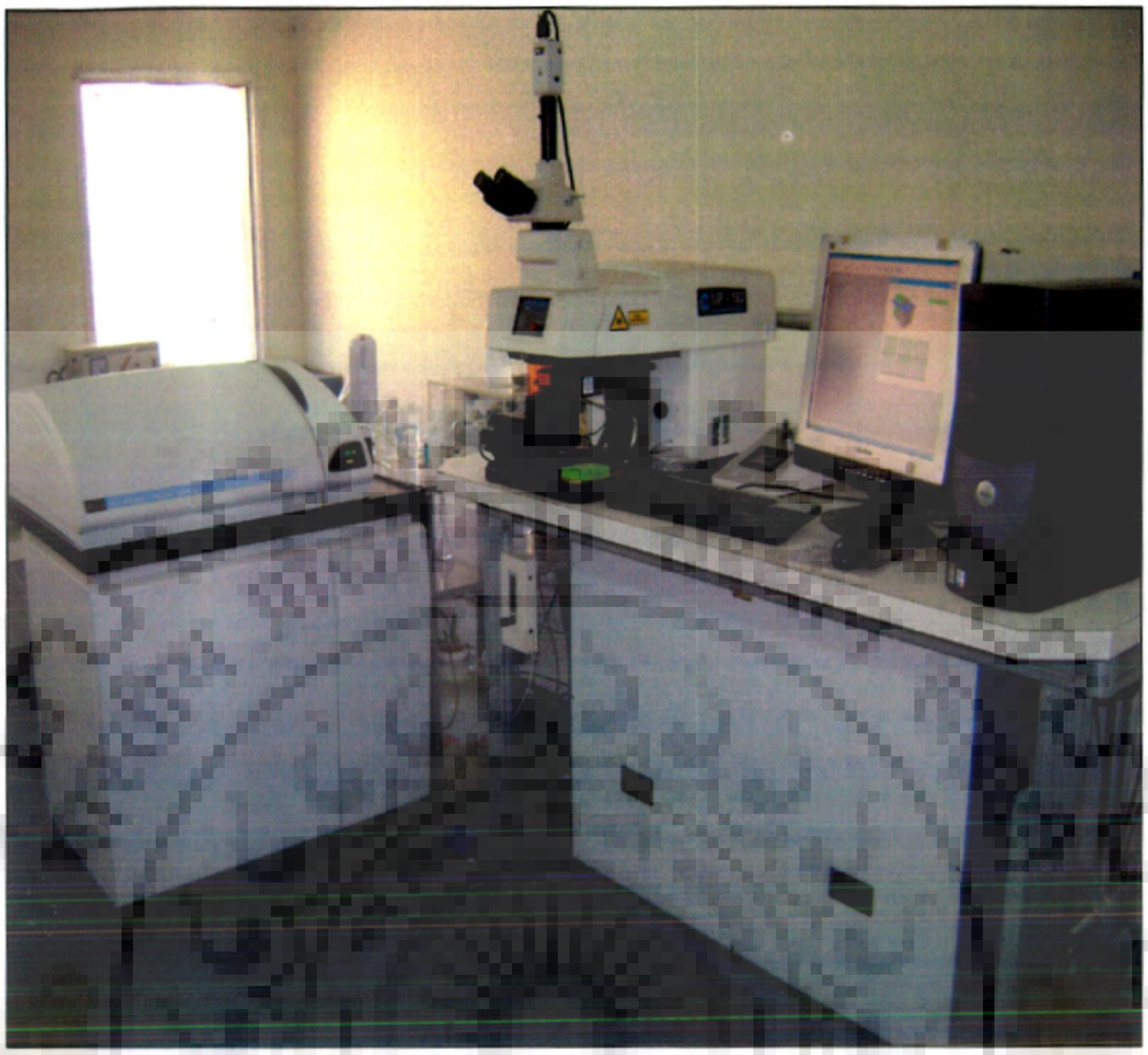


Figure 3.15 ICP-MS

3.5.5.5 Analysis

Chemical analyses were performed according to methods corresponding to specific elements. Before each use of the AAS/ICP-MS the instrument was configured, tuned, and calibrated for the metals of interest. Laboratory blanks were tested along with standard solutions. Three replicates of each sample were measured.

3.5.5.6 Calibration Method for Metals Analysis

The instrument was optimized and initialized at zero before calibration. A standard solution was measured for five times for a stability check of the instrument. The instrument was assumed to be stable when the relative standard deviation (RSD) of the *absorbance signal was less than 5% for all 5 replicates. The calibration points were* obtained from the calibration blank and calibration standards, and a new rational curve was fitted (automatically by the instrument) to the data, which was used as a calibration curve. A new calibration curve was created after measuring 20 samples. Three replicates of each sample were measured. The RSD of the concentrations estimated from the calibration curve for replicates was calculated automatically by the instrument. If the RSD was higher than 10%, the measurement was discarded and another measurement was made. After measuring two samples, a calibration blank was analyzed to ensure no carryover of the metal of interest and to check if the analytical system was free from contamination. The calibration curve was also verified with a standard solution after analyzing four samples at varying concentrations (Bin Shafique et al., 2002).

3.5.5.7 Metals Analyzed

In the present study the metals such as Iron (Fe), Zinc (Zn), Manganese (Mn), Nickel (Ni), copper (Cu) and Cadmium (Cd) have been selected for analysis. These elements were chosen as they reasonably represent both primary and secondary elements, which are known to leach from the ash. Iron is a major oxide and Cd, Cu and Zn are mainly accumulated in the exchangeable and bound to carbonate fraction (Polya ak et al., 2001). Great care is required for disposal of fly which is enriched with those metals. Cd and Ni are considered as carcinogenic and therefore they were selected for analysis.

3.5.5.8 TDS, pH and Conductivity

In addition to measuring concentrations, the pH, conductivity, and TDS were measured. The leachates, groundwater samples, ash pond effluent and slurry water were analyzed for pH, electrical conductivity and TDS with the help of Sension 156 portable Multiparameter meter Hach (USA) as shown in Figure 3.16.

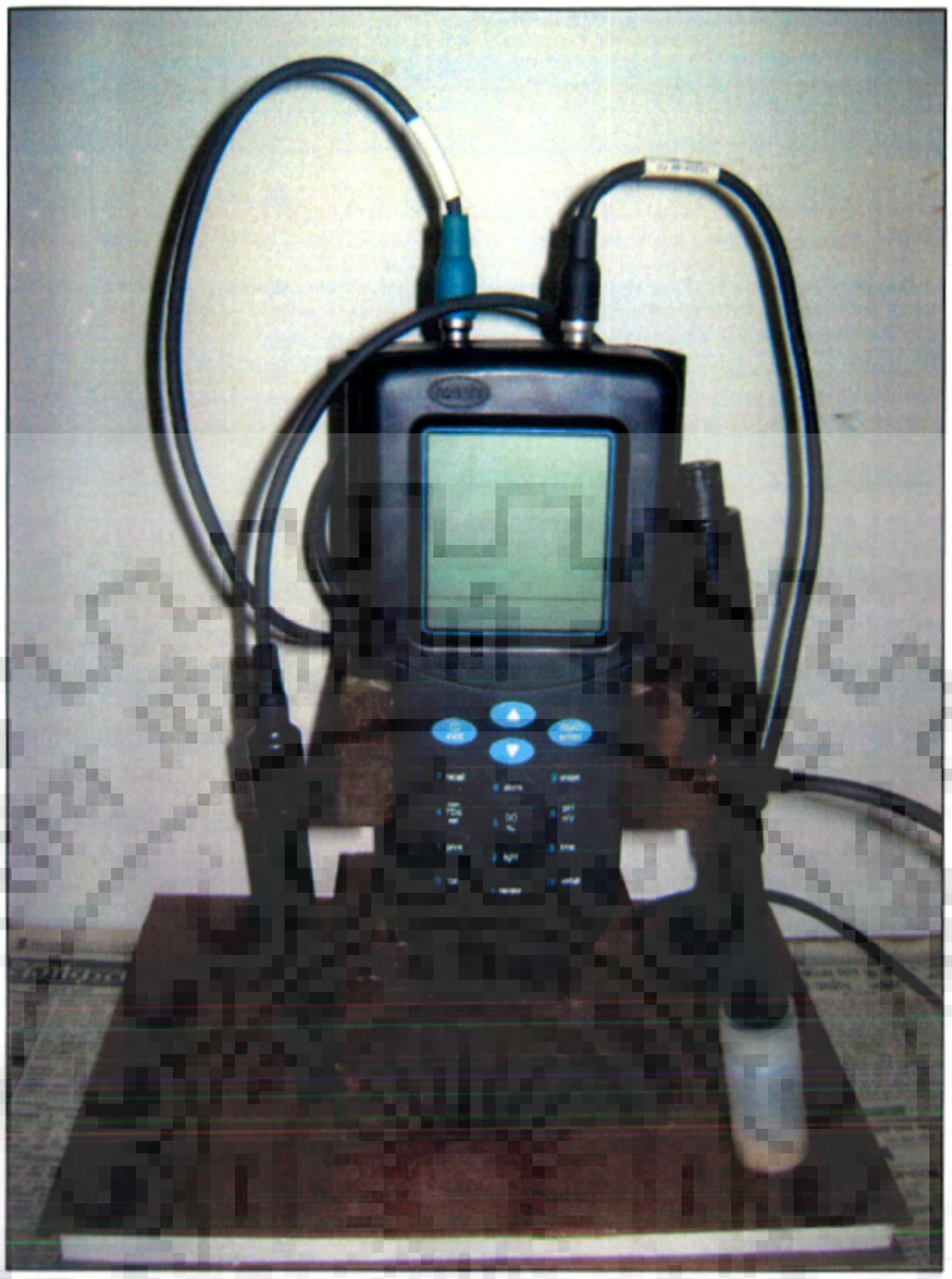


Figure 3.16 Portable Multiparameter meter Hach (USA) Sension 156.

3.6 CONCLUDING REMARKS

In order to characterize the fly ash various instruments such as XRD, SEM, SEM-EDAX, AFM and Laser particle size analyzer were used. Physical properties such as color, specific gravity, specific surface area of fly ash was by Blain's air permeability method, falling head permeability, maximum dry density, optimum moisture content were investigated. Major oxides were determined with XRF analysis. To check the toxicity of fly ash for disposal TCLP test was performed.

In order to simulate field conditions (recurrent flushing of fly ash by rainwater or groundwater) cascade leaching test at initial pH 4 and pH 7 were carried out. Open percolation soil column studies were carried out with fly ash slurry in order to check the transport of metals through the soil column. Collected samples of ash pond surface water, immediately disposed slurry water, effluent samples and groundwater at Kotamgaon and Hinganvedhe villages near to Nashik thermal power plant ash pond were analysed for selected metals composition.

CHAPTER 4

CHARACTERIZATION OF FLY ASH

4.1 GENERAL

Safe disposal of the ash without adversely affecting the environment is great challenge. Fly ash is heterogeneous material derived from combustion of coal for generation of power in the coal fired power plant. Knowledge of physical and chemical properties of coal fly ash, including the physical features, mineralogy, elemental composition, solubility of fly ash particles is essential for utilization of fly ash as well as disposal of fly ash. From utilization point of view, particle size distribution in conjunction with mineralogy provides an important index. Physical properties are also helpful in monitoring post disposal conditions.

The leaching characteristics therefore depend not only on the chemical composition of the combustion residue but also largely depend on its mineralogy and morphology. In order to understand the potential benefits and hazards associated with land application or disposal of fly ash, information is required on its physical and chemical characteristics and weathering behavior. The chemical properties of the coal ash greatly influence the environmental impacts that may arise out of their use/disposal as well as their engineering properties. The adverse impacts include contamination of surface and subsurface water with toxic heavy metals present in the coal ashes, loss of soil fertility around the plant sites, etc. Any poorly planned dry or wet disposal storage facility causes many social and socio-medical problems in the region and creates environmental hazard in the region as well (Prakash. K.,et al., 2009). Proper planning and good waste management practices are helpful to tackle the problems arise due to dry or wet disposal of fly ash. Hence this requires for a detailed study of their chemical composition, particle size, morphology and mineralogy, the details of which are presented in this chapter.

4.2 CHEMICAL COMPOSITION OF FLY ASH

The physical and chemical properties of coal ashes are dependent on coal geological origin, combustion conditions, efficiency of particulate removal and degree of weathering before final disposal (Andriano, D. C., et al.,1980). The chemical analysis of the Bhatinda Fly ash (BFA), Dadri Fly ash (DFA), Nashik Fly ash (NFA) and Suratgarh Fly ash (SFA) by X-Ray Fluorescence are presented in Table 4.1. The sum of the oxides presented does not equal to 100% due to the presence of trace elements. The sum of the SiO_2, Al_2O_3, & Fe_2O_3 fractions is 92.19%, 93.7%, 92.59% and 93.84% for Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash respectively. Thus the fly ash is classified according to ASTM C 618 as "Class F." The loss on ignition (LOI), an indication of unburned carbon, is 1.34%, 0.41%, 0.94% and 0.62% for Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash respectively. Low value of loss on ignition for Dadri fly ash and Suratgarh fly ash means better usability of those ashes compared to Bhatinda and Nashik fly ash. Indian fly ash samples contain low Ca and therefore produce either neutral or mildly acidic leachate pH value. This poses more danger to the environment compared to many other countries (Kanungo, S. B., et al., 2000). Major and minor oxides in the fly ash samples of different power plants are given in Table 4.2.

Table 4.1 Bulk chemical analysis of samples of fly ash from four power plants

Oxides	Bhatinda Fly ash	Dadri Fly ash	NAshik Fly ash	Suratgarh Fly ash
SiO_2	56.55	58.81	61.22	61.93
Al_2O_3	31.96	31.53	27.48	28.25
Fe_2O_3	3.68	3.36	3.89	3.66
CaO	1.04	0.9	1.7	0.6
P_2O_5	0.306	0.372	0.172	0.272
K_2O	0.87	1.11	0.86	1.05
MgO	0.42	0.48	0.51	0.4
TiO_2	1.93	1.76	1.3	1.54
MnO	0.048	0.037	0.061	0.042
Na_2O	0.1	0.1	0.18	0.1
* LOI	1.34	0.41	0.94	0.62

* LOI- Loss on ignition at 900°C

As the sum of oxides of Si, Al, Ti, K and P is greater than or equal to 90% (Table 4.2), the fly ash can be classified as Sialic having high acid tendency (Vassilev, S. V., et al., 2007). Same is also confirmed through acid base behavior of fly ash in later section. Sialic fly ash is generated from dominantly from the anthracite, bituminous and to a lesser extent from sub-bituminous coal. This is also confirmed by the fuel used in the all the studied power plant, which is bituminous coal. Total elemental compositions of trace metals are determined as per the acid (HNO_3+HF) digestion method and presented in Table 4.3.

Table 4.2 Summation of oxides of Si, Al, Ti, K and P

Oxides	Bhatinda Fly Ash	Dadri Fly Ash	Nashik Fly Ash	Suratgarh Fly Ash
SiO_2	56.55	58.81	61.22	61.93
Al_2O_3	31.96	31.53	27.48	28.25
P_2O_5	0.306	0.372	0.172	0.272
TiO_2	1.93	1.76	1.3	1.54
K_2O	0.87	1.11	0.86	1.05
Sum of oxides	91.62	93.59	91.03	93.04

Table- 4.3 Total elemental concentrations in mg/kg

Sr. No	Metal	Bhatinda	Dadri	Nashik	Suratgarh	Range in literature
1	Zn	64.8	62.3	66.2	54	7.9-300 [a]
2	Ni	108.3	117.5	96.6	124.6	56-290 [a]
3	Pb	37.9	36.5	39.8	37.98	5.3-85 [a]
4	Cd	8.1	7.3	10.5	6.4	1-12 [b]
5	Cu	69.3	46.7	58.9	63.1	43-190 [a]
6	Fe	10407	12312	10774	13800	277-21100 [c]
7	Mn	189.7	184.6	192.5	187.9	30.5-294 [c]
8	Ba	902	711	708	518	Not reported
9	Cr	178	151	147	215	58.8-222 [a]
10	V	201	190	165	185	57-266 [a]
Sum of elements		12166	13819	12259	15192	

[a]Negi B. S., (1991); [b] Hajarnavis (2000); [c] Twardowska. I., et al., (2003).

The elements such as As, B, Se, Co and other metals are also likely to be present in the fly ash and their total composition is not reported in the present study.

4.3 TOXICITY CHARACTERISTIC LEACHING TEST PROCEDURE

After the Resource Conservation and Recovery Act (RCRA) 1976, the US Environmental Protection Agency (USEPA) developed specific criteria for two different fly ash extraction procedures, called EPTOX and TCLP test (USEPA Method 1311). There is no leaching protocol available in India to check the toxicity of coal fly ash, however, Tare, V., et al., (2005) and Benito Y., et al., (2001) advocated the checking of the toxicity characteristics of ashes before utilization or disposal. In view of this TCLP test was carried out with acetic acid solution at pH 3. A liquid to solid ratio of 20:1(Acetic acidified water: Fly ash) is used for extraction and then it was analyzed with the help of atomic absorption spectrophotometer for the elements Fe, Zn, Ni, Cu, Cd, Pb, Mn and Cr. The results of the TCLP test are given in Table 4.4

Table 4.4 Toxicity Characteristics Leaching Test for studied fly ashes

Metals	Bhatinda Fly Ash	Dadri Fly Ash	Nashik Fly Ash	Suratgarh Fly Ash	TCLP limit mg/lit
pH	4.9	6.6	8.4	8.0	-
EC	88.8	121.4	292	98.6	-
TDS	42.1	57.7	140.4	46.8	-
Fe	1.881	1.668	1.418	1.681	0.2
Mn	1.562	1.947	1.353	1.767	50
Zn	0.769	0.378	0.35	0.45	5
Cu	0.219	0.043	0.016	0.020	3.0
Pb	0.0145	0.014	0.01	0.013	0.015
Cd	0.0043	0.0032	0.0025	0.0026	0.005
Ni	0.005	0.048	0.01	0.043	0.05
Cr	0.1	0.09	0.01	0.035	5.0

Under the tested leaching protocol for toxicity, Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash passes the TCLP test for (selected in the present study) heavy metal toxicity. It can be easily utilized or land disposed. Testing of the other elements prescribed in TCLP protocol is not reported in the present study.

4.4 ACID BASE CHARACTERIZATION OF FLY ASH

The acid base behavior of fly ash indicates the extent of the pH of the contact liquid which is affected by the acidic and alkaline components of the ash. The same has been determined by measuring pH of demineralized water at L/S ratio of 100 after 1 and 10 minutes contact time. As suggested by Van der Sloot, (1984), the fly ashes can be classified as acidic: pH 10 min< 7, alkaline: pH 1 min > 10, and neutral:7<pH<10. System is not yet seriously affected by solubility limitations, therefore the stabilized value pH value of the contact liquid was measured after 1 min and 10 min. Fly ash can be categorized as acidic and alkaline on the basis of pH of fly ash. Acidic fly ash has pH less than 7.0. Fly ash with pH of about 6.0 to 7.0 is mildly acidic, 6.0 to 5.0 is moderately acidic; below that fly ash is considered as highly acidic. Alkaline fly ash has pH more than 7.0 Fly ash with pH between 7.5 to 8.0 is mildly alkaline; 8.0 to 9.0 is moderately alkaline; and above that fly ash is considered as alkaline. In the present study the acid base categories for the ash samples of different power plants are given in Table 4.5

It is observed from the Table 4.5 that Bhatind fly ash is mildly acidic and Dadri as well as Suratgarh fly ash are neutral. Whereas Nashik fly ash is alkaline. Sikka (1994) observed that ash directly collected from electrostatic precipitator of Bhatinda thermal power station found to be low in pH. Earlier works also indicate that fly ash of Northern and Eastern parts of Indian Thermal power plants are acidic in nature (Thakre, R., 1996).

Table 4.5- Acid-Base categorization of fly ash

Fly ash	1 min pH	10 min pH	Nature
Bhatinda fly ash	6.0	6.7	Mildly acidic
Dadri fly ash	6.9	7.0	Neutral
Nashik fly ash	8.5	8.7	Alkaline
Suratgarh fly ash	7.8	7	Neutral

4.5 PHYSICAL PROPERTIES OF FLY ASH

Physical properties of fly ash (Adriano et al., 1980) are largely depends on the nature of parent coal, condition of combustion, type of emission control devices, storage and handling methods. Color of Bhatinda fly ash (LOI-1.34%) as well as Nashik fly ash (LOI-0.94%) is dark grey and that of Dadri (LOI-0.41%) and Suratgarh (LOI-0.62%) fly ash is light grey. It is also confirmed by the loss on ignition (LOI) value of respective fly ash, which is an indication of unburned carbon and it imparts color to fly ash. More value of LOI means darker the color of fly ash. More LOI value limits the utilization of fly ash in cement production or in concrete and enhances the possibility of land disposal of fly ash. The physical properties of the fly ash samples of all the four power plants considered in the present study are given in Table 4.6. The fineness of fly ash can be expressed as its specific surface (i. e., surface area per unit mass of the substance). Blain's air permeability method is recommended procedure to determine the specific surface of fly ashes (IS: 1727, 1967). Blain's air permeability is given in Table.4.6 and it is in the range given in literature (Shridhran et al., 2001) 1300- 5300 cm^2/gm. In addition to the initial surface area, the change in surface area as the reaction progresses is also important in a long-term leaching process.

Table 4.6 Physical Properties of Fly Ashes

Property	Bhatinda Fly Ash	Dadri Fly Ash	Nashik Fly Ash	Suratgarh Fly Ash
Color	Dark gray	Light gray	Dark gray	Light gray
Particle size- wet sieve analysis below 75 μm	79.8%	89%	79.2%	96.8%
Blain's Air Permeability cm^2/gm	2928	3533	2641	3966
Specific gravity	2.0	2.1	2.0	2.3
Dry density	0.6-1.2	0.9-1.2	0.9-1.3	0.99-1.4
Optimum Moisture Content %	25.4	19.5	24.2	19.4
Permeability falling head cm/sec	3.1×10^{-5}	1.3×10^{-5}	4.3×10^{-5}	1.3×10^{-5}

Wet sieve analysis is carried out by taking 500 gm of fly ash on 75 μm sieve and is washed with water. Particles greater than 75 μm will be retained on sieve and less then 75 μm will get escape through the water. The particles retained on the sieve are oven dried and sieve analysis is carried out. It was found that 79.8%, 89%, 79.2% and 96.8% particles are less than 75 μm found in Bhatinda fly ash (BFA), Dadri fly ash (DFA), Nashik fly ash (NFA) and Suratgarh fly ash (SFA) respectively as shown in Figure 4.1.

Based on the wet sieve analysis all the fly ash samples are classified as predominantly silt sized (0.002-0.075 mm). It is also observed that 20.2%, 11.0%, 20.8% and 3.2% sand sized particles found in sand sized range (0.075 mm-4.75 mm) for Bhatinda fly ash (BFA), Dadri fly ash (DFA), Nashik fly ash (NFA) and Suratgarh fly ash (NFA) respectively. Specific gravity of fly ashes were determined as per (IS 2720:1980). The specific gravity of Bhatinda, Dadri, Nashik & Suratgarh power plant fly ashes are 2.0, 2.1, 2.0 and 2.3 respectively. When fly ash slurry was prepared in glass cylinder for all above ashes, it was observed that particularly for Bhatinda and Nashik fly ash floaters were observed on the water surface. The low specific gravity of coal ashes is attributed to the presence of floating particles or hollow particles. Same can be observed with the help of scanning electron micrographic studies for Bhatinda and Nashik fly ash. Presence of more silt sized particles indicates that permeability of fly ash is less which was observed through the values of the falling head permeability as given in Table 4.6. The significant difference in the particle sizes is reflected in greater surface area and lower hydraulic conductivity of fly ash.

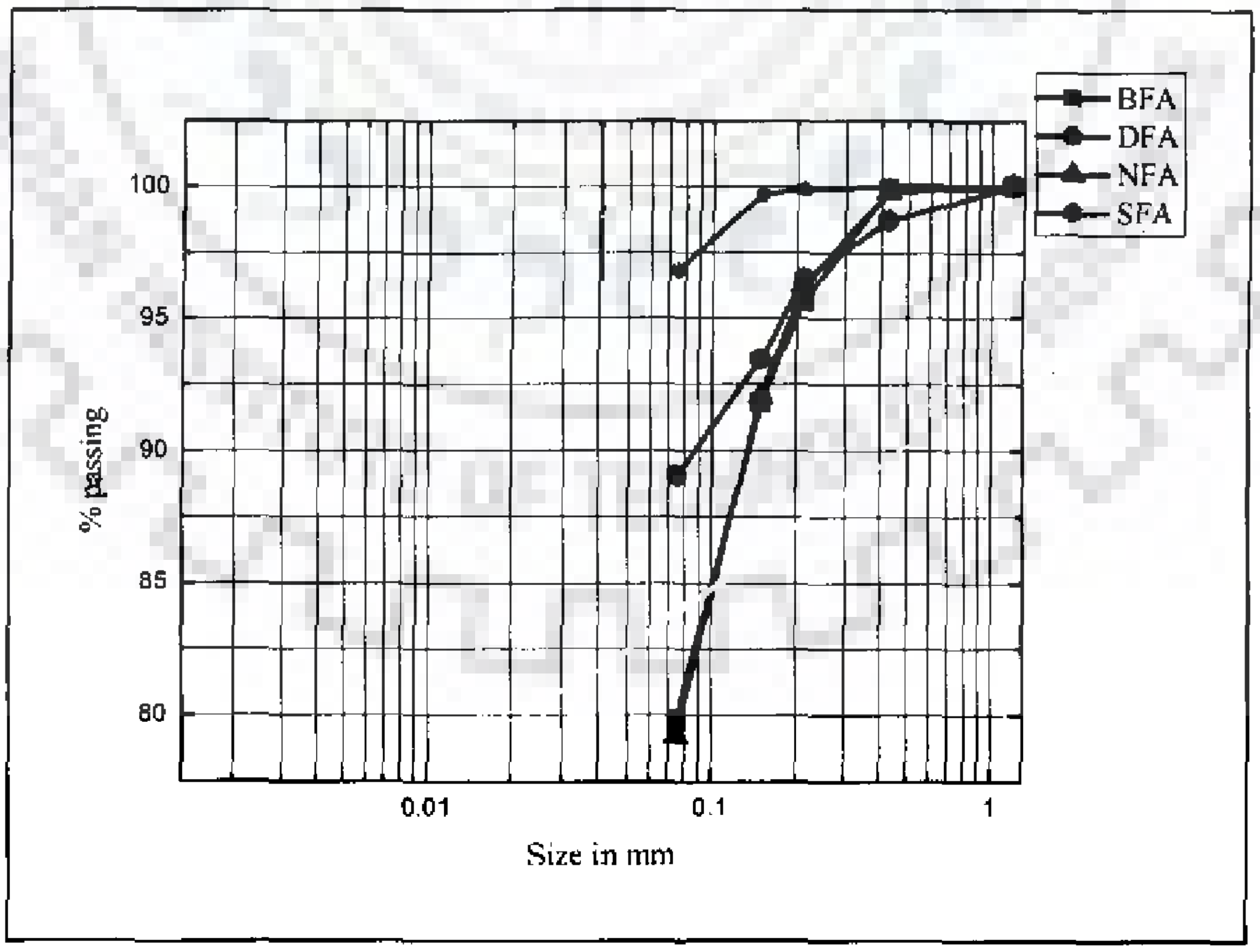


Figure 4.1 Wet sieve analysis of fly ash

4.6 MINERALOGY OF FLY ASH

The mineralogy of a fly ash refers to both amorphous and crystalline phases and other mineral fractions in the fly ash. X-ray diffraction studies were carried out to determine the phase compositions of the Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash. The leaching behaviour of fly ash can be related to their mineralogical characteristics. More attention should be paid to the major phases which may control leaching chemistry and the host phases of toxic elements which directly associate with the release of the elements, in order to understand the leaching processes. Glass phases, ferrite spinel or other silicates are preferably formed in high temperature combustion. Although this trend may not be exactly the same for various combustion residues, the major fraction of the residues is usually composed of amorphous phases of silicon, aluminium and iron such as the glasses, magnetic spinel and some aluminosilicates. It is widely accepted that an impure aluminosilicate glass constitutes the bulk of the coal fly ash matrix (Fisher and Natusch, 1979; Roy et al., 1985). According to Chatterjee (2001), the glass content of Indian fly ashes is low and often the glass particles are devitrified. It has been found that (Sharma and Krishnamurthy 1992) the glass content of 20 class F Indian fly ashes to be in the range of 16–35%. The glass content of the U.S. fly ashes is much higher, in the range of 54–87% (Yudhbir and Honjo, 1991).

The release of species from solid wastes in an aqueous solution depends on the mineral patterns of the species existing in the solid wastes. Most trace elements exist as a solid solution in the combustion residues, especially in coal fly ash. The leaching behaviours of these elements are usually determined by their host phases. In most cases, the glass phases and magnetic fraction in the combustion residues contain most of the potentially toxic trace elements. The majority of trace elements in the aluminosilicate matrix of ashes are concentrated in the glass phases, while the crystalline phases have low concentrations. The mullite-quartz phase, for example, is relatively more pure than the glass phase. The glass phases and magnetic fraction are potentially the most important hosts for many toxic trace elements in the combustion residues (EPRI, 1983; Zevenbergen, 1994).

XRD analysis identified the minerals Quartz (SiO_2), Mullite ($3Al_2O_3$, $2SiO_2$) in most predominant phase and Hematite (Fe_2O_3) and Magnetite (Fe_3O_4) in minor phase. Sillimanite (Al_2O_3, $2SiO_2$) was additionally observed in Dadri fly ash. The peak at 2θ 26.6 and corresponding d-spacing is 3.4 which indicates quartz to be one the of major constituent as shown in Figures 4.2, 4.3, 4.4 and 4.5 for Bhatinda, Dadri, Nashik and Suratgarh fly ash respectively. Therefore fly ash is classified as amorphous ferro-alumino silicate minerals. The minerals obtained through study of XRD analysis are consistent with previously done XRD studies for Indian fly ashes (Kolay. P. K., et al., 2001 Trivedi. A., et al., 2002, Kaniraj., S. R., et al., 2004, Gaikwad P. G., et al., 2009). *Quartz in fly ash* originates from silt and clay in the coal that is not fluxed by other inorganic materials. Mullite is principal aluminium containing phase in class F fly ash. It crystallizes directly from the molten ash or by devitrification of the glass after cooling. Its formation requires temperature above 1000°C. The predominant minerals in studied ash resulting from combustion of coals are Quartz and Mullite. This ash is referred to as ASTM class F fly ash. Primary fuel used in Guru Hargobind Thermal power plant (Lehra Mohabat) Bhatinda Punjab state, Dadri Thermal Power Plant Uttarpradesh, Nashik Thermal Power Plant Eklahara, Maharashtra State and Suratgarh Super Power Plant, Rajasthan State of India, is Bituminous coal. Class F fly ash is produced from burning of anthracite and bituminous coal. *Major mineralogical phases (quartz and mullite) make it inert.*

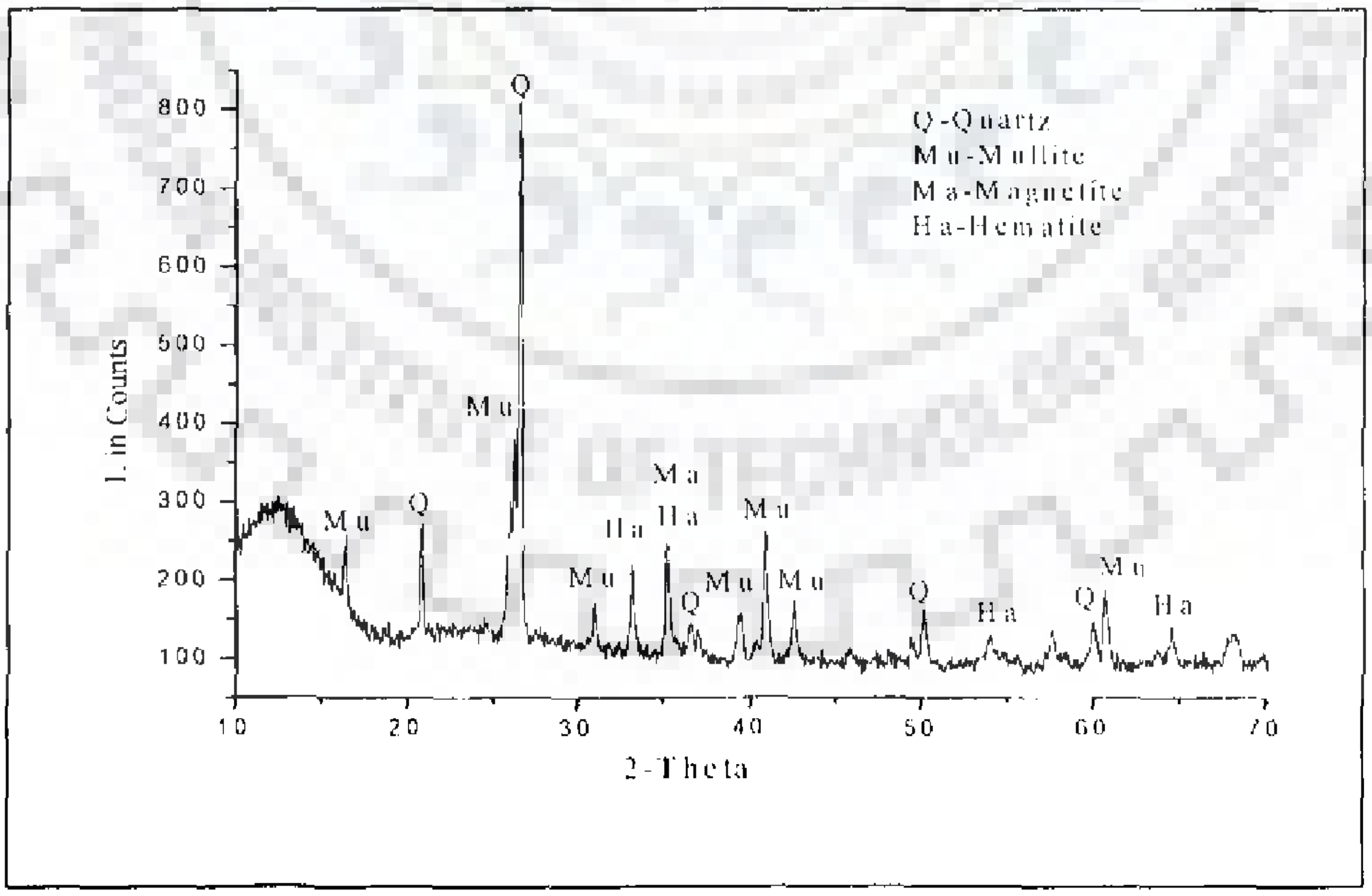


Figure 4.2 XRD pattern for Bhatinda fly ash

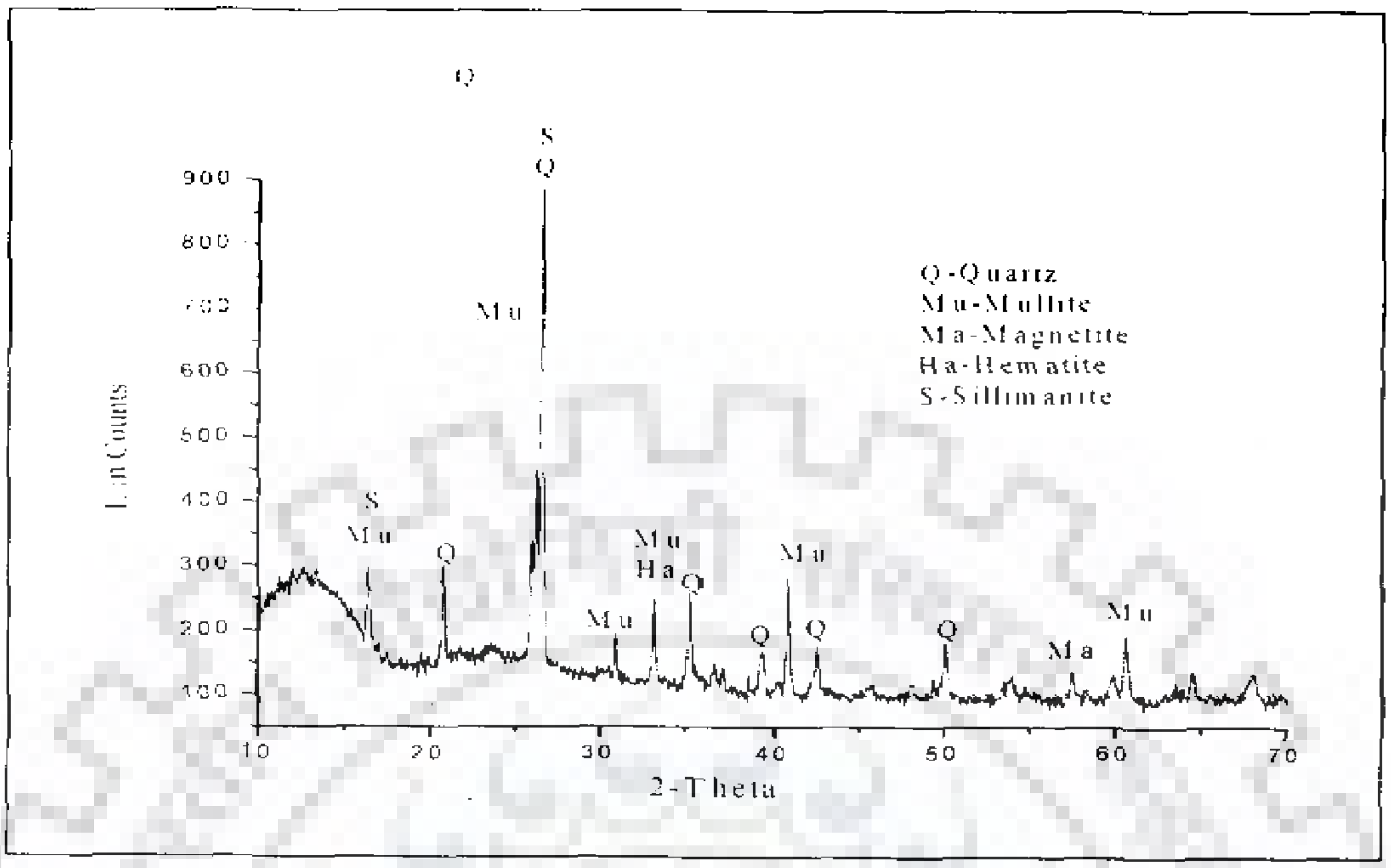


Figure 4.3 XRD pattern for Dadri fly ash

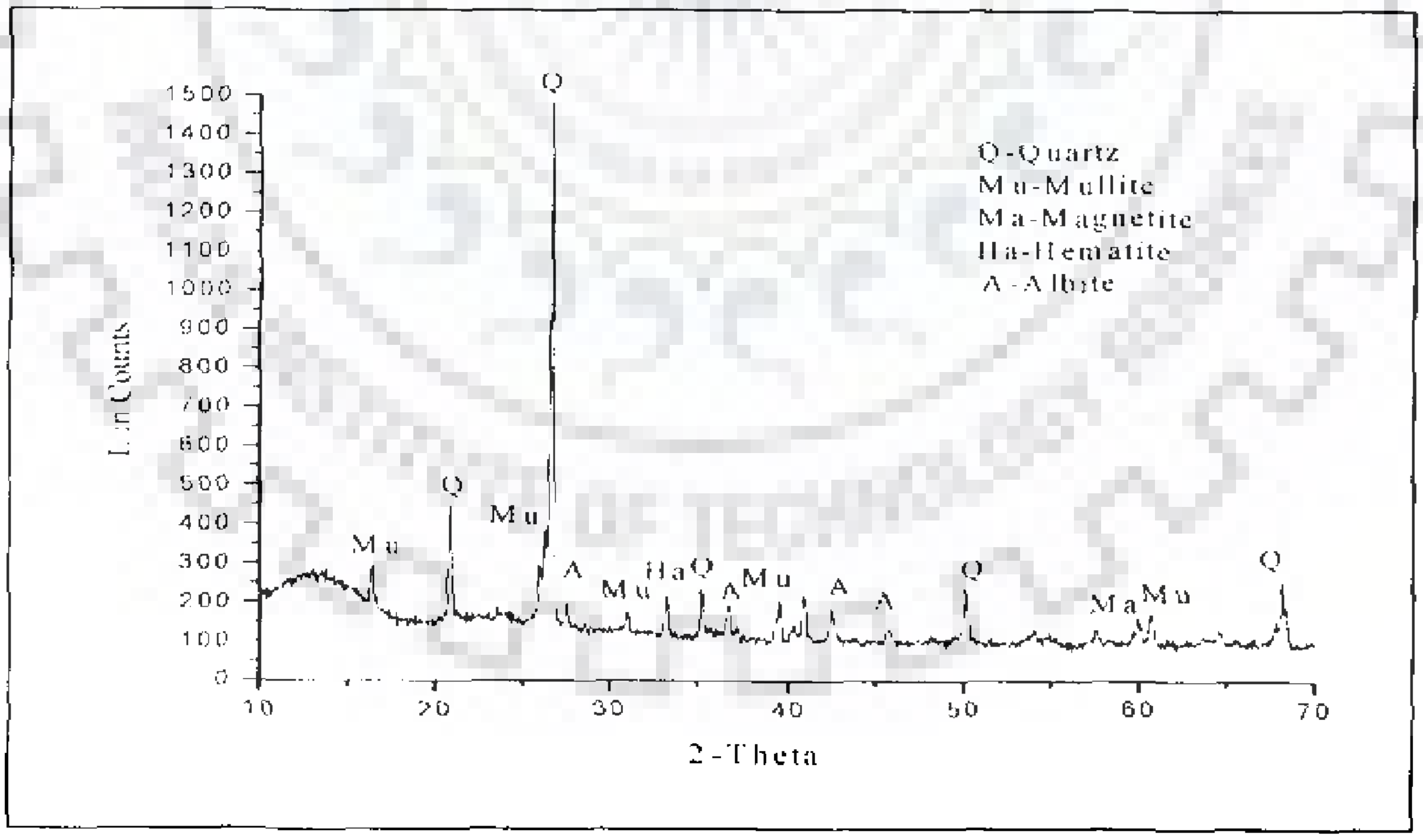


Figure 4.4 XRD pattern for Nashik fly ash

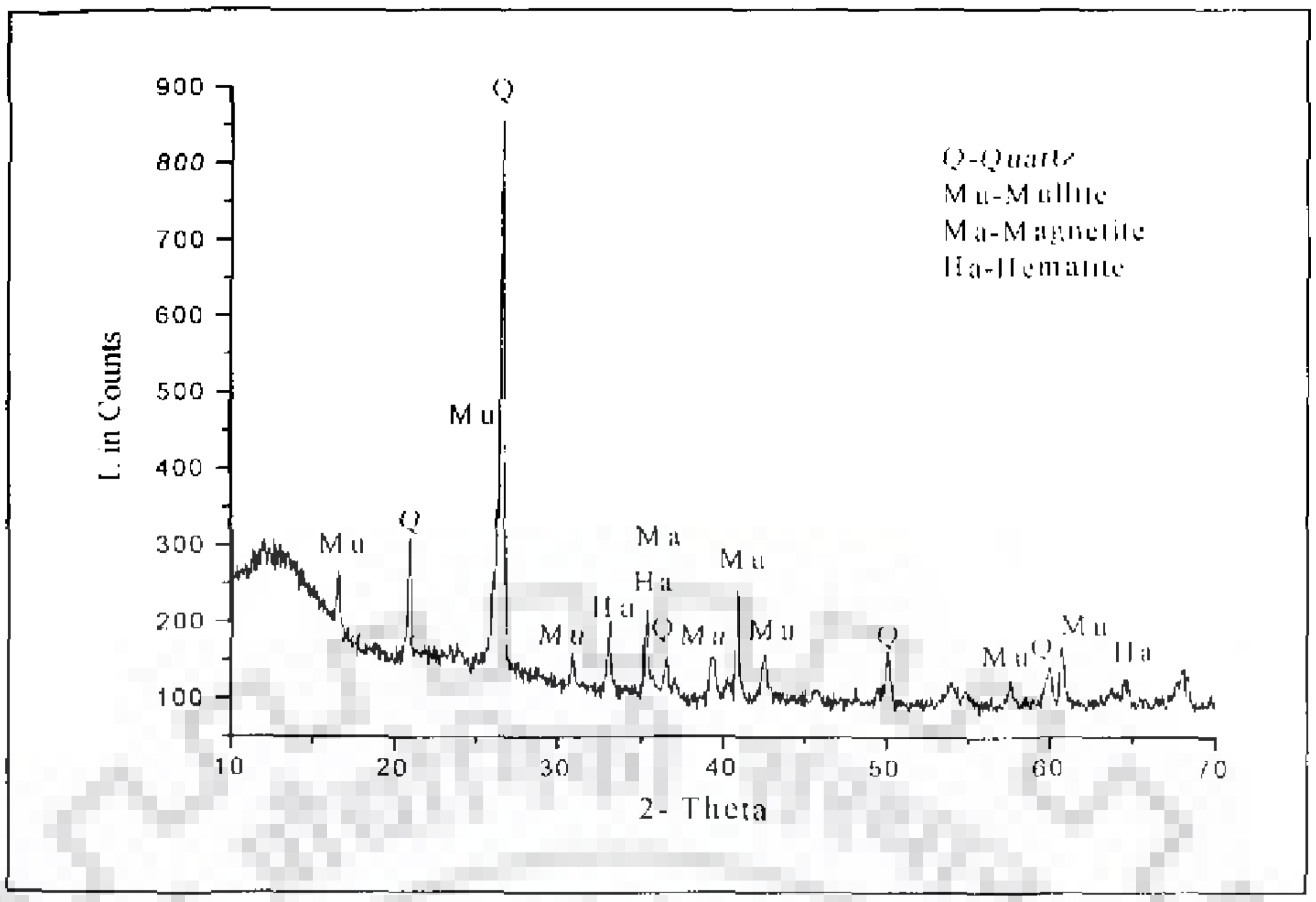


Figure 4.5 XRD pattern for Suratgarh fly ash

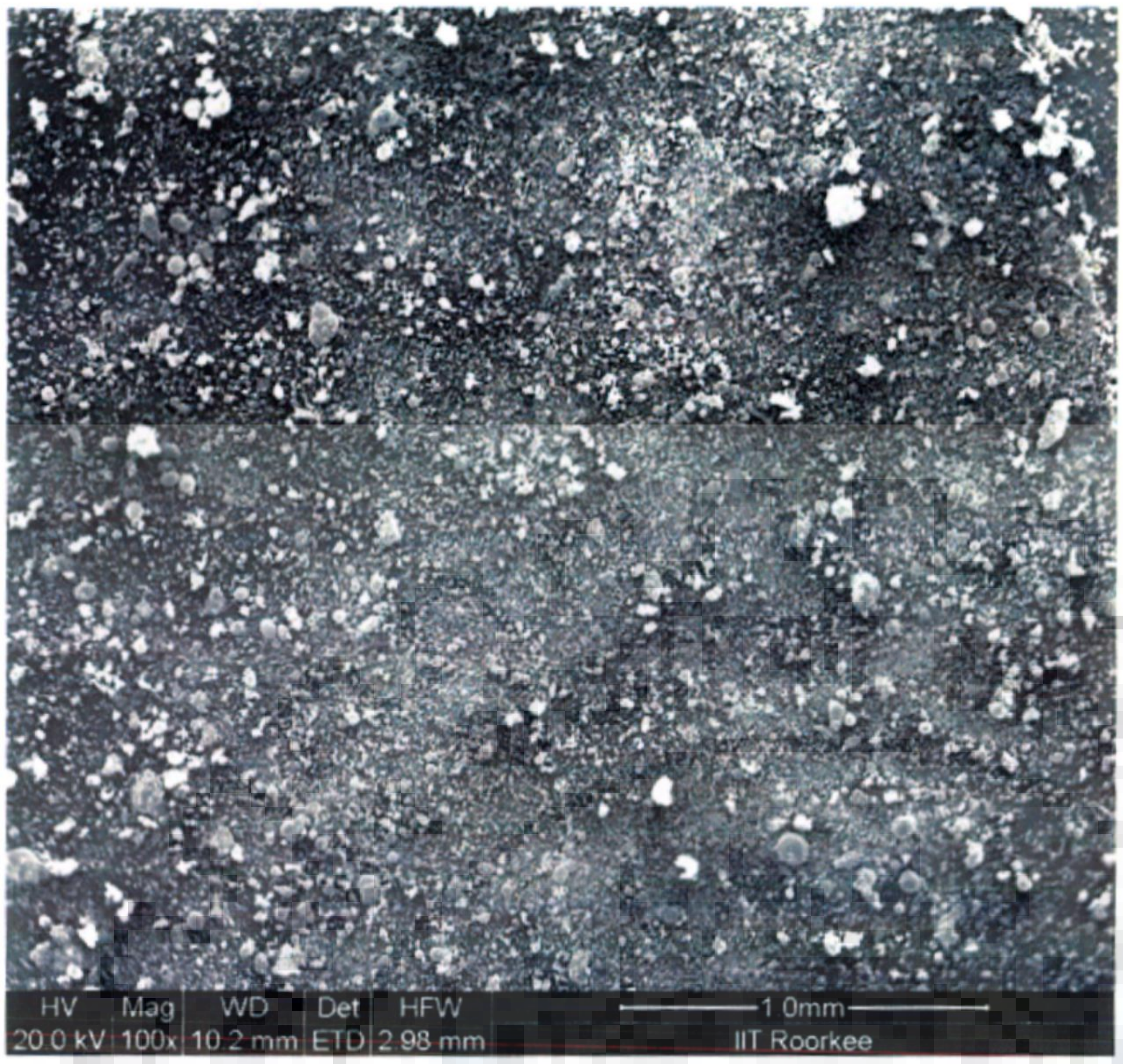
4.7 SCANNING ELECTRON MICROGRAPHIC AND ENERGY DISPERSIVE X-RAY STUDIES

Scanning Electron Microscopy (SEM) is one of the most useful and well known analytical techniques for ash characterization (Kutchko, B. G., et al., 2006).The Field Emission Scanning Electron Microscope (FE-SEM) is configured similar to a conventional SEM, additionally the instrument is fitted with Energy Dispersive X-ray (EDAX) for the determination of elemental composition. The characteristic X-ray emitted from the sample serve as finger prints and give elemental information of the samples including semi quantitative analysis, quantitative analysis, line profiling and spatial distribution of elements. SEM with X-ray analysis is a versatile tool to carry out surface analysis.

Here gold coated samples are subjected for FE-SEM-EDAX analysis, in which Scanning Electron Micrograph is obtained and its chemical composition is also obtained. Depending upon the requirement, total elemental composition as well as surface texture of individual particles can be obtained. In some EDAX spectra, an unidentified spectra is for gold coating. Fly ash has high amount of carbon content (BFA- 57.33%, DFA-39.58%, NFA-40.43%, SFA- 39.37%) beside high concentration of oxygen coming from oxides of various elements such as Al (BFA-7.1%, DFA-14.66, NFA-8.48, SFA-10.05), Si (BFA-8.61%, DFA-13.29%, NFA-11.59%, SFA-15.02%), Fe (BFA-1.34%, DFA-1.82%, NFA-1.72%, SFA-2.61%), Ca (BFA-0.4%, DFA-0.68%, NFA-0.72%, SFA-0.6%), B, Mg, Ti, Mn, Ba, Cr, Cu, Zn, Ni, and Sc present in the sample as depicted in Figures 4.6, 4.7, 4.8 and 4.9 for Bhatinda, Dadri, Nashik and Suratgarh fly ash respectively.

Because of low calcium content and high carbon content, it is classified as class F fly ash. Due to low calcium content, class F fly ash does not find widespread supplementary usage. EDAX spectra with strong peak for Si, is indicative of the presence of quartz and which is also confirmed through XRD studies. EDAX spectrum in Figures 4.6, 4.7, 4.8 and 4.9 displays a very strong peak for Si followed by less strong peak for Al. This suggest strongly the presence of a mineral with composition of ($3Al_2O_3$, $2SiO_2$) most likely mullite. Same is also identified through XRD studies. Major elements obtained through EDAX studies are Al, Si and O, and Fe in minor peak along with other trace metals indicating that it is ferro- aulmino-silicate mineral.

Scanning Electron Micrograph with EDAX spectra along with elemental composition for the magnetic fraction is shown in Figures 4.10, 4.11, 4.12 and 4.13 for Bhatinda, Nashik ,Suratgarh and Dadri,fly ash respectively. Spherical particle covered with thin cover of triangular, hexagonal and dendritic shaped crystalline grains are magnetic particles and same particles are observed through Scanning Electron Micrographs. The corresponding EDAX spectra reveal that there are strong peaks for Fe, Al and Si. The composition of Fe (BFA-32.12%, NFA- 52.25%, SFA-42.99% DFA-25.94%), Al (BFA-11.6%, NFA-4.36%, SFA-5.62% DFA-19.26%), Si (BFA-13.31%, NFA-8.35%, SFA-7.47 % DFA-18.5%). This confirms that fly ash is not homogeneous material. These magnetic particles are also identified through XRD studies as magnetite with minor inclusion of hematite. The investigations into the morphology and chemical composition of non magnetic and magnetic fraction of fly ash particles carried are shown to be consistent with findings of other investigators given in literature (Das, S. K., 2005 XUE, Q. F., et al., 2008).



Element	Wt %
C	57.33
O	21.72
Na	0.12
Mg	0.43
Al	7.1
Si	8.61
S	0.22
Cd	0.47
K	0.35
Ca	0.4
Ti	0.64
V	0.05
Cr	0.23
Mn	0.11
Fe	1.34
Ni	0.41
Cu	0.22
Zn	0.25

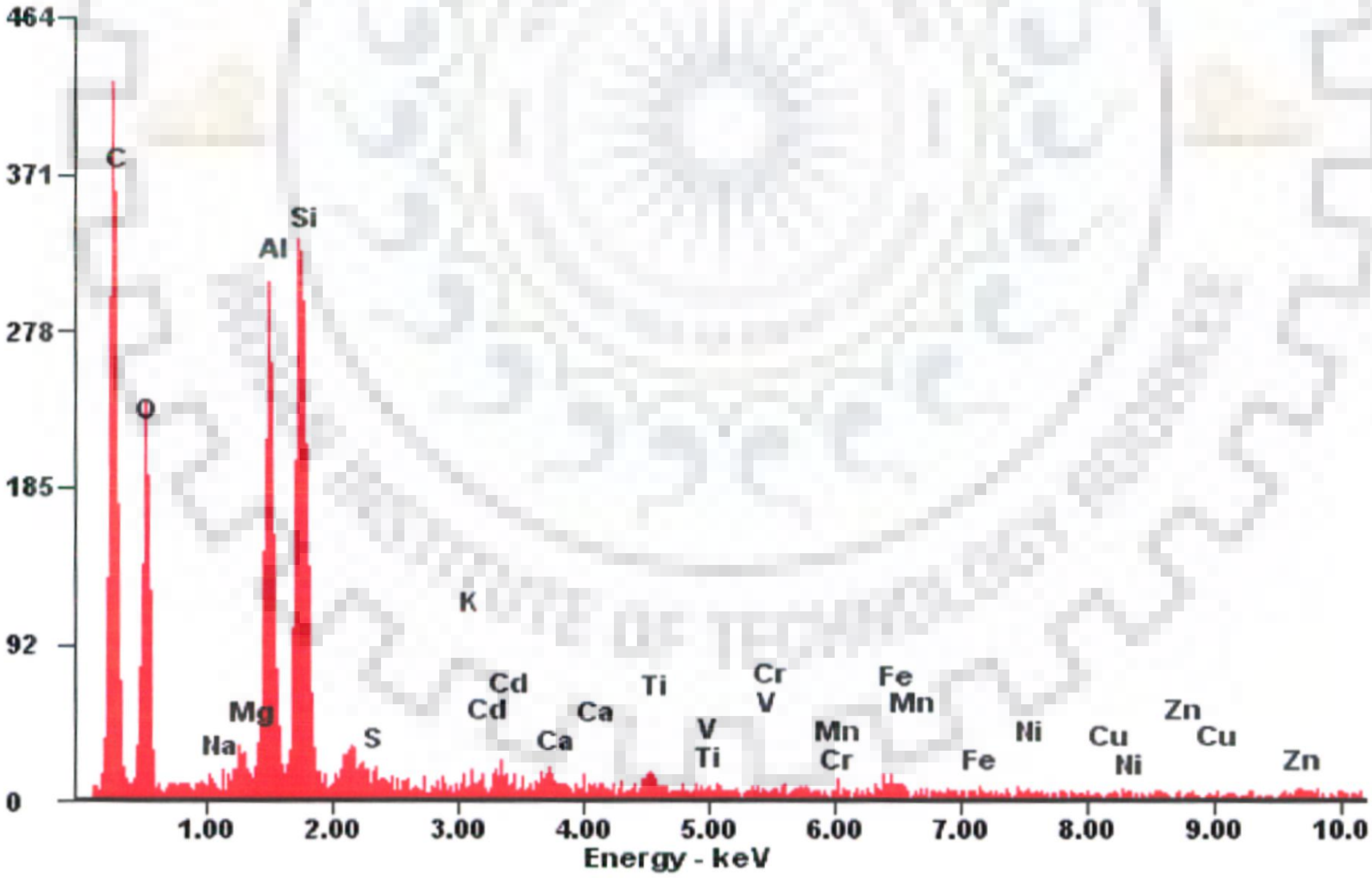
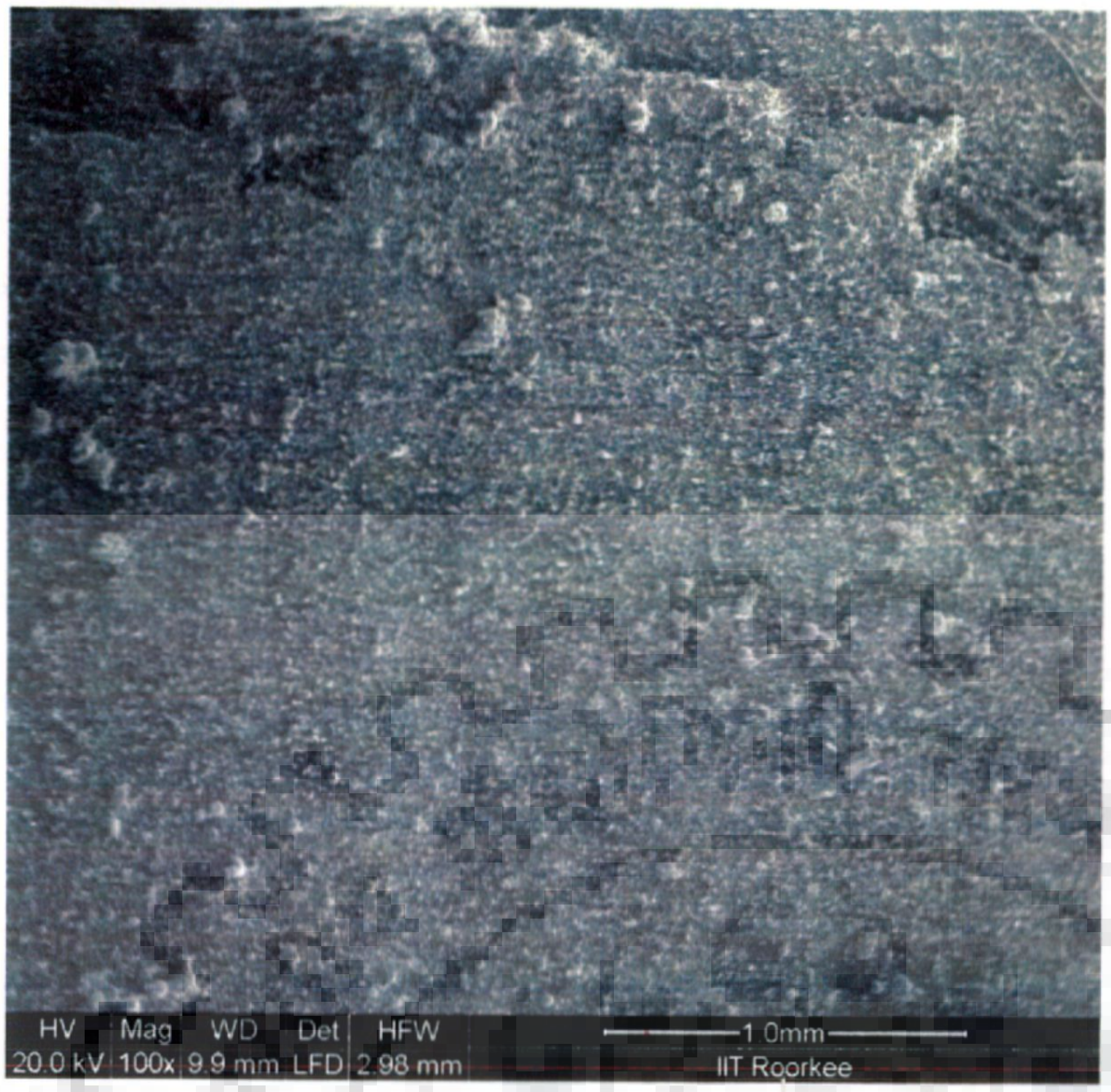


Figure 4.6 Scanning Electron Micrograph with EDAX spectra along with elemental composition for Bhatinda fly ash



Element	Wt %
C	39.58
O	24.7
Na	0.21
Mg	0.65
Al	14.66
Si	13.29
S	0.22
Cd	0.32
K	0.76
Ca	0.68
Ti	0.67
V	0.27
Cr	0.2
Mn	0.33
Fe	1.82
Ni	0.48
Cu	0.41
Zn	0.75

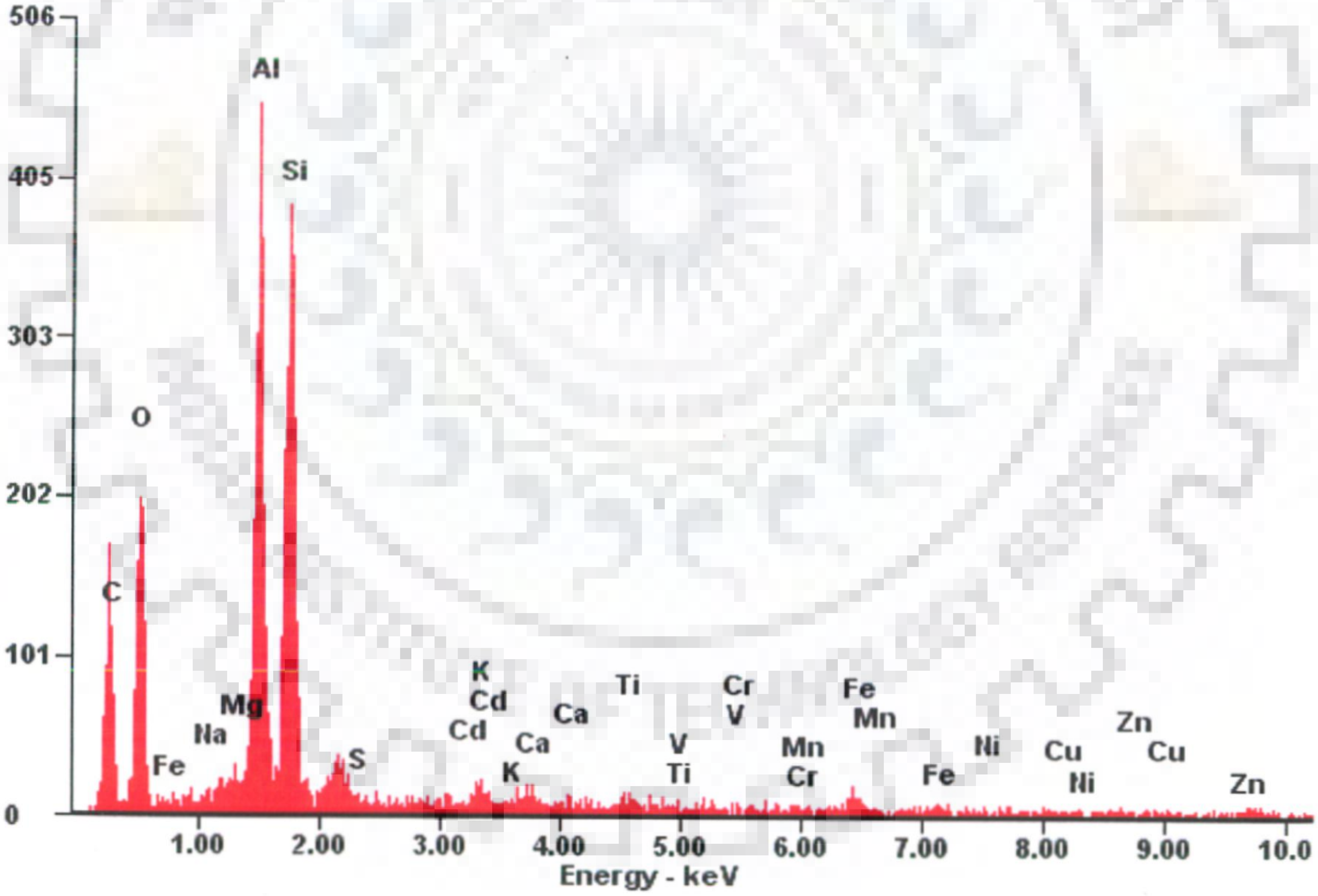
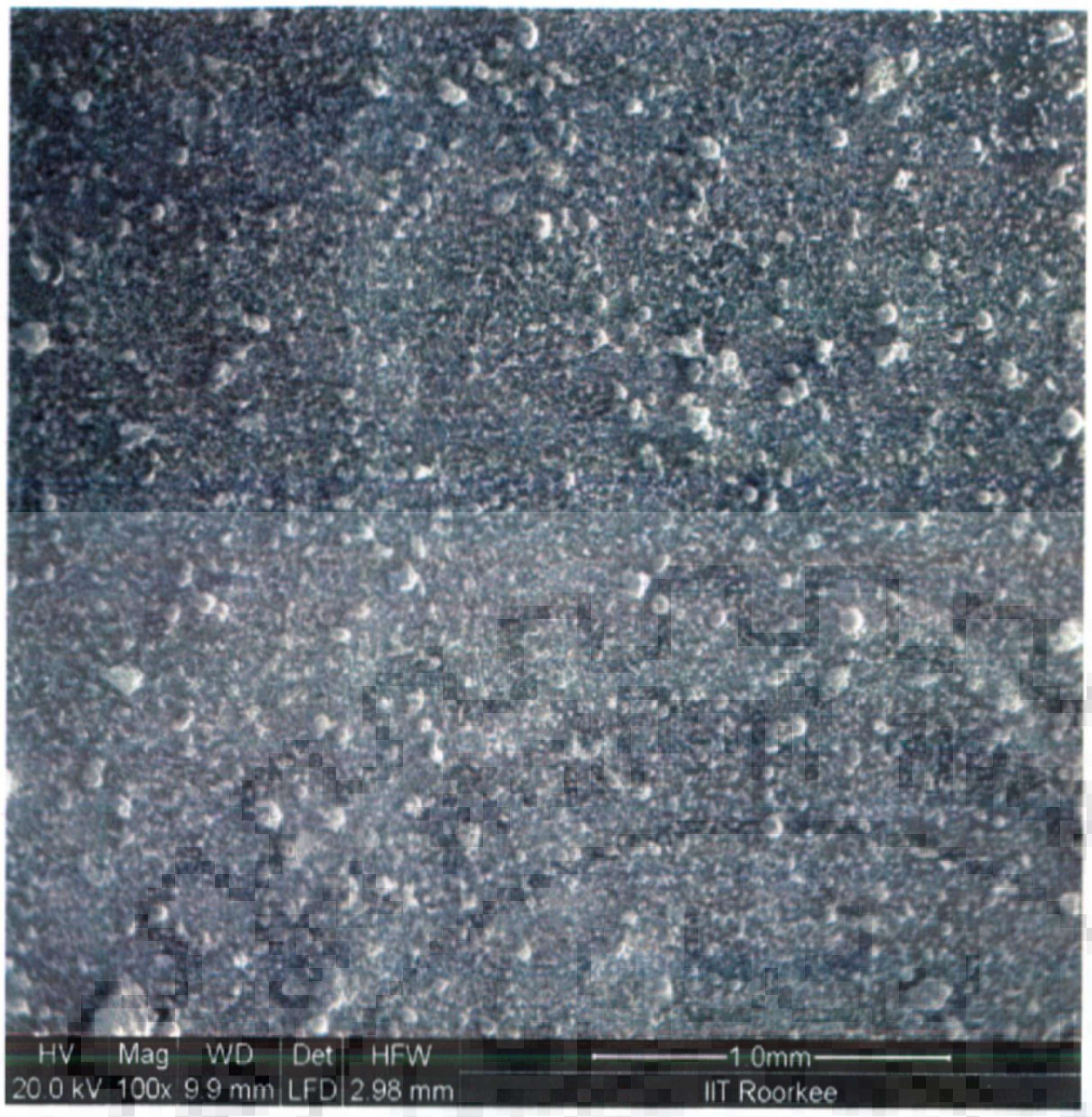


Figure 4.7 Scanning Electron Micrograph with EDAX spectra along with elemental composition for Dadri fly ash



Element	Wt %
C	40.43
O	22.32
B	10.11
Mg	0.21
Al	8.48
Si	11.59
Se	1.38
Ba	0.81
K	0.39
Ca	0.72
Ti	0.4
V	0.09
Cr	0.07
Mn	0.21
Fe	1.72
Ni	0.35
Cu	0.48
Zn	0.24

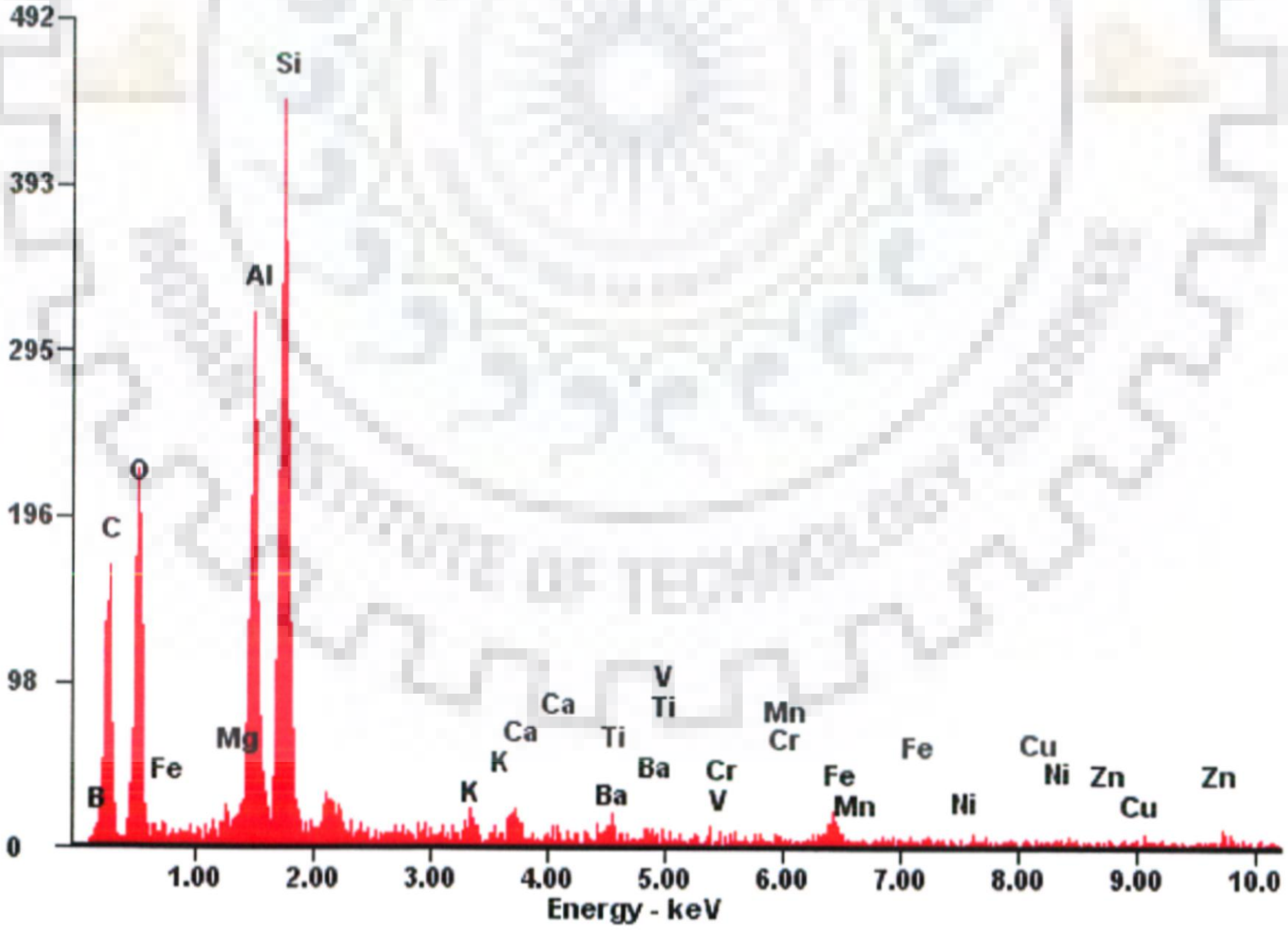
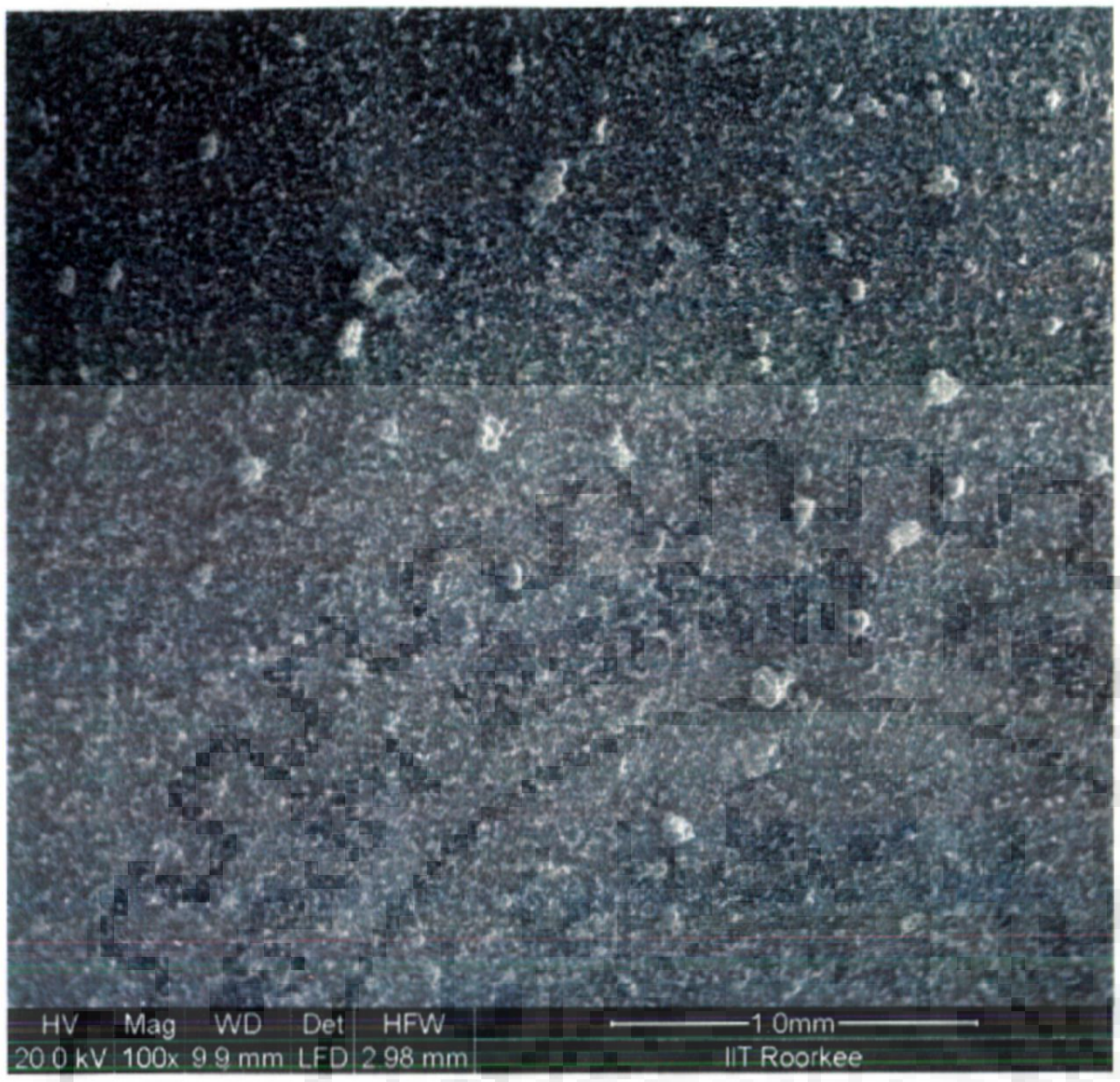


Figure 4.8 Scanning Electron Micrograph with EDAX spectra along with elemental composition for Nashik fly ash



Element	Wt %
C	39.37
O	27.0
Na	0.12
Mg	0.32
Al	10.05
Si	15.02
Ba	0.27
Cd	0.38
K	0.6
Ca	0.6
Ti	0.97
V	0.4
Cr	0.57
Mn	0.37
Fe	2.61
Ni	0.54
Cu	0.39
Zn	0.36

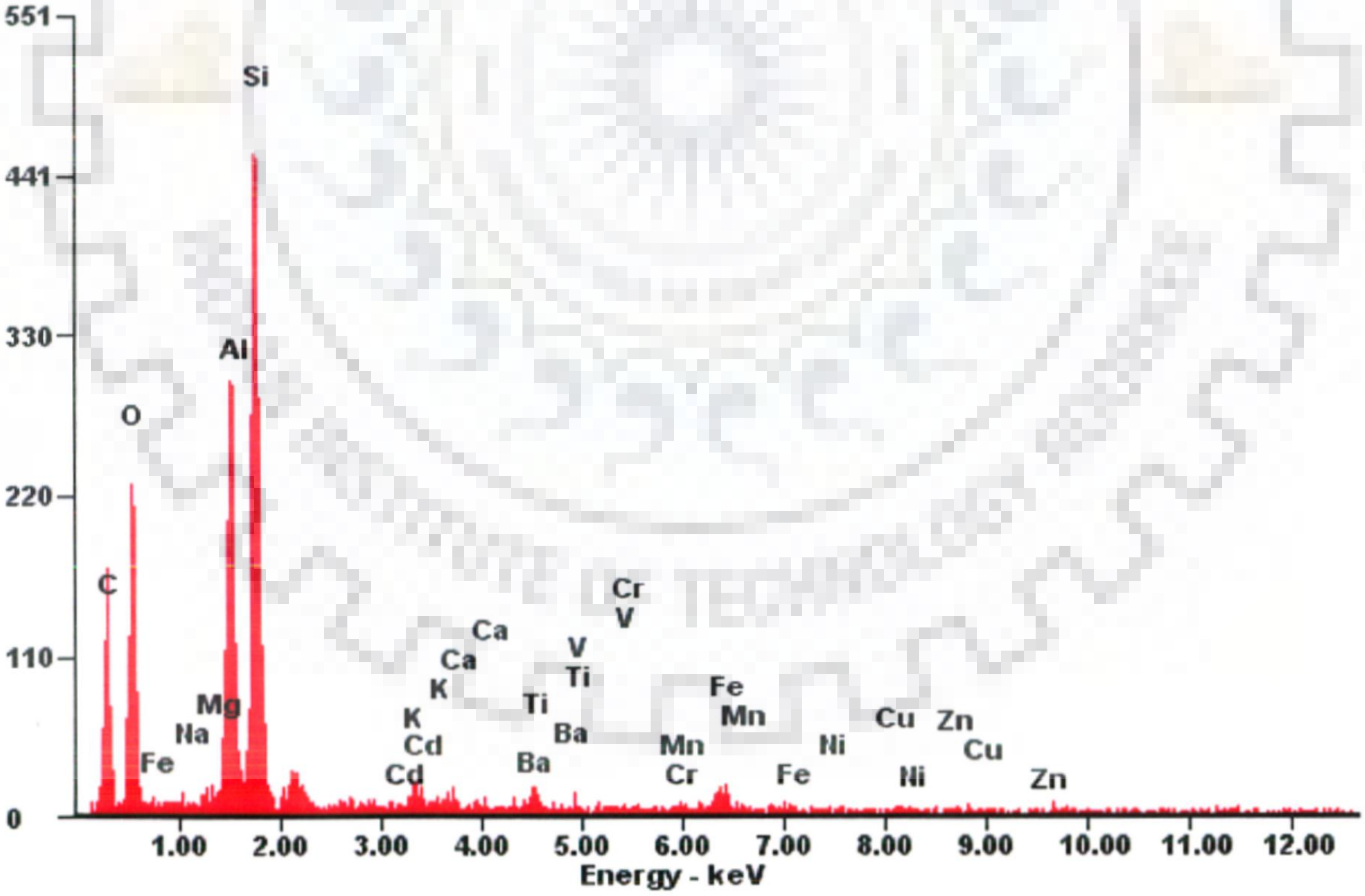
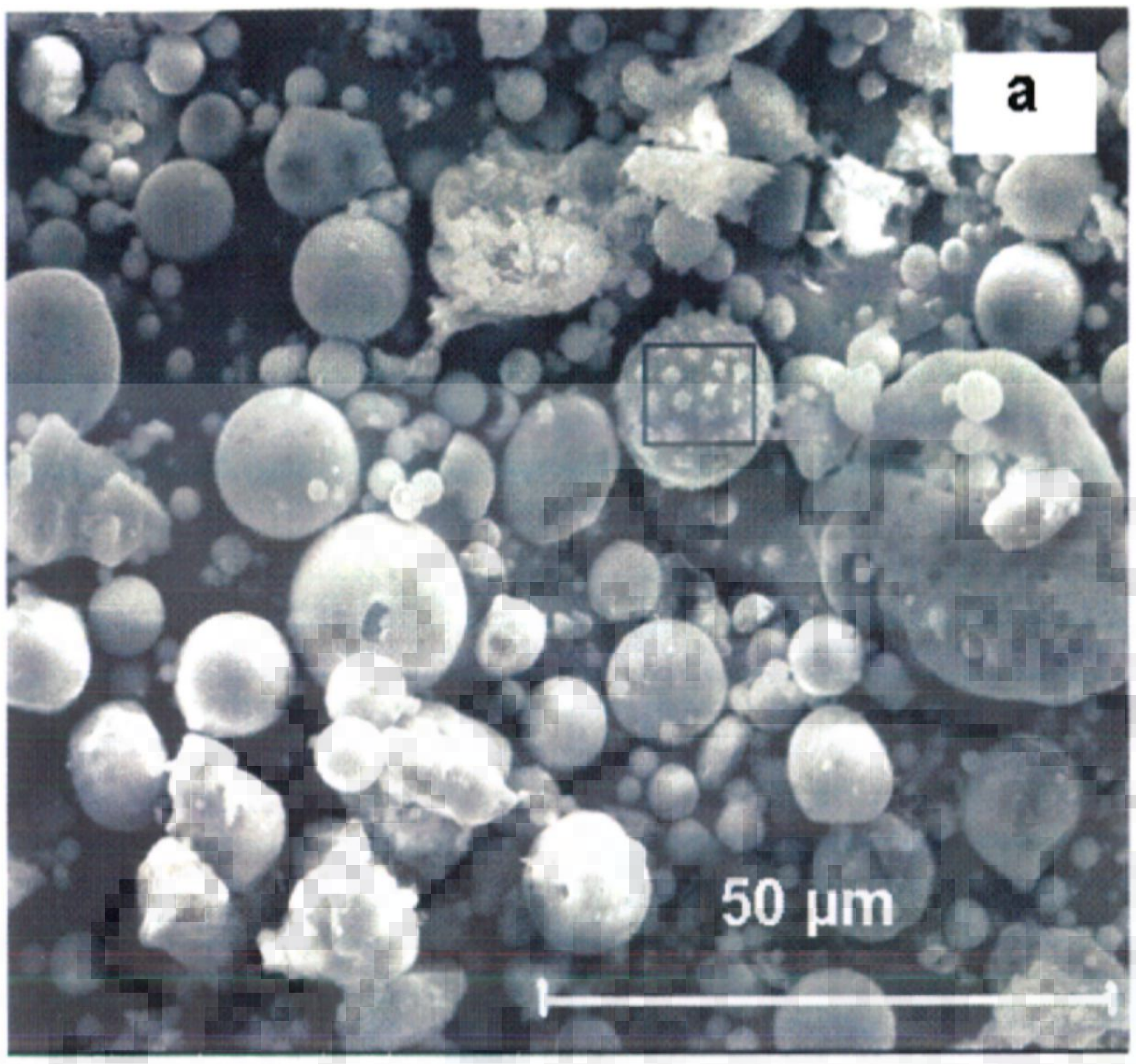


Figure 4.9 Scanning Electron Micrograph with EDAX spectra along with elemental composition for Suratgarh fly ash



Element	Wt %
C	9.71
O	26.67
Na	0.37
Mg	0.31
Al	11.60
Si	13.31
K	0.8
Ca	0.83
Ti	0.94
V	0.36
Cr	0.45
Mn	0.6
Fe	32.12
Ni	0.56
Cu	0.63
Zn	0.74

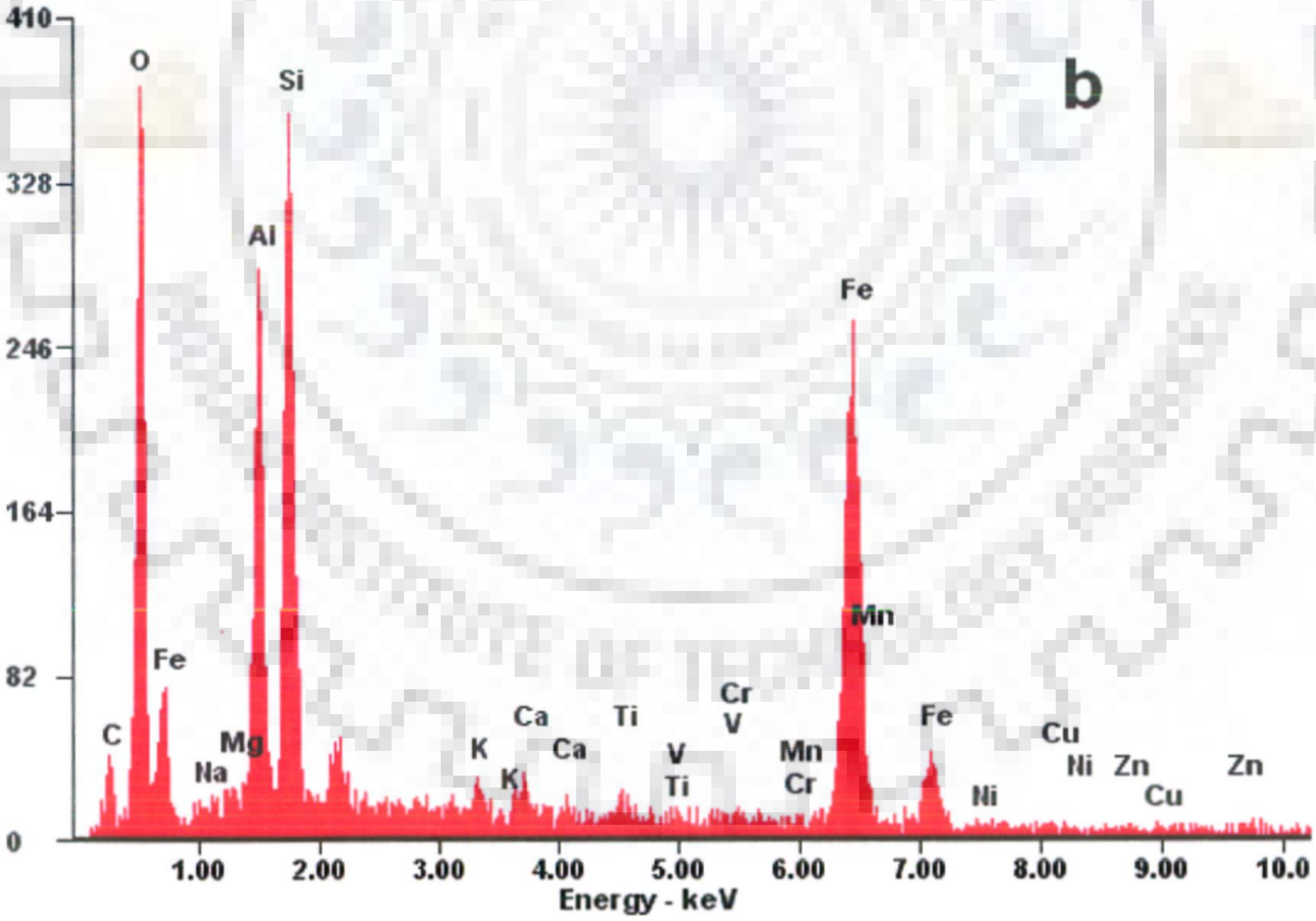
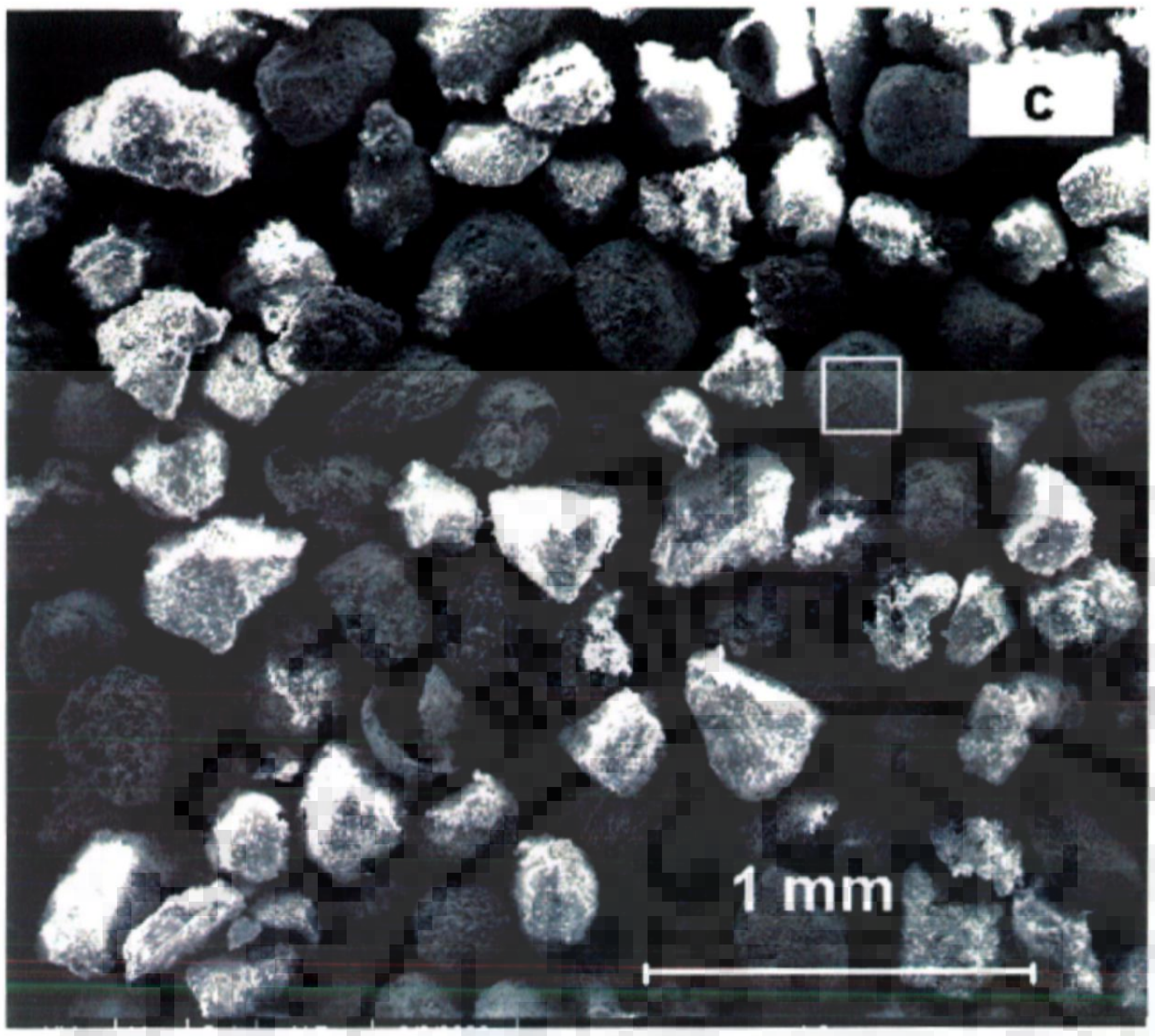


Figure 4.10 Scanning Electron Micrograph with EDAX spectra along with elemental composition for the magnetic fraction of Bhatinda fly ash



Element	Wt %
C	2.51
O	22.61
Mg	0.36
Hg	2.86
Al	4.36
Si	8.35
K	0.46
Ca	1.13
Ti	0.46
V	0.51
Cr	0.36
Mn	2.64
Fe	52.25
Ni	0.61
P	0.52

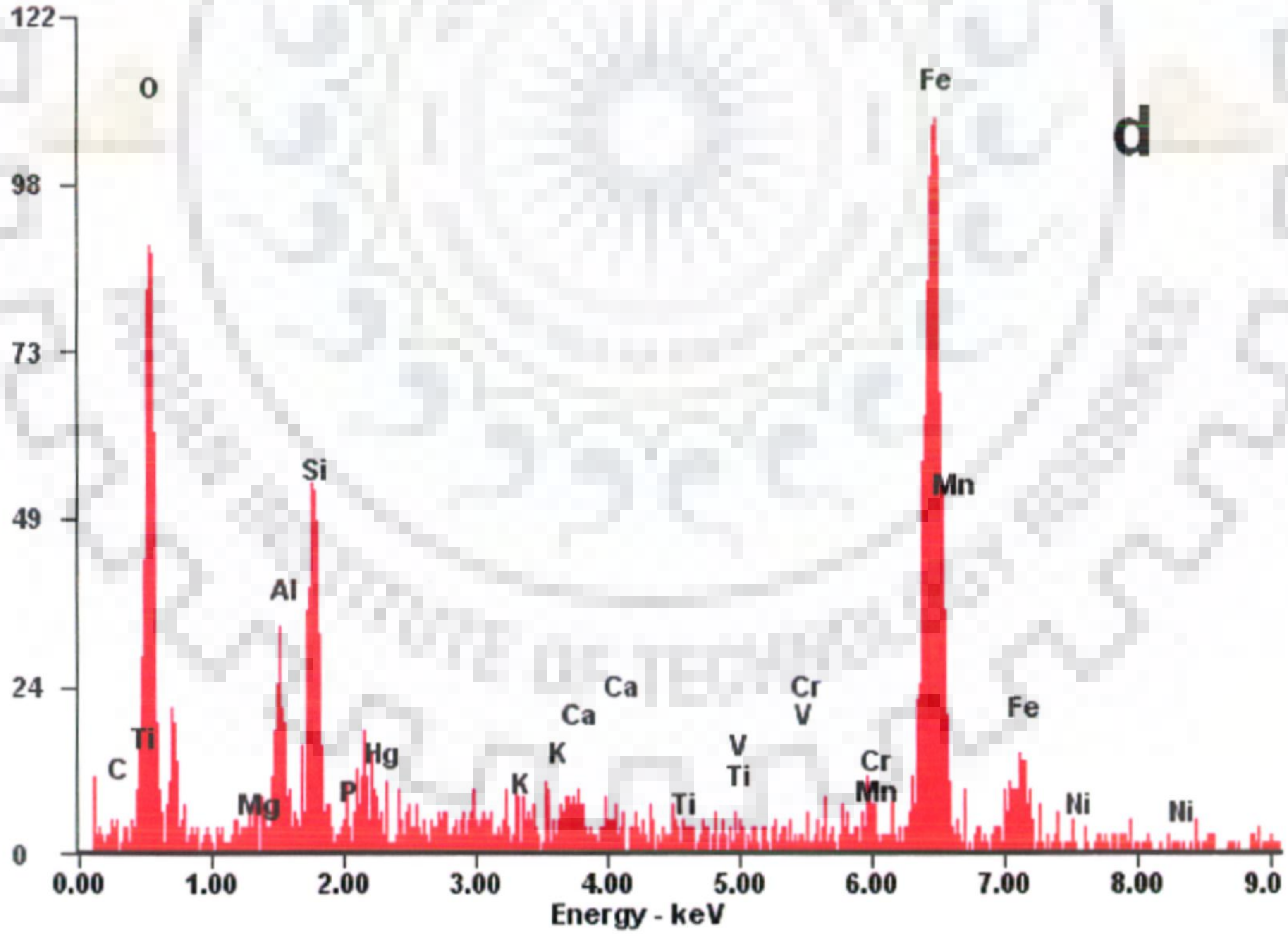
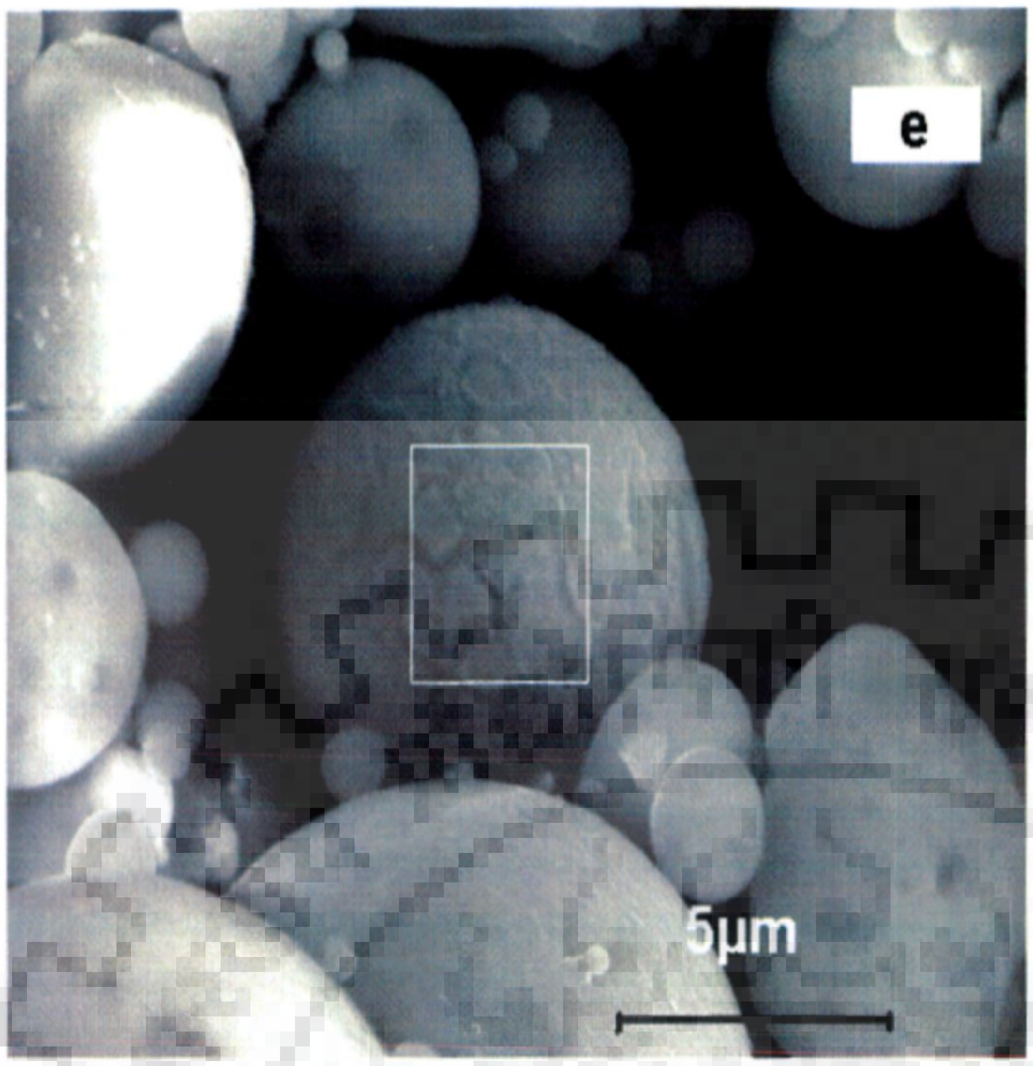


Figure 4.11 Scanning Electron Micrograph with EDAX spectra along with elemental composition for the magnetic fraction of Nashik fly ash



Element	Wt %
C	17.27
O	21.99
Mg	0.66
Al	5.62
Si	7.47
K	0.25
Ca	0.62
Ti	0.34
Cr	0.36
Mn	1.03
Fe	42.99
Ni	0.18
Cu	0.88
Zn	0.38

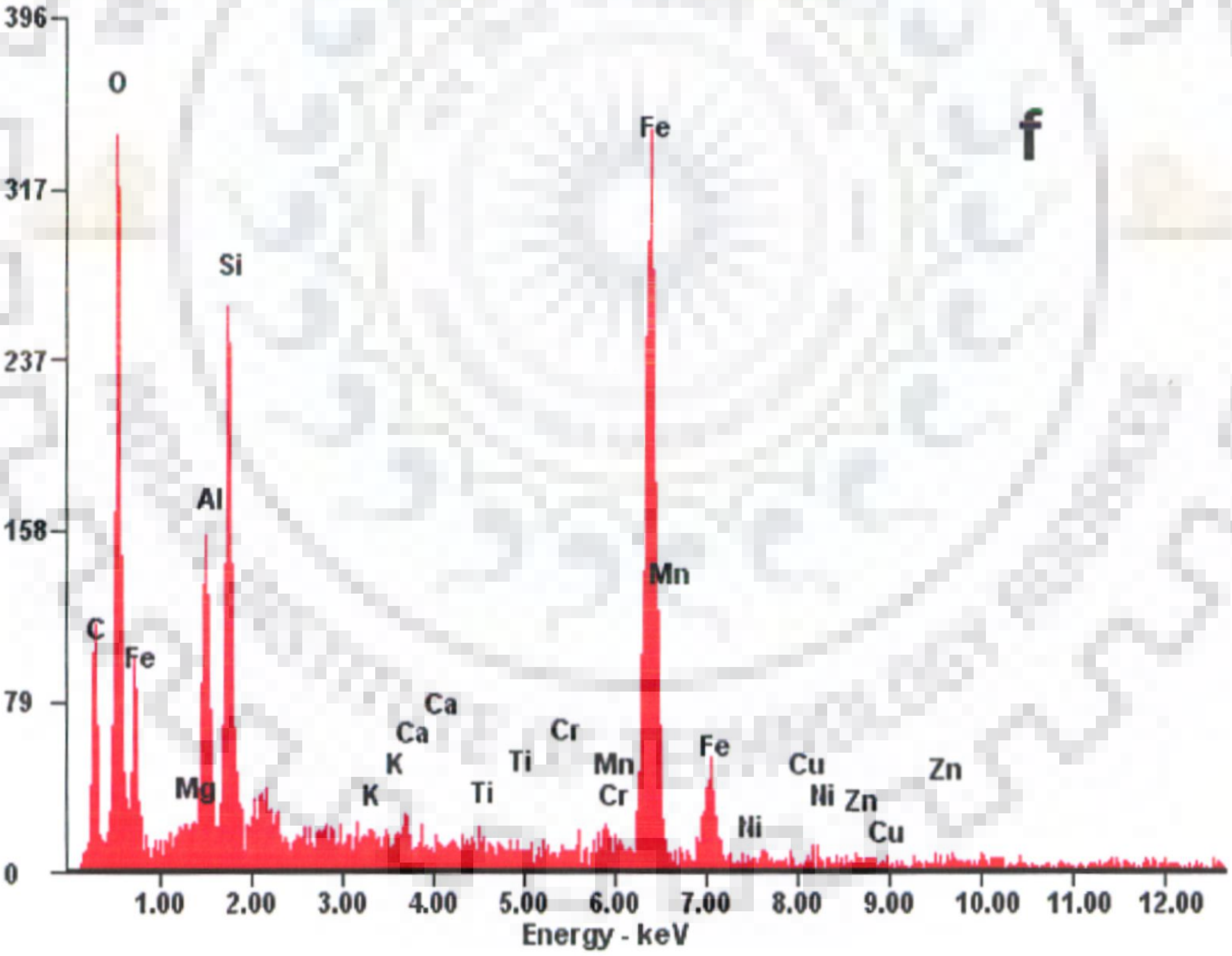
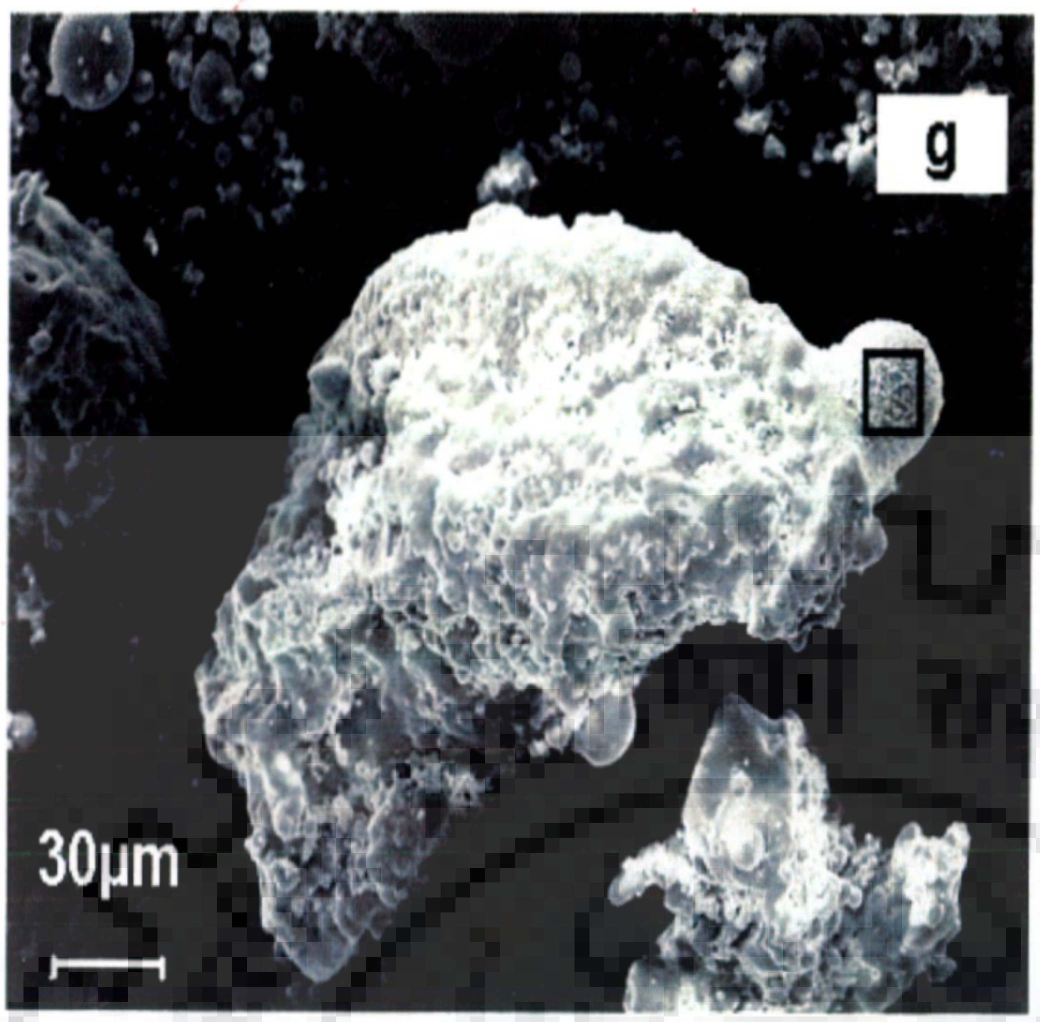


Figure 4.12 Scanning Electron Micrograph with EDAX spectra along with elemental composition for the magnetic fraction of Suratgarh fly ash



C	11.26
O	17.07
Mg	0.37
Al	19.26
Si	18.5
K	0.44
Ca	0.76
Ti	0.63
Cr	0.39
Mn	1.2
Fe	25.94
Ni	0.49
Cu	1.01
Zn	0.79
Se	1.39

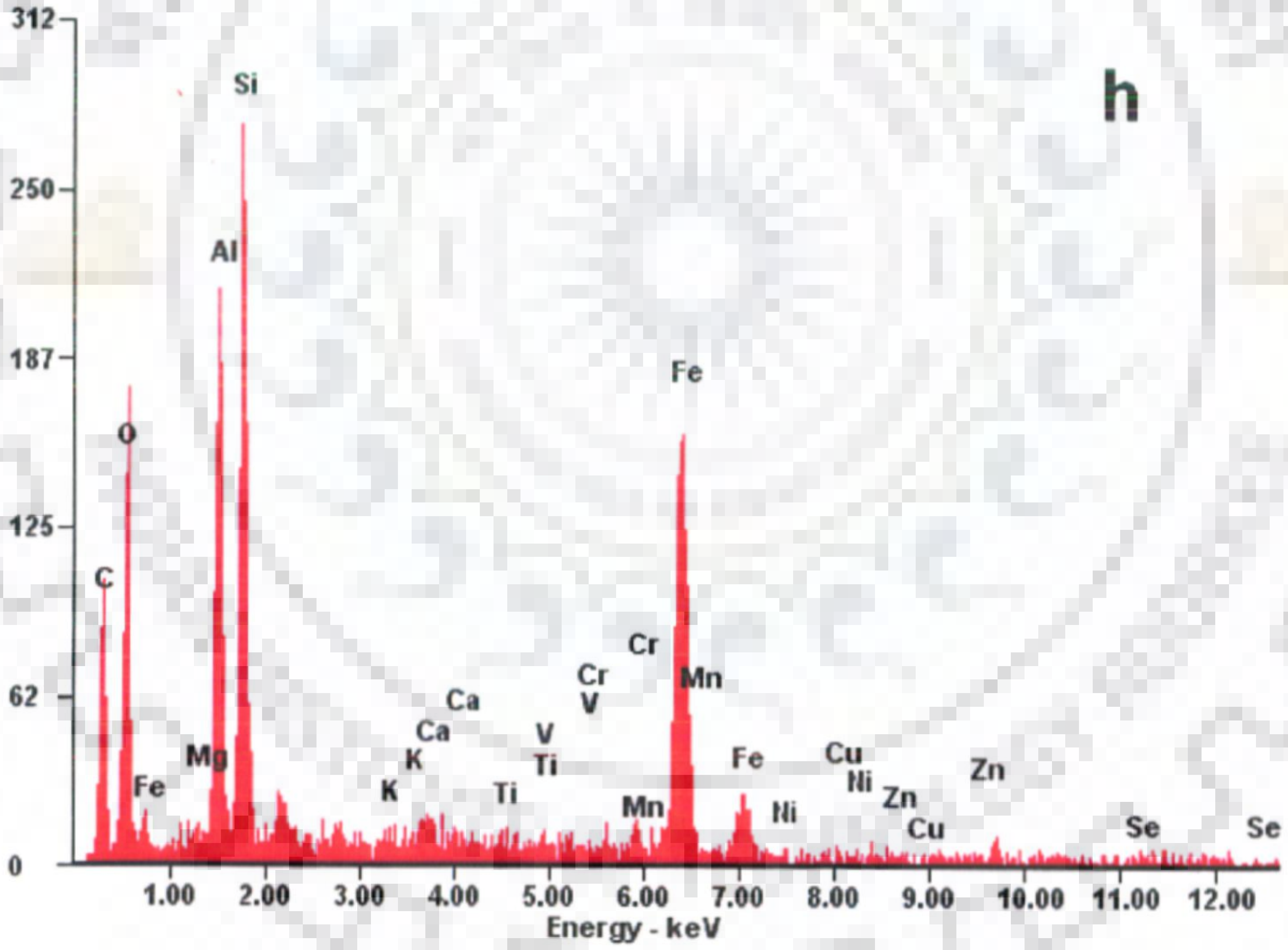


Figure 4.13 Scanning Electron Micrograph with EDAX spectra along with elemental composition for the magnetic fraction of Dadri fly ash

4.8 MORPHOLOGY OF FLY ASH

Morphology of fly ash is controlled by combustion temperature, cooling rate, solidifying process and residence time of particle during combustion. The morphology of the fly ash particles was studied by Scanning Electron Microscopy (SEM). The morphology observed through scanning electronic micrographs reveal solid spherical particles, hollow spheres (cenospher), small spheres enclosed in bigger one (plerosphere), irregular shape, Swiss cheese like, irregular holey (clinker-like) particles, platy particles etc. The majority of the particle are observed are in the range of 1μm to 100μm and consisted of spherical shape. Leaching is a function of the surface exposed to the leaching fluid. The ratio of the particle surface area to the volume occupied by the particles, the average particle size, and internal pore structures in the material, all control the surface area where dissolution from solid to the liquid can occur (Van der Sloot et al.,1997). Smaller particle sizes produce large surface area, allowing for increased contact between the solid material and the leaching fluid, resulting in increased contact between the leaching fluid and leachable constituents.

Fly ash collected from electrostatic precipitator, typically displayed spherical morphology. Spherical shape indicates that it is fresh ash and suggests that it does not have any previous contact with water. Spherical particles, less than 10 μm in size (finer fraction), were abundant in the Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash which is indicated in Figuress 4.14 and 4.15. The plerosphers are formed due differential melting of particles and influence of gases generated by decomposition of $CaCO_3$ and carbon present on the surface or inside of ash particles and dehydration of clay minerals (Goodarzi, F. et al., 2009). Micro spheres are formed due to intimate contact of minerals and pulverized coal during combustion. During combustion fused silicates shell forms around encapsulated ash particles.

Cenospheres are formed by gaseous generation within molten slag droplets. Cenosphers have density less than water that is why they are floating on water surface.

therefore they are sometimes also called as floaters. Ash with proportion of such floaters or cenosphers is readily dispersed by wind when stockpiled or spread over lagoons and can cause storage problems. Because cenospheres transport heavy metals relevant from the hygienic and health point of view (Goldsmith, J. R., 1977) into the environment, particularly V, Fe, Ni, Cr, Zn and Mn as oxides and sulphates.

Irregular shape of fly ash particle showing cavities are formed by gaseous emission during crystallization. Agglomerated particles and irregular shaped amorphous particles may have been due to inter-particle contact or rapid cooling. Particle morphology for Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash is given *in Figures 4.16, 4.17, 4.18 and 4.19 respectively. Similar findings for fly ash* morphology are being reported by various researchers (Fisher, G. L., et al., 1978; Del Monte, M., et al., 1984; Diamond, S., 1986; Dudas, M. J., et al., 1987; Kolay, P. K., et al., 2001; Goodarzi, F., et al., 2009) in the literature.

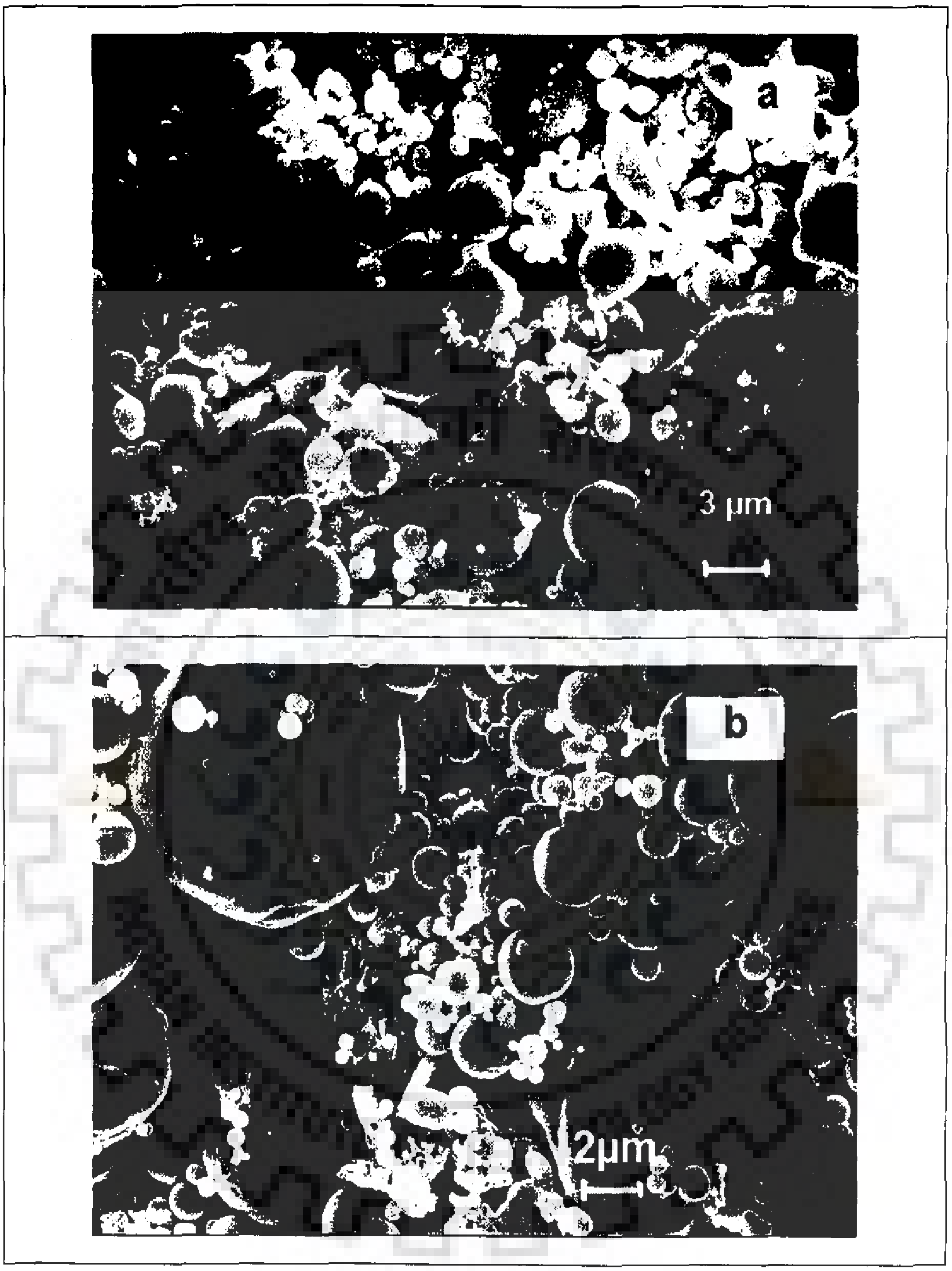


Figure 4.14 Spherical particles of fly ash in finer fraction
(a) Bhatinda fly ash, (b) Dadri fly ash

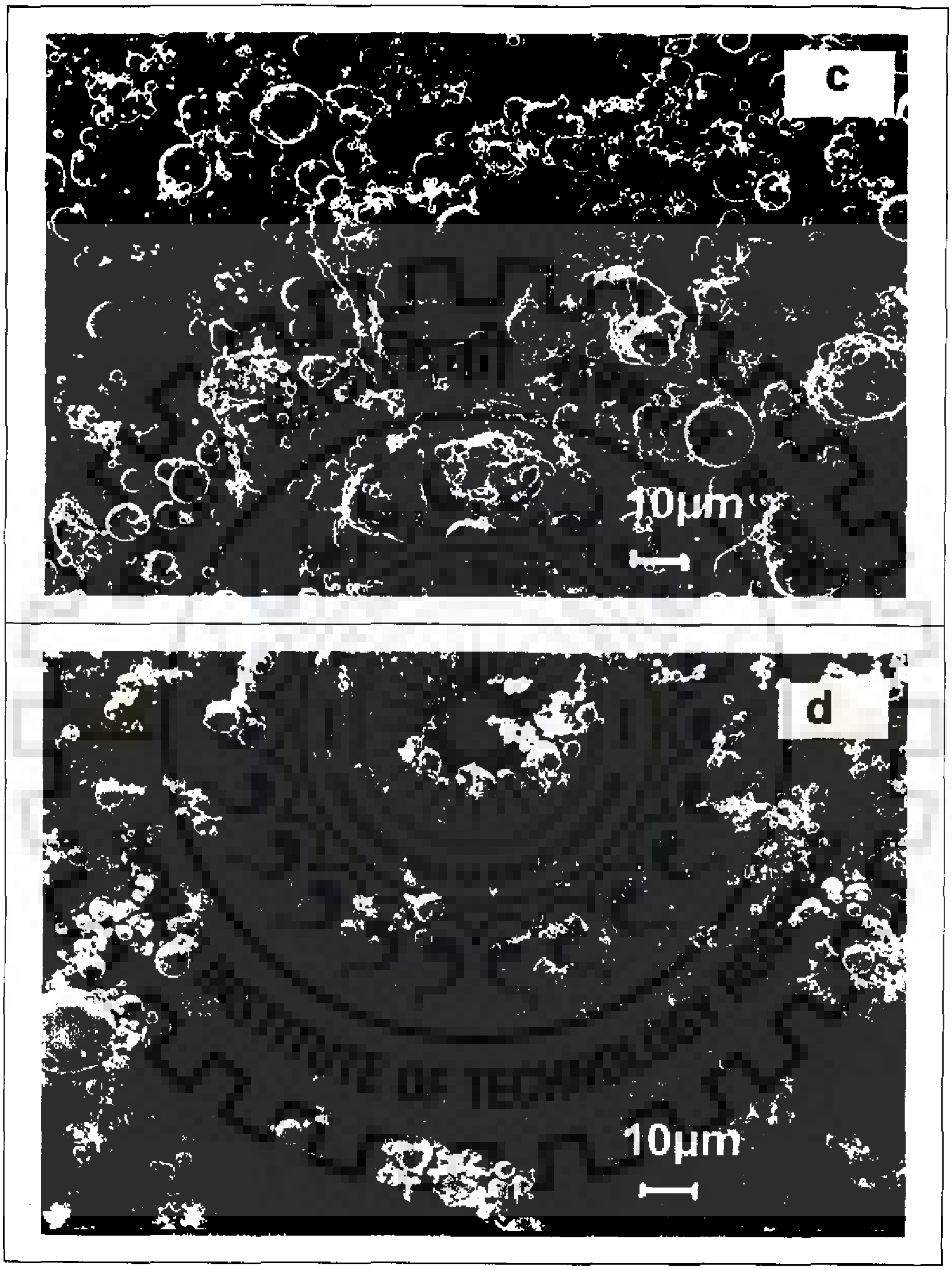


Figure 4.15 Spherical particles of fly ash in finer fraction
(c) Nashik fly ash, (d) Suratgarh fly ash

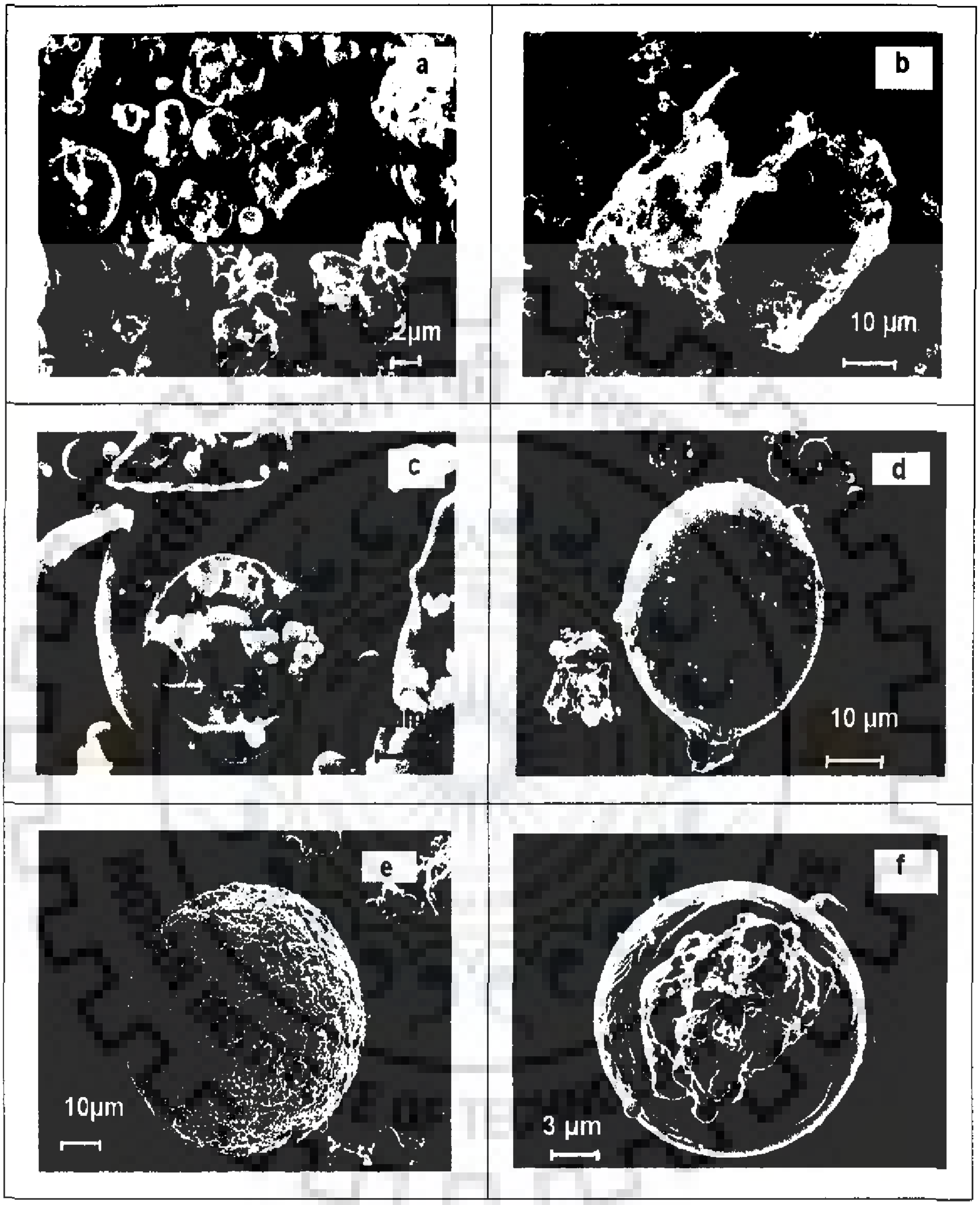


Figure 4.16 SEM for Bhatinda fly ash (a) Typical spherical morphology (b) Irregulary spongy paricle (c) Plerosphere (d) Solid sphere with submicron particle attached (e) Magnetic sphere (f) Solid sphere with attached cluster of submicron particle with some cavities.

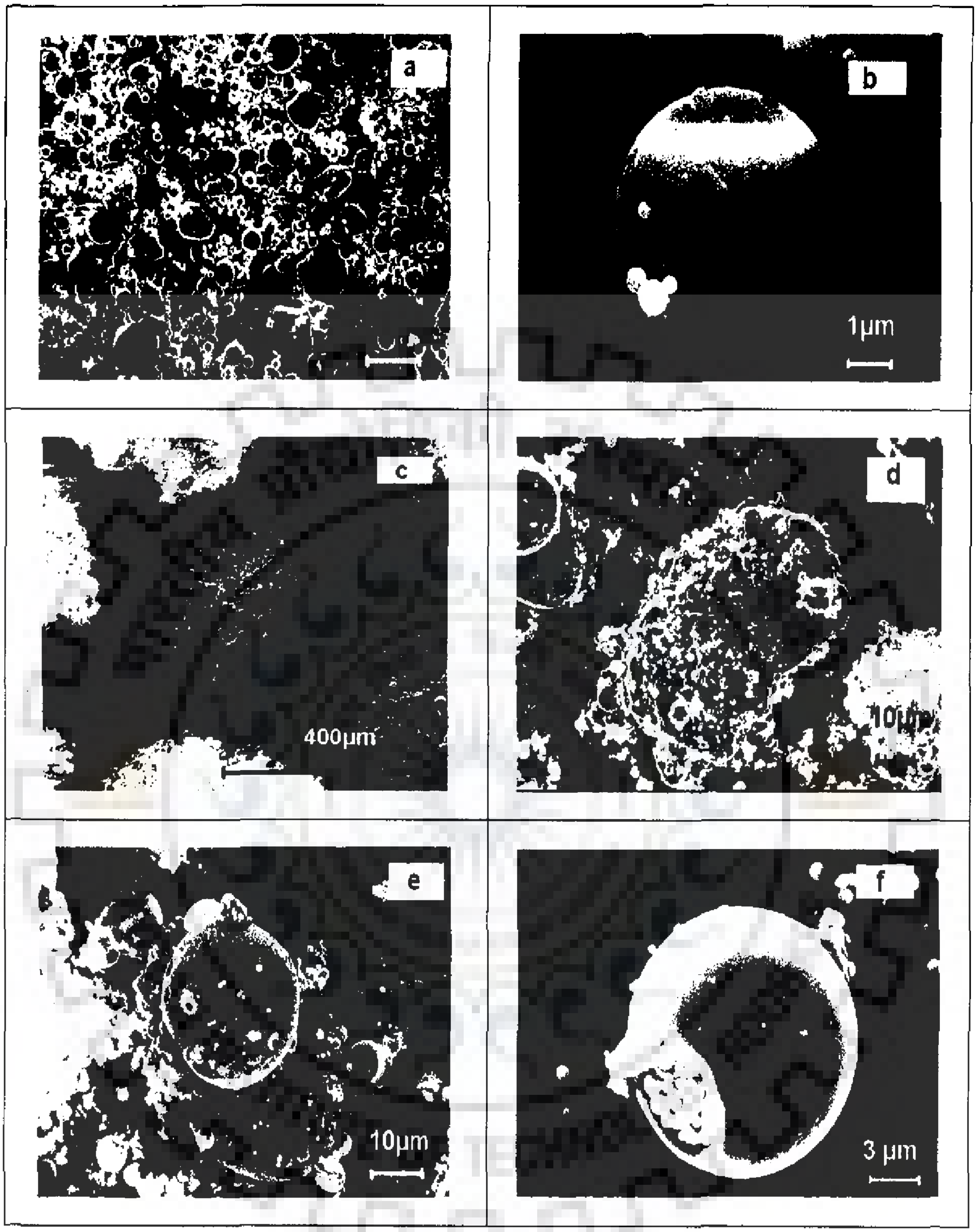


Figure 4.17 SEM for Dadri fly ash (a) Spherical particles, (b) Solid spherical particle with submicron spheres attached, (c) spongy carbon particle with submicron spheres attached, (d) Irregular alumino silicate matrix with submicron particles (e) Potato shape particle along with submicron particle (f) Plerosphere

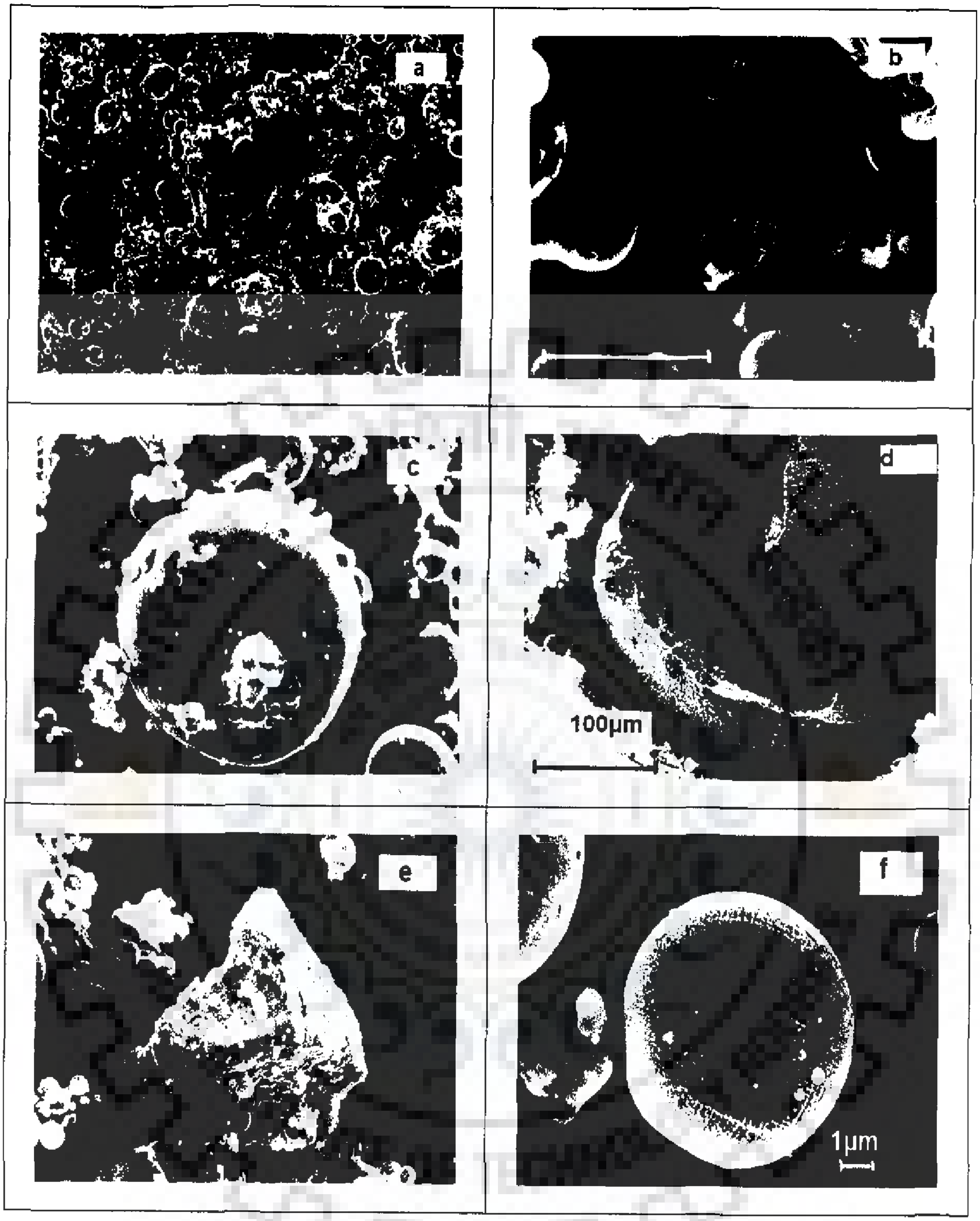


Figure 4.18 SEM for Nashik fly ash (a) Typical spherical morphology, (b) Irregular holey particle (c) Plerosphere (d) Broken cenosphere (e) Silicate particle with micospheres attached (f) Dendritic ferrosphere

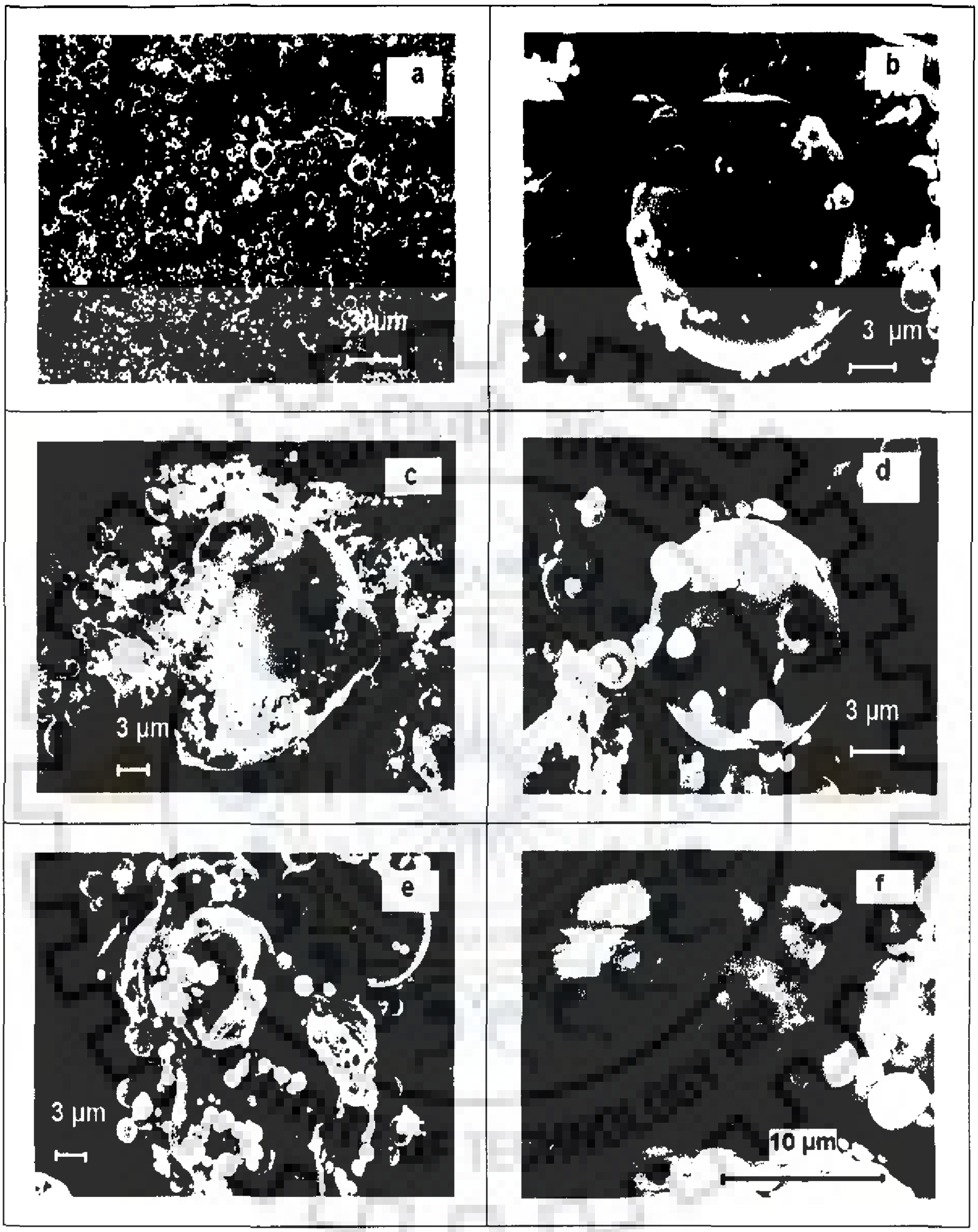


Figure 4.19 SEM for Suratgarh fly ash (a) Typical spherical morphology, (b) Solid sphere with submicron particles attached, (c) Agglomerated particles and irregular shaped, (d) Cenosphere, (e) Alumino silicate matrix with micro cavities, (f) Irregular platy particle

4.9 ATOMIC FORCE MICROSCOPIC STUDIES

Scanning Electron Microscopy provides general overview of the surface texture of fly ash particles. Atomic Force Microscopy (AFM-make-NT-MDT, Ntegra) gives significant information on the shape of the fine particles of fly ash up to nanoscale. By AFM a sharp tip is scanning over a sample surface and three dimensional images having resolution at nanometer levels are obtained at atmospheric condition. Advantage of AFM-make-NT-MDT, Ntegra is that it gives surface roughness (nm), particle size (nm) and number of grains directly. Figures 4.20, 4.21, 4.22 and 4.23 shows atomic force micrographs for Bhatinda fly ash (BFA), Dadri fly ash (DFA), Nashik fly ash (NFA) and Suratgarh fly ash (NFA) respectively.

Figure 4.20 (a), (c), and (e) depicts 2-Dimensional Atomic Force Micrograph of Bhatinda fly ash and in Figure 4.20 (b) 3D image showing elongated particles, of fly ash with particle size 222 nm and surface roughness 61 nm. Figure 4.20 (d) shows 3D image of columnar particle indicating presence of silica by white color, with particle size 33 nm and surface roughness 9 nm, whereas in Figure 4.20 (f) 3D image of globular particles with particle size 23 nm and surface roughness 6 nm is shown.

Figure 4.21 (a), (c) and (e) shows 2-Dimensional Atomic Force Micrograph of Dadri fly ash. In Figure 4.21 (b) 3D image showing elongated peaks of fly ash, particles with particle size 146 nm and surface roughness 42 nm. Figure 4.21 (d) shows 3D image of columnar particle, with particle size 83 nm and surface roughness 24 nm, whereas Figure 4.21(f) represents 3D image of fly ash with crest and trough indicating presence of silica by white color particles with particle size 29 nm and surface roughness 8 nm.

Figure 4.22 (a), (c), (e) gives 2-Dimensional Atomic Force Micrograph for Nashik fly ash. Figure 4.22 (b) shows 3D image showing elongated peaks of silicate particles of fly ash with cavity, with particle size 145 nm and surface roughness 37 nm. Figure 4.22 (d) gives 3D image of columnar particle indicating presence of silica by white color and big particle with cavity with particle size 136 nm and surface roughness 33 nm, whereas

Figure 4.22 (f) shows 3D image of fly ash with small globular particle and platy particle with trough with particle size 44 nm and surface roughness 11 nm.

Figure 4.23 (a), (c) and (e) shows 2-Dimensional Atomic Force Micrograph for Suratgarh fly ash, whereas Figure 4.23 (b) shows 3D image showing elongated peaks of silicate particles of fly ash and larger platy particle with cavity, particle size 160 nm and surface roughness 40 nm. Figure 4.23 (d) shows 3D image of columnar particle of white color indicating presence of silica and irregular shape particle with cavities particle size 130 nm and surface roughness 27 nm and Figure 4.23 (f) gives 3D image of fly ash with crest and trough, particle size 19 nm and surface roughness 6 nm.

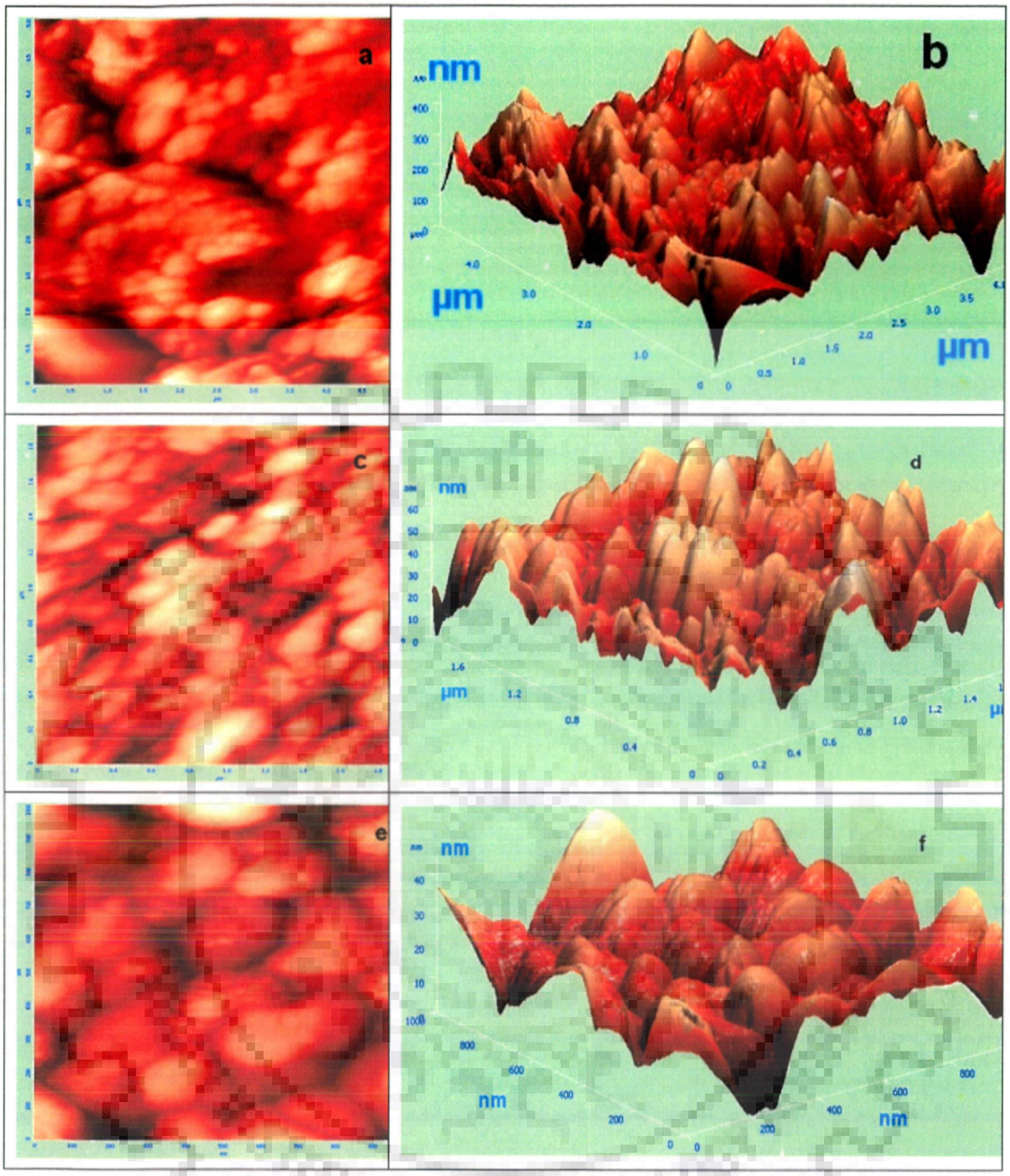


Fig 4.20 AFM of Bhatinda fly ash particles (a) 2D image of fly ash, (b) 3D image showing elongated particles, of fly ash, (c) 2D image of fly ash particle, (d) 3D image of columnar particle indicating presence of silica by white colour, (e) 2D image of spherical particles, (f) 3D image of globular particles

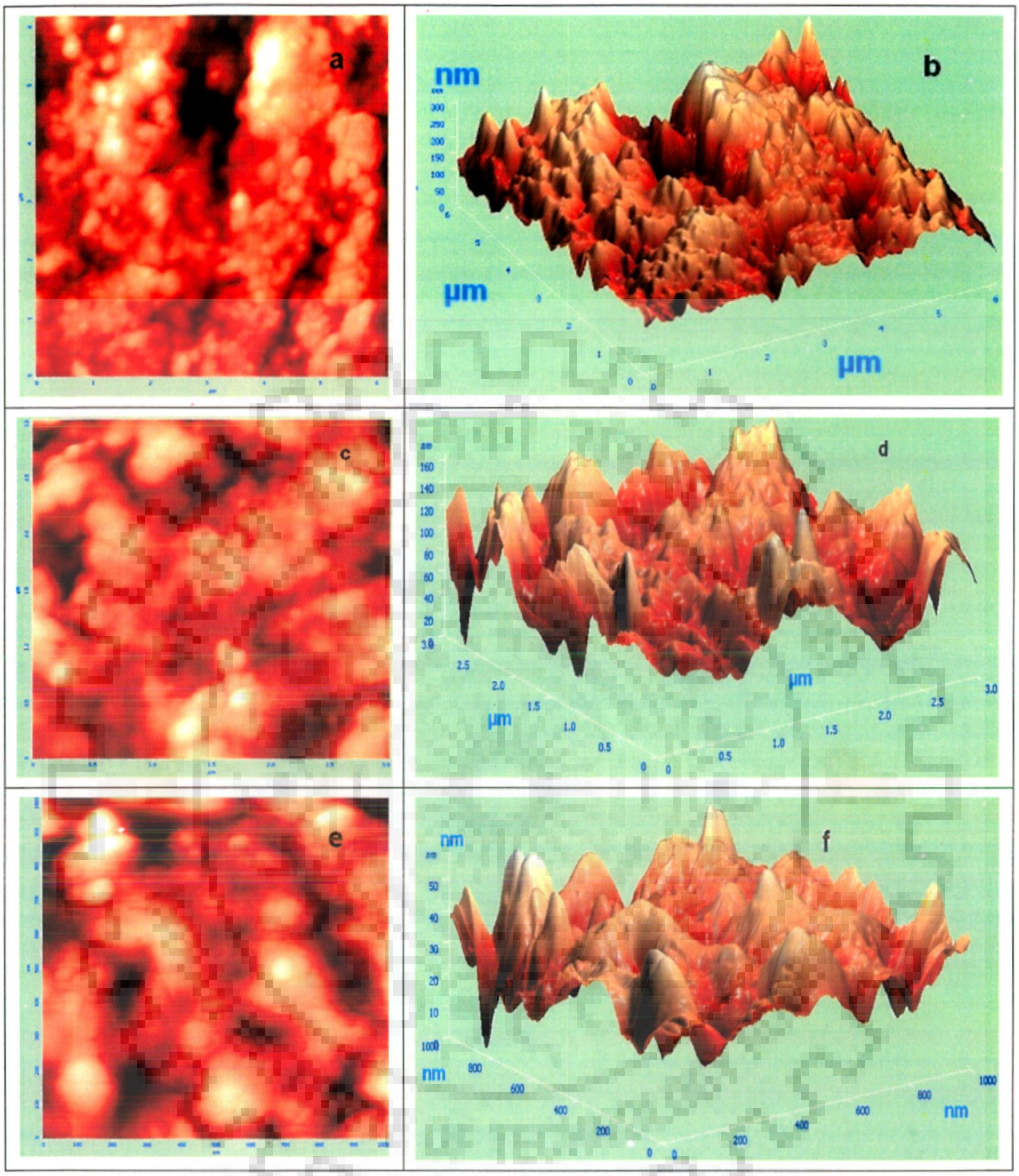


Figure 4.21 AFM for Dadri fly ash (a) 2D image of fly ash, (b) 3D image showing elongated peaks of fly ash, (c) 2D image of fly ash particle with cavities, (d) 3D image of columnar particle (e) 2D image of spherical particles, (f) 3D image of fly ash with crest and trough indicating presence of silica by white color.

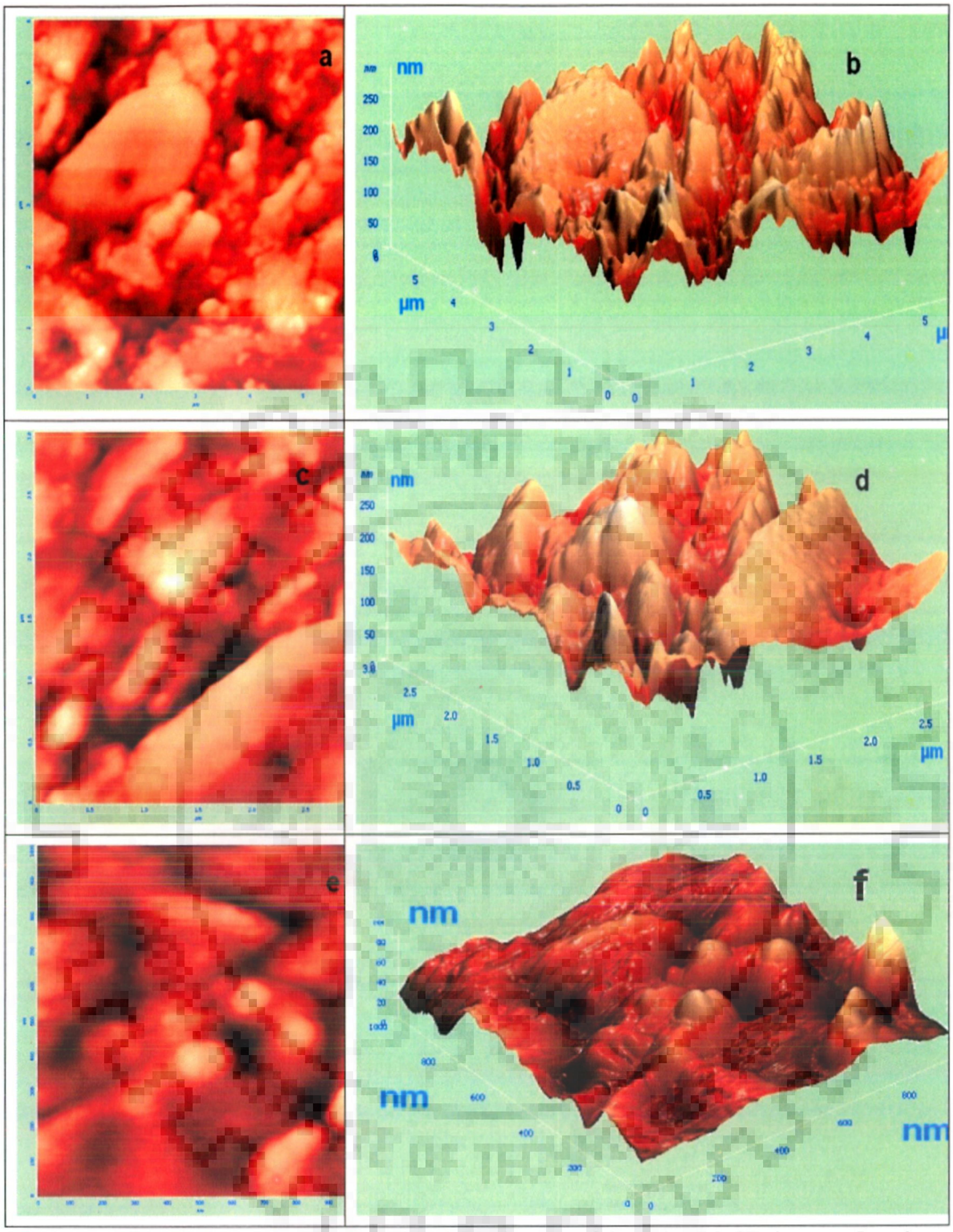


Figure 4.22 AFM for Nashik fly ash (a) 2D image of fly ash, (b) 3D image showing elongated peaks of silicate particles of fly ash with cavity, (c) 2D image of fly ash particle with cavities, (d) 3D image of columnar particle indicating presence of silica by white color and big particle with cavity (e) 2D image of fly ash particles with cavities,(f) 3D image of fly ash with small globular particle and platy particle with trough.

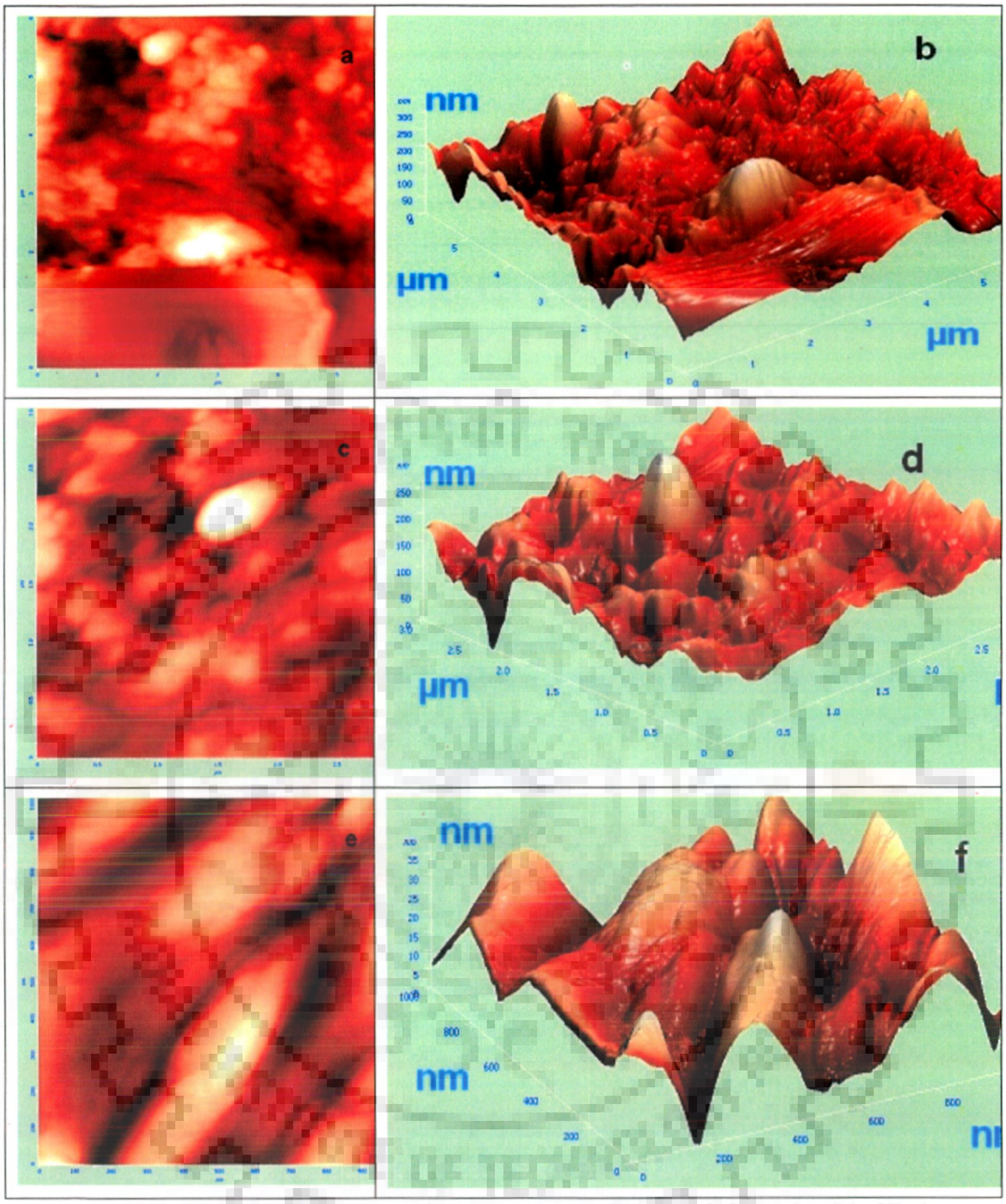


Figure 4.23 AFM for Suratgarh fly ash (a) 2D image of fly ash, (b) 3D image showing elongated peaks of silicate particles of fly ash and larger platy particle with cavity, (c) 2D image of fly ash particle with cavities, (d) 3D image of columnar particle of white color indicating presence of silica and irregular shape particle with cavities (e) 2D image of fly ash particles with cavities,(f) 3D image of fly ash with crest and trough .

4.10 LASER PARTICLE SIZE ANALYSIS

Through wet sieve analysis, it was found that 79.8%, 89%, 79.2% and 96.8% particles are less than 75 µm found in Bhatinda fly ash (BFA), Dadri fly ash (DFA), Nashik fly ash (NFA) and Suratgarh fly ash (SFA) respectively. For the analysis of finer ash particles laser particle size analysis was carried out and same samples are also observed through scanning electron micrographs for confirmation as depicted in Figures 4.24, 4.25, 4.26 and 4.27 for Bhatinda fly ash (BFA), Dadri fly ash(DFA), Nashik fly ash (NFA) and Suratgarh fly ash (SFA) respectively. Particle size analyzer reveal that more than 90% particles are in the range of 0.1 µm-40 µm, 0.1µm-30µm, 0.1µm-65µm and 0.1µm-10µm for Bhatinda fly ash (BFA), Dadri fly ash(DFA), Nashik fly ash (NFA) and Suratgarh fly ash (SFA) respectively. Particle size distribution of fly ash samples for all the power plants considered in the present study are given in Table 4.7

Table 4.7 Particle size distribution of fly ash

Fly ash	D_{10}	D_{30}	D_{50}	D_{60}	D_{90}	Cu	Cc	Span
Bhatinda Fly Ash	0.45	0.8	1.24	2.1	5.94	4.66	0.67	4.42
Dadri Fly Ash	0.4	0.6	0.98	1.5	4.72	3.73	0.6	4.4
Nashik Fly Ash	0.99	2	3	3.5	6.15	3.53	1.15	1.72
Suratgarh Fly Ash	0.58	1.9	3	3.5	5.33	6.04	1.77	1.58

D_{10} - Effective size

D_{50} - Mean size

Cu- Coefficient of Uniformity, $Cu = D_{60} / D_{10}$

Cc- Coefficient of Curvature, $Cc = D_{30}^2 /(D_{10} \times D_{60})$

$Span = (D_{90} - D_{10})/ D_{50}$

Here D_{10}, D_{30}, D_{50}, D_{60} and D_{90} represent the equivalent particle diameters corresponding to 10%, 30%, 50% 60% and 90% fines on the grain size distribution curve respectively. From utilization point of view, particle size distribution in conjunction with mineralogy provides very useful information. Fly ash particles with less than 10µm size are amenable to better compaction (Mehta, P. K., 1998). These particles contribute towards improvement in concrete performance in more than one ways. They reduce water requirement of the concrete, strengthen the "Transition Zone" (Masao, K., 1993), cause lesser bleeding during the preparation of concrete mix, and increase the long-term compressive strength.

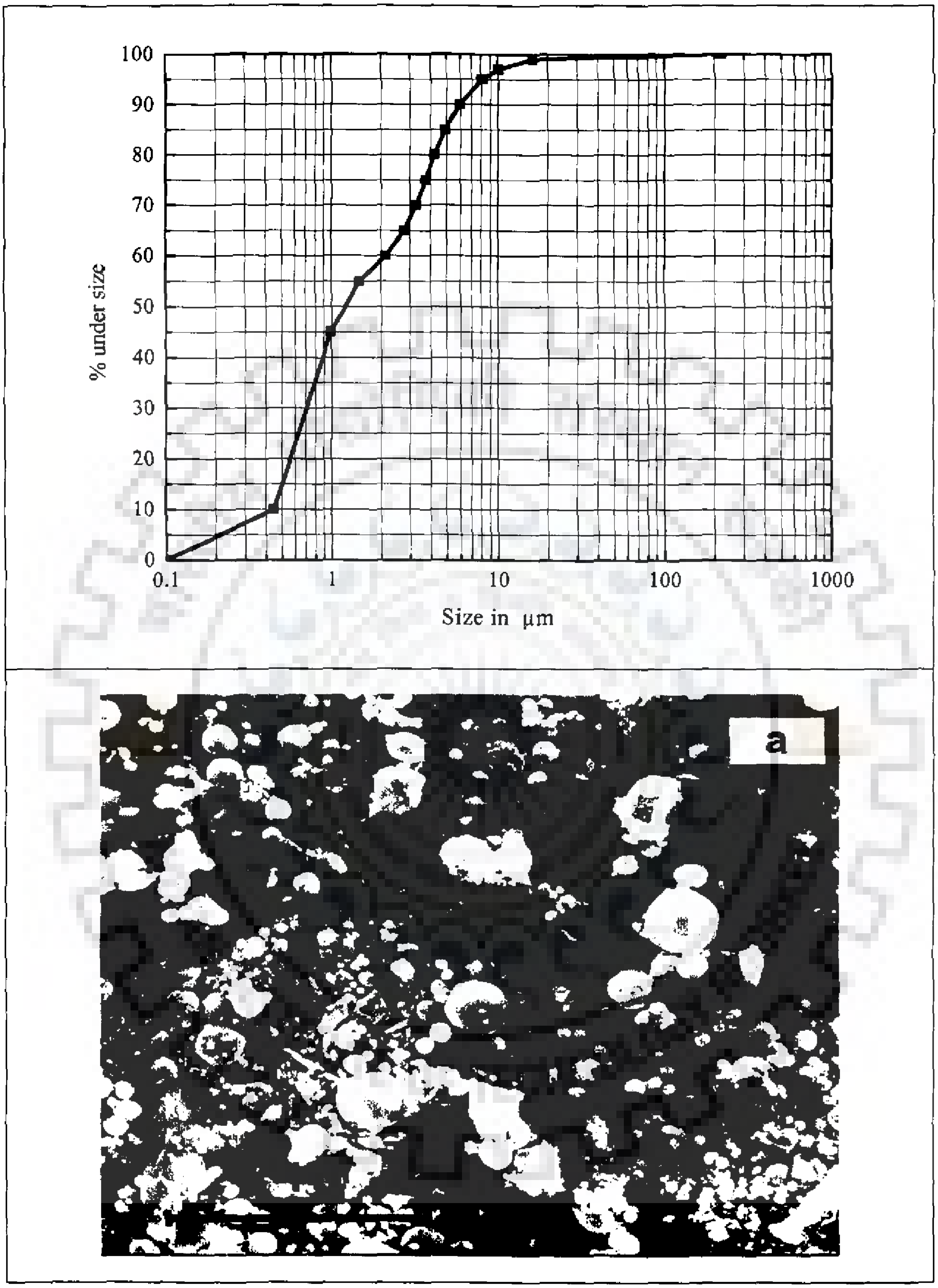


Figure 4.24 Particle size analysis and SEM of Bhatinda fly ash

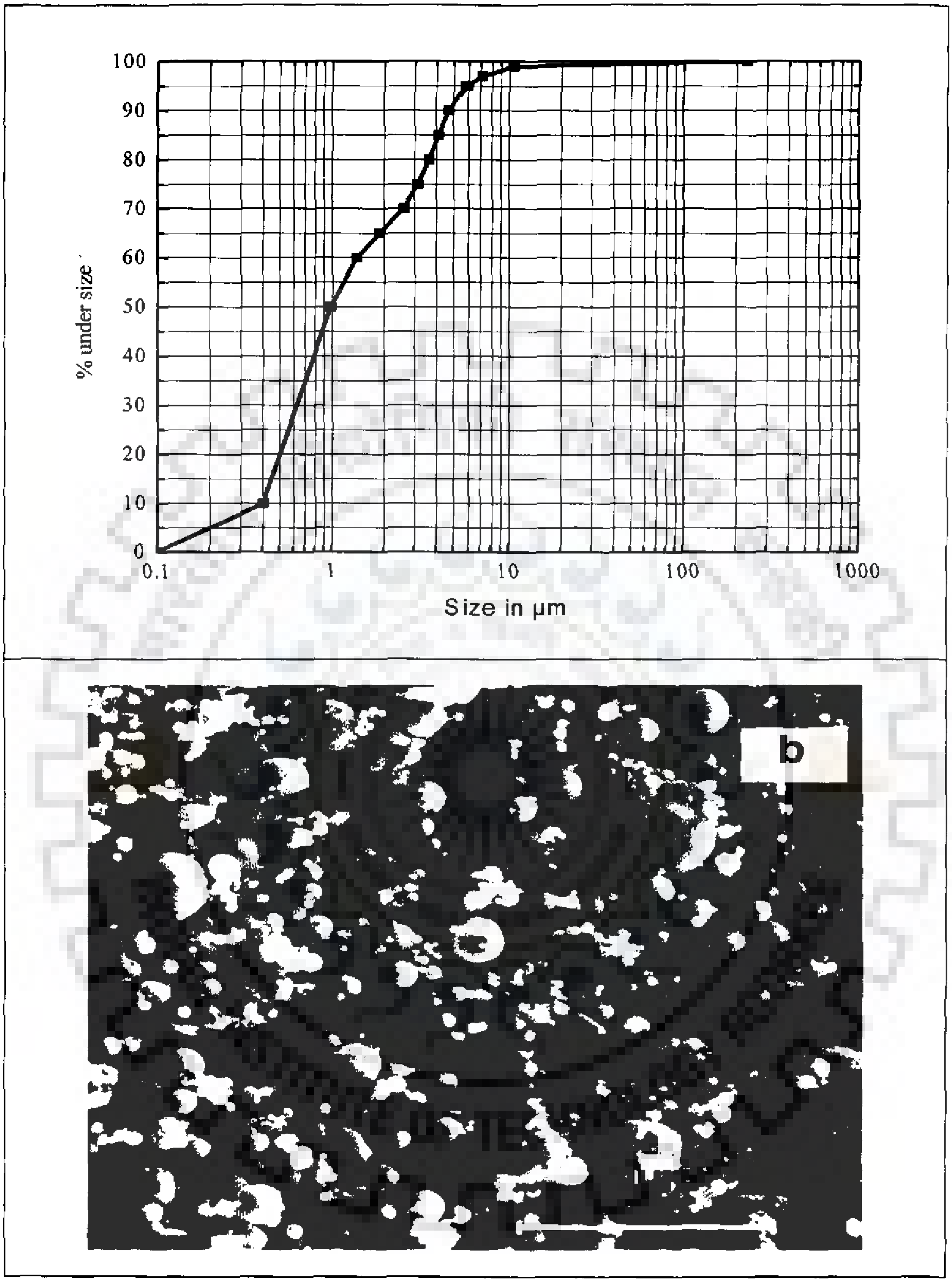


Figure 4.25 Particle size analysis and SEM of Dadri fly ash

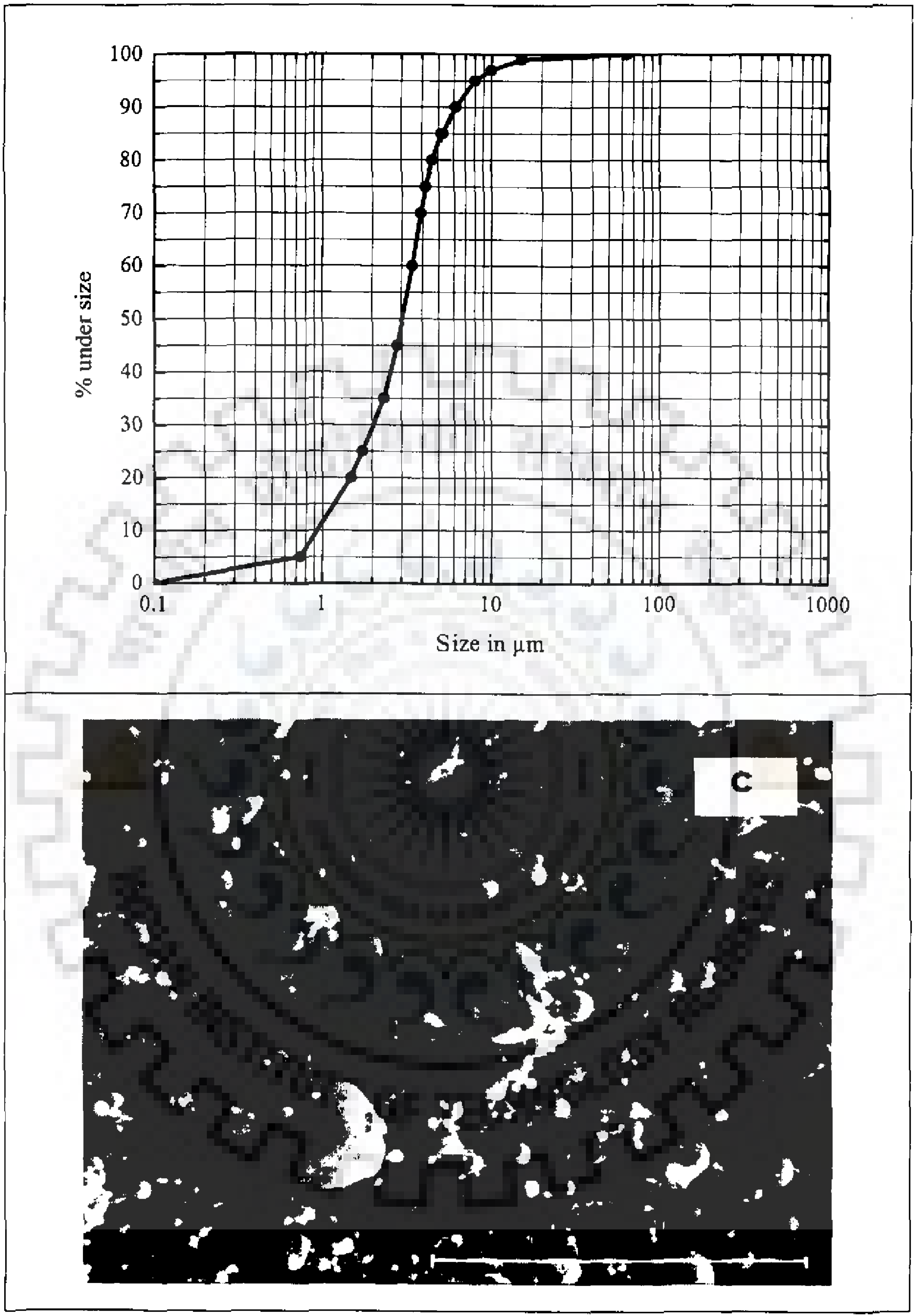


Figure 4.26 Particle size analysis and SEM of Nashik fly ash

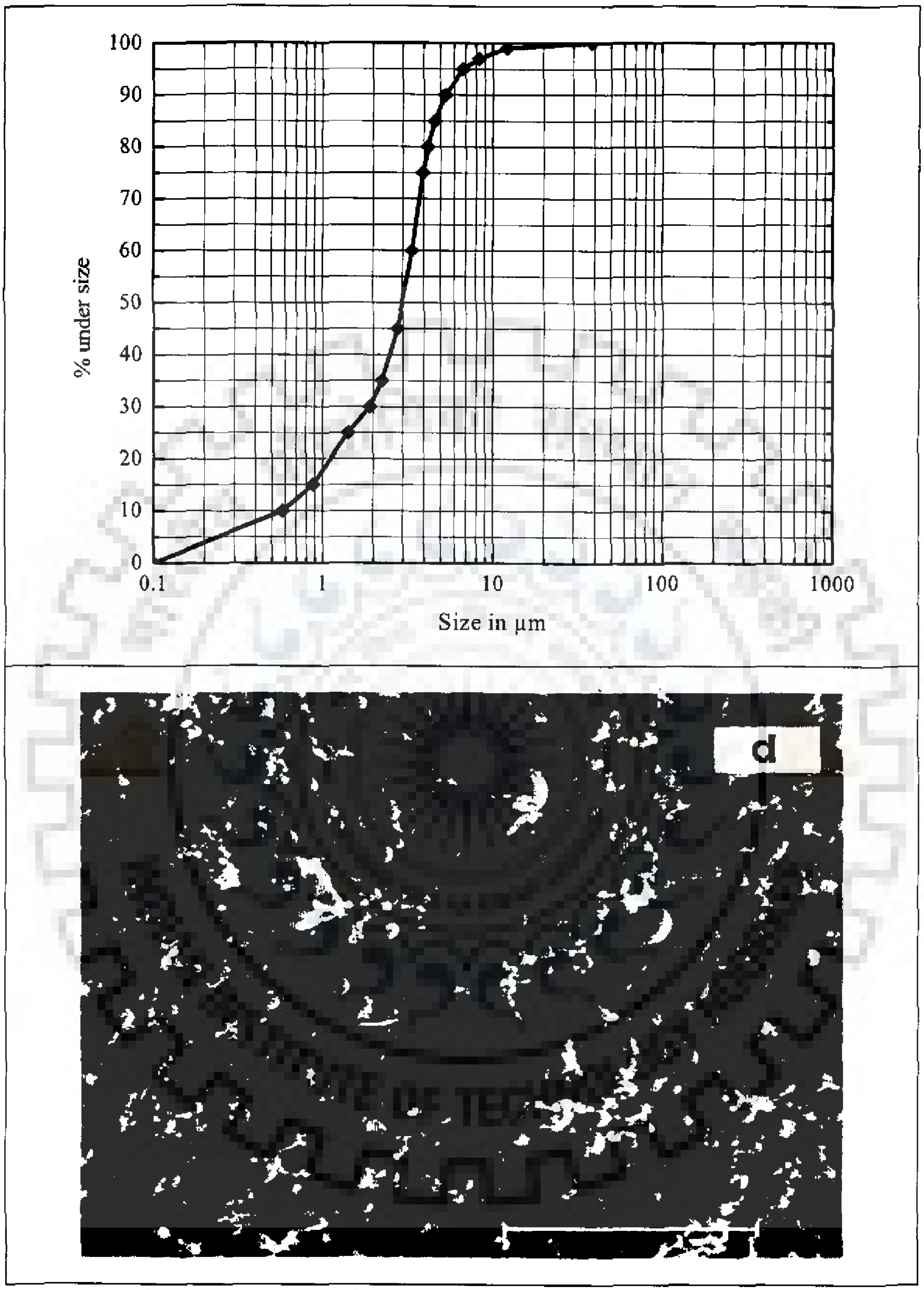


Figure 4.27 Particle size analysis and SEM of Suratgarh fly ash

4.11 UTILIZATION OF FLY ASH

Mehta P. K., (1998) observed that the pozzolanic properties of fly ash are not only affected by chemistry of fly ash but the mineralogy and particle size of the fly ash plays an important role. Fine fly ash has a larger surface area to provide the silica and alumina compounds for pozzolanic reaction (Theerawat S., et al., 2006). Fly ash particles under 10 µm are the ones that contribute to the 7 and 28 days strengths. Particles between 10 to 45 µm are ones that slowly react between 28 days and about one year, while particles above 45 microns are considered as inert. Fly ash with small particle size increases ultimate strength as well as rate of strength gain of fly ash cement mortar (Chai.J., et al.,1999). Very fine fly ash could be used effectively for reducing the expansion and improving sulfate resistance of mortar (Theerawat S., et al., 2006).

Laser particle size analysis reveals that in the finer fraction of fly ash less than 90% particles are less than 10 µm and it has better prospect of utilization in self compacting concrete as well as fly ash cement mortar. Low permeability and presence of dominant fine particles in characterized fly ash makes it suitable for use in filling application and hearting material in case of dam. Laboratory studies have shown that alkaline fly ash was chemically equivalent to approximately 20% of reagent grade $CaCO_3$ in increasing soil pH and supplying Ca to the plants (Phungs et al., 1979). Nashik fly ash is alkaline and it can be utilized in agricultural application. Of course it is kept in mind that addition of unweathered (Electrostatic precipitator ash) fly ash is not advisable as it may substantially increase the soil salinity. Khan A. A., et al., (2007) reported that 20% amendment of fly ash to soil is found to be better for the growth and yield of potato, onion and garlic crops. Fly ash is also useful for stabilization of organic or peat soil. Usage of coal ash for wasteland development improves the soil fertility, enhances the plant growth, increases the crop yield and saves irrigation water without affecting the food quality (Fly Ash Mission, India). Fly ash with some amendment with local available soil can be effective as liner for landfill site. Even Sachdev et al., (1983) investigated the utilization of fly ash as liner and they aimed for hydraulic conductivity of 10^{-5} cm/sec. With this value the fly ash used in present investigation is suitable as liner (with % wise addition) for landfill.

4.12 CONCLUDING REMARKS

In the present study all the studied fly ash samples are classified as Sialic-High Acid (S-HA)-Inert and as per ASTM C 618-99, it is classified as Class F fly ash. Low Ca ash produces either neutral or mildly acidic leachate pH, which is a matter of environmental concern. Presence of low Ca makes it susceptible to land disposal and reduces its chances of utilization in construction or cement production.All the fly ash samples were comprised mainly of amorphous alumino-silicates spheres and a smaller amount of iron rich spheres. The major elemental concentrations, as determined by EDAX, were consistent with X-ray diffraction data. Scanning electron micrographic study confirms the presence of spherical particles, cenosphers, plerosphers, potato shape, irregular, holey (clinker like) particles, platy particles, and broken sphere. Atomic force microscopy gives surface roughness and particle size in nano scale,and also number of grains are displayed directly, which can be helpful for analysis of surface morphology.

Laser particle size analyzer disclose that more than 90% particles are in the range of 0.1 μm-40 μm, 0.1μm-30μm, 0.1μm-65μm and 0.1μm-10μm for Bhatinda fly ash (BFA), Dadri fly ash(DFA), Nashik fly ash (NFA) and Suratgarh fly ash (SFA) respectively and it is also confirmed with scanning electron micrographic observations. Environmental problem may arise due to finely dispersed crystalline silica and possible high concentrations of certain lithophile trace elements in glass and silicates, which could be slightly mobile under alkaline environment during storage or processing of such combustion residues. Predominantly silt size particles have potential to become airborne in certain conditions. With the particle size analysis, it can be concluded that it is suitable as filling material.

CHAPTER 5

CASCADE LEACHING TEST ON FLY ASH

5.1 PREAMBLE

To assess the environmental risk associated with the utilization of fly ash or wet disposal, it is necessary to study the leachable or extractable fraction of fly ash under field condition. Various leaching tests have been used by researchers for the study of leaching characteristics of fly ash. In India as such there is no leaching protocol available like USA and European countries. In the prediction of environmental impacts, the leaching characteristics of fly ash in aqueous and weakly acidic solutions are most important although many leaching tests use more aggressive leaching media than those which occur in a natural environment. Van der Sloot (1984) manifested that one of the effective means of assessing leaching behavior by combining tests related to time, L/S ratio (Liquid to Solid ratio) and release of metals at different pH condition. Fly ash is disposed in ash pond by mixing it with water by making slurry at L/S ratio 3.5 or 10 (Sear, L. K. A. 2001) or even at 20 (Mukherjee, A. B. et al., 2006) depending upon availability of water. When water percolates through ash pond, cumulative leaching occurs in a cascade manner (Singh, D. N., et al., 2001). To simulate recurrent flushing by rainwater at ash pond cascade leaching test is employed in this research work. Leaching potential of selected constituents from the four fly ash samples i.e. collected from four power plants has been determined by performing the cascade leaching tests. Leachate concentrations obtained through cascade leaching test are used for quantitative estimation of pollution likely to occur due to wet disposal of fly ash. Post leached samples were also subjected to SEM analysis to investigate the changes occurred in surface morphology of fly ash due to leaching.

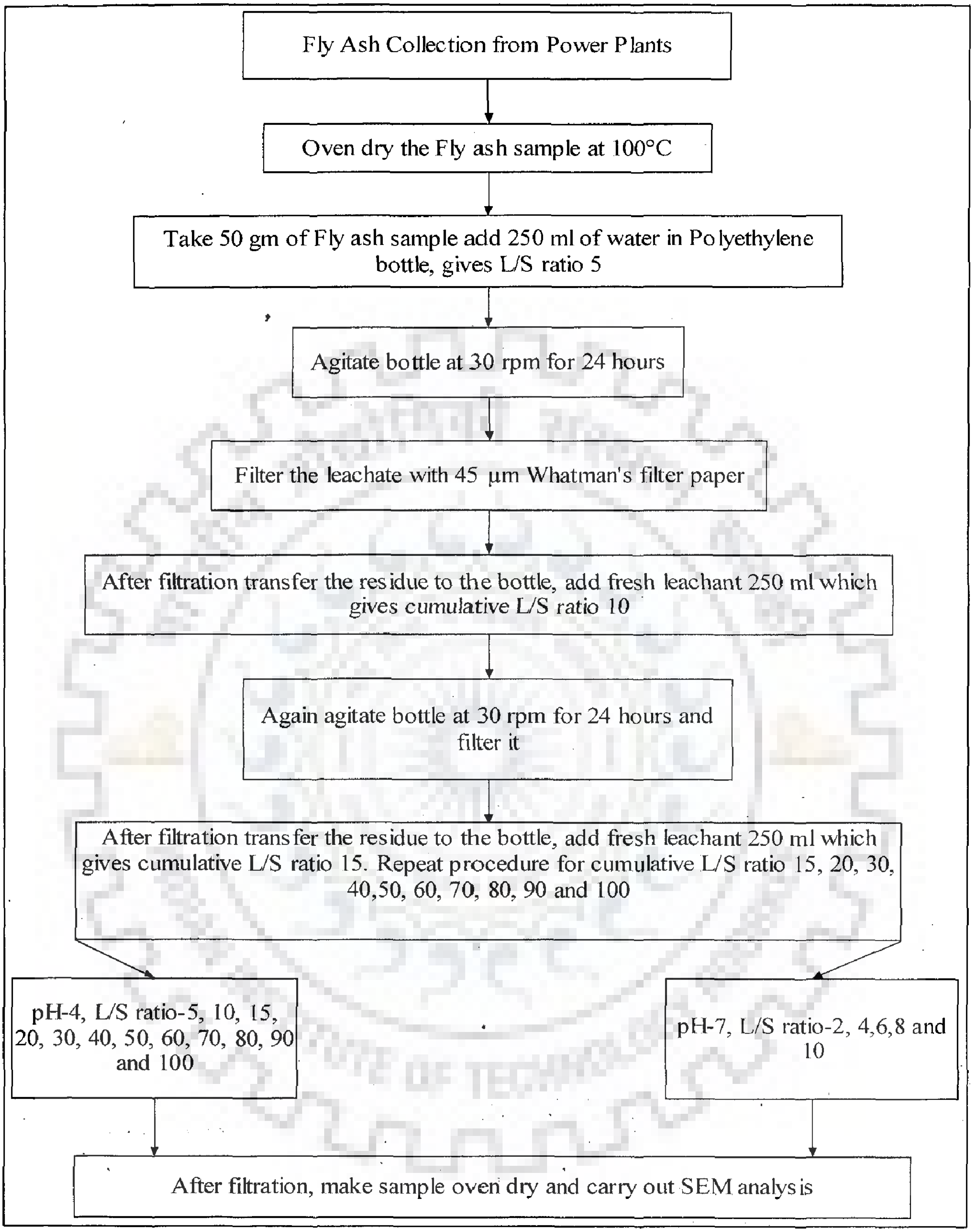


Figure: 5.1 Flow chart of Cascade leaching test for fly ash

5.3.1 Characterization of Leachates for pH, TDS and Electrical conductivity

One of the major leaching effects in an aqueous environment is the acid-base properties of fly ash. The pH value of the leachate is important for the environment and also for the dissolution of the fly ash matrix. Investigation carried out by Killingley et al., (2000) elucidated that the pH of ash water system depends on the balance between the concentrations of alkaline earth elements such as Ca and Mg in the ashes and the proportion of potentially acid generating SO_3 on the other hand. Figure 5.3 presents the pH change patterns for Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash when ash was added to the aqueous solution and equilibrium is reached. The pH of leachate were observed in the range of (7.3-7.0), (7.1-7.1), (9.2-8.7) and (8.2-7.27) for Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash respectively. This result reflects that pH of leachates are slightly acidic to neutral and alkaline for Bhatinda fly ash, Dadri fly ash and Suratgarh fly ash. For Nashik fly ash leachate pH (9.2-8.7), is alkaline in nature which is beyond the prescribed limit for drinking water and industrial effluent or leachates. Oxides on ash surfaces supply hydroxyl ions responsible for the elevated pH. Increase in pH for Nashik fly ash has been attributed to concurrent hydrolytic reaction of calcium, magnesium, potassium and sodium (Talbot, R. B., et al., 1978). The surface coating of amorphous iron oxide is particularly plays major role in aqueous media in deciding acidic component aqueous phase (Theis,T. L.,et al.,1977). Due to release of iron in leachate, pH of leachate decreases, which is also observed through the respective concentration of Fe in leachate for Bhatinda fly ash, Dadri fly ash and Suratgarh fly ash whereas the concentration of Fe in Nashik fly ash leachate is less, that is why it has produced alkaline leachate.

Total Dissolved Solids (TDS mg/lit) and Electrical conductivity (EC µs/cm) in general shows initial high value to lower value at later stage as leaching progresses and cumulative L/S ratio increases which is presented in Figure 5.4 and Fig. 5.5. Gradual decrease of TDS and EC indicates the fly ash with high capacity for leaching soluble salts as L/S ratio increases. The TDS and EC values are high at early stage due to dissolution of elements and when L/S ratio is increased TDS and EC values are decreased via dilution.

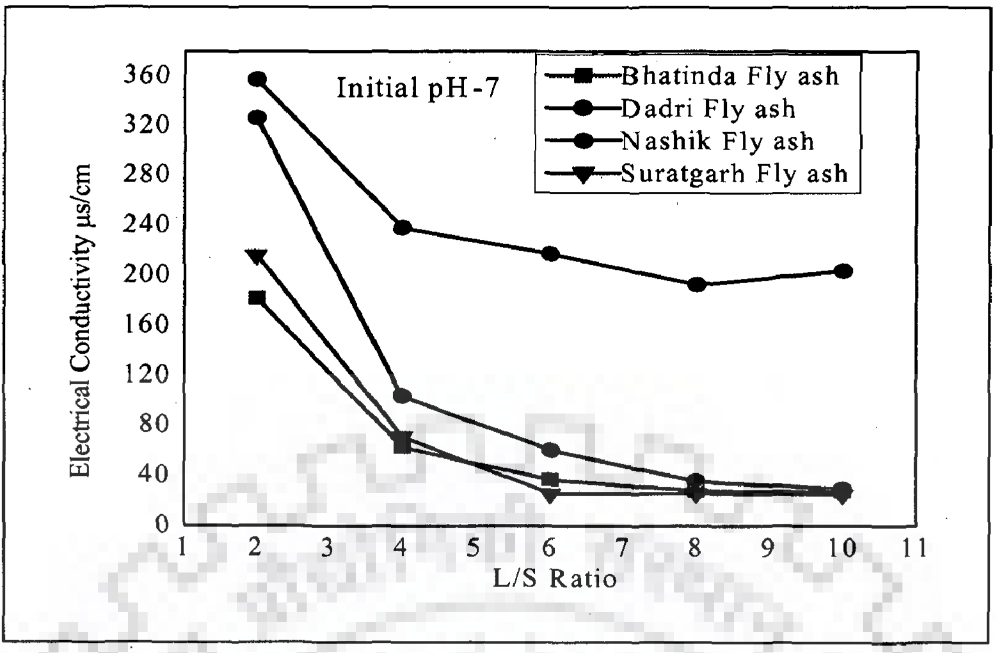


Figure 5.5 Variation of EC of leachate as a function of L/S ratio at Initial pH-7

5.3.2 Release of metals as a function of liquid to solid ratio at pH=7

Results of metals leached through cascade leaching test are given in Table 5.1 for Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash. The corresponding variation of the cumulative percentage leached with respect to L/S ratio for Bhatinda fly ash, Dadri fly ash, Nashik fly ash and Suratgarh fly ash are presented in Figure 5.6, Figure 5.7, Figure 5.8 and Figure 5.9 respectively. In general high concentrations are leached for Bhatinda fly ash, Dadri fly ash, Suratgarh fly ash compared to Nashik fly ash. Iron is distributed on the surface as well as within the matrix of aluminosilicate phases of fly ash (Henry and Knapp, 1980; Hulett et al., 1980; Hansen et al., 1984). According to Theis, T. L., et al., (1979) the range of surface concentration of trace metals on fly ash are: Cd- <2-58% of total, Cu- 25-75 % of total, Ni- 5-42% of total, Zn- 10-70% of total. Dissolution of major elemental components of fly ash begins immediately after the water contact. In the present study it is found that the Fe is released 0.03%, 0.037% and 0.029% for Bhatinda fly ash, Dadri fly ash, Suratgarh fly ash compared to Nashik fly ash which is only 0.007%. High concentrations of Fe indicate that it is one of the major elements and this is consistent with the results obtained by Van

Table 5.1 Metal concentrations leached through cascade leaching test at pH = 7

Metal	Cum.L/S ratio	Bhatinda Fly ash	Dadri Fly ash	Nashik Fly ash	Suratgarh Fly ash
Fe mg/l	2	0.8	1.1691	0.098	0.7191
	4	0.22	0.7109	0.091	0.595
	6	0.21	0.1661	0.07	0.26
	8	0.19	0.123	0.05	0.25
	10	0.18	0.12	0.01	0.19
Mn µg/l	2	58.2	42	8.4	42.3
	4	37.2	30	7.9	39.6
	6	19.2	28.5	5.3	30
	8	18.8	21	3	26.4
	10	17.3	10	2.5	23.4
Zn µg/l	2	43.7	51.4	45.1	38.5
	4	43	30.1	3.6	30.9
	6	30.4	28.5	2	6.4
	8	9	27.3	1.8	5
	10	7.4	8.7	1.4	2.1
Cd µg/l	2	9	5.4	4.5	6.2
	4	4	4.3	3.6	6
	6	3.8	4	2.9	4.1
	8	2.3	3.5	1.9	3.6
	10	2	1.9	1.5	3.4
Cu µg/l	2	9.4	35	10.2	30
	4	Bdl	9.9	Bdl	Bdl
	6	Bdl	Bdl	Bdl	Bdl
	8	Bdl	Bdl	Bdl	Bdl
	10	Bdl	Bdl	Bdl	Bdl
Ni µg/l	2	19.2	56	36.7	25
	4	10	24	Bdl	10
	6	Bdl	Bdl	Bdl	Bdl
	8	Bdl	Bdl	Bdl	Bdl
	10	Bdl	Bdl	Bdl	Bdl

Bdl- Below detection limit

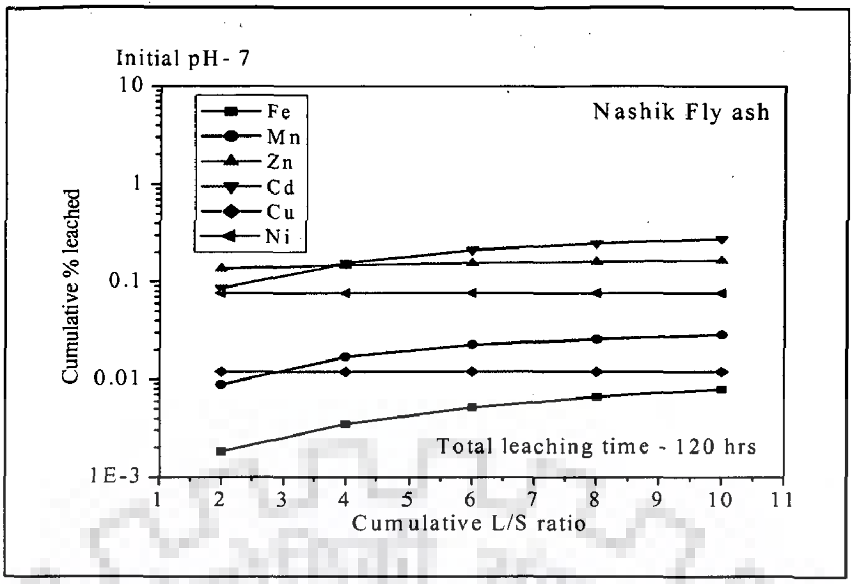


Figure 5.8 Cumulative percentage leached from Nashik fly ash as a function of L/S ratio at pH-7

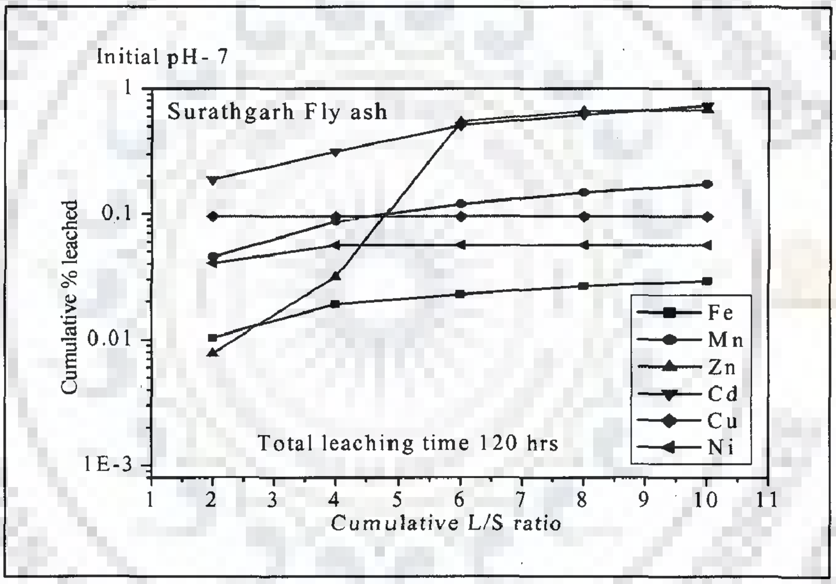


Figure 5.9 Cumulative percentage leached from Suratgarh fly ash as a function of L/S ratio at pH-7

5.4. CASCADE LEACHING TEST AT INITIAL pH-4

Rainwater is slightly acidic because atmospheric carbon dioxide dissolves in water to form carbonic acid. Natural emissions of sulfur and nitrogen compounds further affect the pH of rainfall and lowest value of pH-5 is commonly found for rainfall in areas not polluted by man-made emissions. Extraction at pH - 4 is assumed to represent the lowest natural pH (The Institution of Engineering and Technology fact file, 2006).

5.4.1 Leachate pH, TDS and electrical conductivity

As described in the previous sections, leachate pH, TDS and Electrical Conductivity for all the four power plant fly ash have been determined at pH- 4. The variation of pH of leachate with cumulative L/S ratio is presented in Figure 5.11. The variation of EC and TDS with respect to cumulative L/S ratio are shown in Figure 5.12 and Figure 5.13 respectively

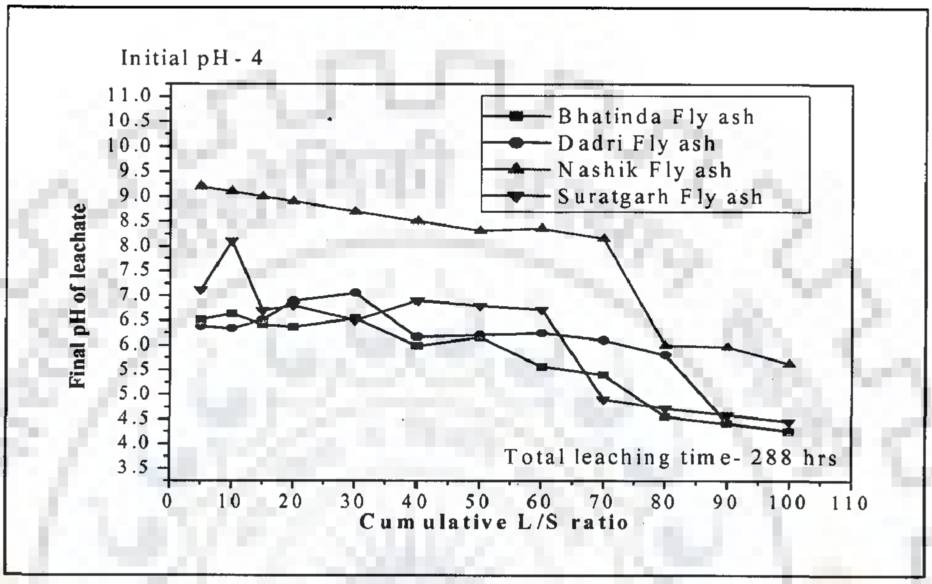


Fig. 5.11: Variation of pH as a function of L/S ratio at pH-4

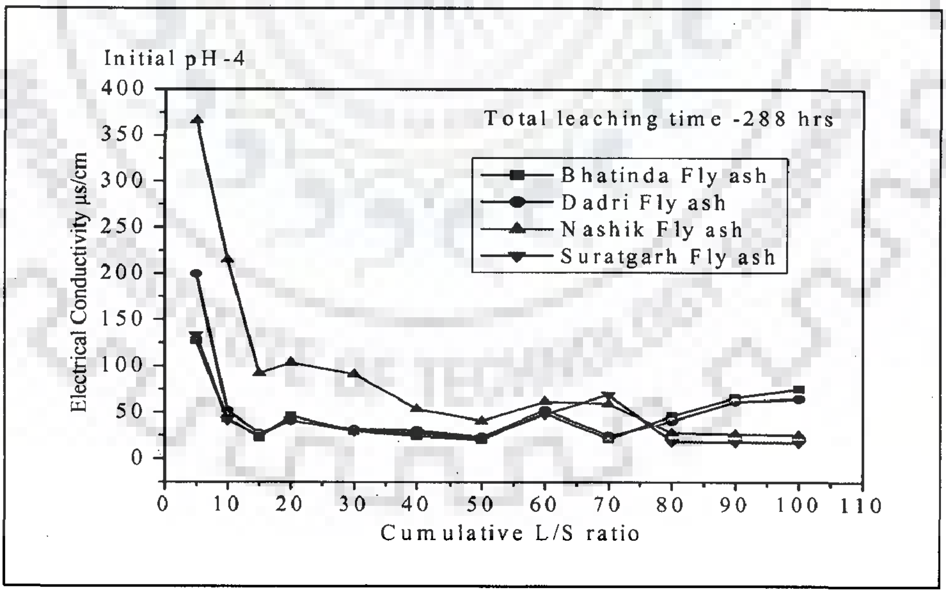


Fig. 5.12 Variation of EC of leachate as a function of L/S ratio at pH-4

Table 5.2 Metal concentrations leached through cascade leaching test in Bhatinda fly ash at pH – 4

Cum L/S ratio	Fe	Mn μg/l	Zn μg/l	Cd μg/l	Cu μg/l	Ni μg/l
5	0.7034	68.2	62	5.3	24.2	68
10	0.4744	51.9	32	4.5	17.8	15.1
15	0.3382	35.8	22	4	17.5	14.9
20	0.2573	34.9	21.2	3.9	13.7	12.3
30	0.2368	24.8	19	3.7	11.1	12
40	0.1706	20.8	17	3.5	4.8	11.2
50	0.166	20.4	15	3.1	3.8	11
60	0.126	17.3	12	3	2.3	10.4
70	0.1023	14.8	10	2.9	2	9.8
80	0.0852	12.8	9.3	2.8	1.9	7.4
90	0.0774	5.5	7.9	2.2	1.3	5.4
100	0.0453	4.4	2.7	1.8	1.2	1.8

Table 5.3 Metal concentrations leached through cascade leaching test in Dadri fly ash at pH - 4

Cum L/S ratio	Fe mg/l	Mn μg/l	Zn μg/l	Cd μg/l	Cu μg/l	Ni μg/l
5	0.761	42	82	7	27.7	78
10	0.3432	35	72	6.3	19.6	69
15	0.1938	27	52	4	10.8	27.2
20	0.1539	20.9	39	3.1	6.5	22
30	0.1501	12.2	34	3	5.5	18.5
40	0.1341	7.2	29	1.9	5.3	10.2
50	0.1309	7.1	14.2	1.5	5	8.3
60	0.1109	4.9	9.2	1.4	4.5	5.2
70	0.1036	4.2	7.3	1.3	3.9	4.4
80	0.0819	3.8	6.3	1.2	3.1	4
90	0.0795	3.2	3	1.1	2.5	3.6
100	0.0788	1.1	2	1	2	1.3

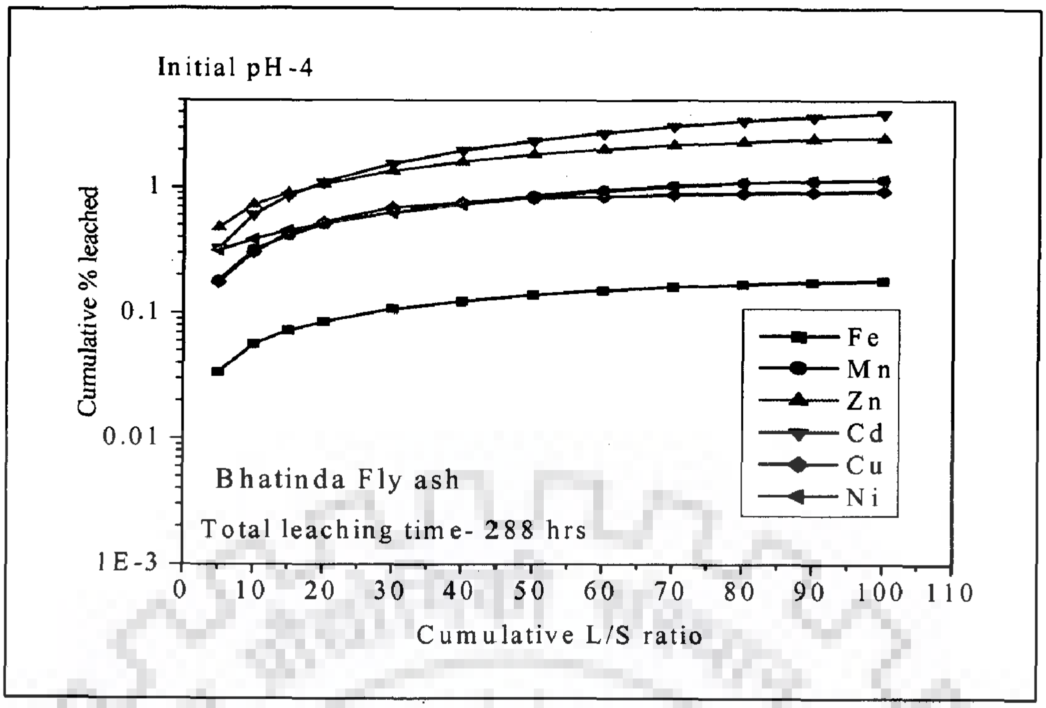


Figure 5.14 Cumulative percentage leached from Bhatinda fly ash as a function of L/S ratio at pH-4

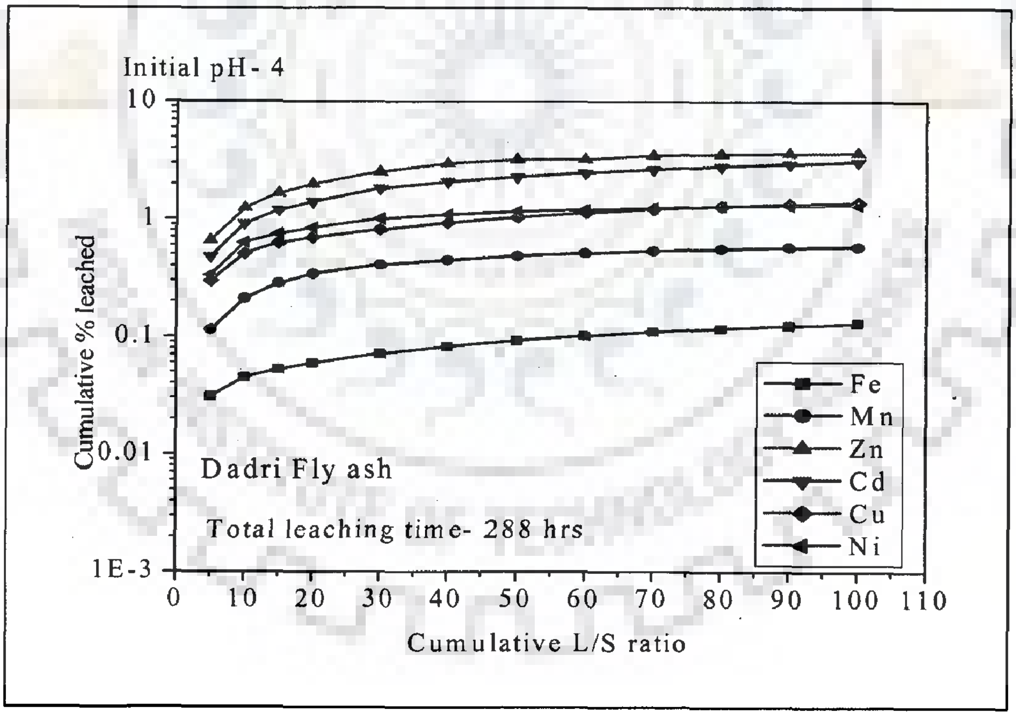


Figure 5.15 Cumulative percentage leached from Dadri fly ash as a function of L/S ratio at pH-4

5.5 RELEASE OF METALS IN FLY ASH TRANSPORT WATER

Depending on the availability of water, generally L/S ratio of 10 is adopted for slurry disposal of fly ash. With this view, the quantity of heavy metals leached or released (in mg/kg) in fly ash transport water are given in Table 5.6

Table 5.6 Release of heavy metals in fly ash transport water (mg/kg)

Metals	Initial pH	Bhatinda Fly ash	Dadri Fly ash	Nashik Fly ash	Suratgarh Fly ash
Fe	4	5.9	5.52	0.7	3.4
	7	3.1	4.57	0.638	4.04
Mn	4	0.37	0.38	0.13	0.38
	7	0.3	0.26	0.054	0.32
Zn	4	0.47	0.77	0.27	0.61
	7	0.26	0.29	0.107	0.16
Cd	4	0.049	0.066	0.06	0.085
	7	0.04	0.038	0.028	0.046
Cu	4	0.21	0.23	0.027	0.032
	7	0.01	0.08	0.007	0.06
Ni	4	0.4	0.735	0.17	0.39
	7	0.08	0.16	0.073	0.07

The results obtained with cascade leaching test suggest that, it has several implications regarding the water quality aspects of wet disposal of fly ash. The acidic solution becomes neutral with time, trace metals will not remain in solution due to shifting of solubility controls. Thus the ash that produces acidic leachate would be more toxic to the aquatic ecosystem when initially disposed to the ash ponds. When potential pollutant reach to its steady state conditions in the ash pond, which gives rise to longer residence times in the ash pond effluent. When such effluent joins the river, aquatic ecosystem is disturbed. Often ash pond effluent is used for irrigation or is disposed on land, which is harmful to plant establishment or to the animals consuming the plants grown on such soil. It ultimately increases the cycling of potentially toxic trace metals through food chain.

Nashik and Suratgarh power plant dumped 1.75 x 10^8 kg, 7.05 x 10^8 kg, 1.117 x 10^9 kg and 9.23 x 10^8 kg of ash on the ash pond respectively, by wet disposal method. With the values of disposed ash quantity (in kg) and elements leached on dry ash basis (in mg/kg: obtained through cascade leaching test), it is possible to estimate the pollution likely to occur due to leaching of elements at ash pond site. The environmental pollution details under neutral environment and pH- 4.conditions are given in Table 5.8 and Table 5.9 respectively.

Table 5.8: Estimation of pollution on (dry basis) at ash pond for the power plants in neutral environment

Metal	Unit	Bhatinda Fly ash	Dadri Fly ash	Nashik Fly ash	Suratgarh Fly ash
Fe	mg/kg	3.1	4.57	0.638	4.04
	ton	0.542	3.22	0.71	3.728
Mn	mg/kg	0.3016	0.263	0.054	0.32
	ton	0.0527	0.185	0.06	0.298
Zn	mg/kg	0.26	0.292	0.107	0.16
	ton	0.0467	0.205	0.12	0.147
Cd	mg/kg	0.04	0.038	0.028	0.046
	ton	0.0065	0.0269	0.0312	0.043
Cu	mg/kg	0.01	0.08	0.007	0.06
	ton	0.00329	0.0633	0.0227	0.0553
Ni	mg/kg	0.08	0.16	0.07	0.39
	ton	0.014	0.112	0.0819	0.064

Table 5.9: Estimation of pollution on (dry basis) at ash pond for respective power plants at initial pH- 4

Metal	Unit	Bhatinda Fly ash	Dadri Fly ash	Nashik Fly ash	Suratgarh Fly ash
Fe	mg/kg	5.9	5.52	0.7	3.4
	ton	1.032	3.89	1.56	3.13
Mn	mg/kg	0.37	0.38	0.13	0.38
	ton	0.063	0.444	0.145	0.341
Zn	mg/kg	0.47	0.77	0.27	0.61
	ton	0.087	0.239	0.234	0.35
Cd	mg/kg	0.049	0.046	0.06	0.085
	ton	0.00857	0.23	0.027	0.0784
Cu	mg/kg	0.08	0.23	0.027	0.032
	ton	0.013	0.051	0.022	0.1052
Ni	mg/kg	0.4	0.735	0.17	0.357
	ton	0.07	0.518	0.189	0.329

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Cu	mg/kg	0.01	0.08	0.007	0.06
	ton	0.00329	0.0633	0.0227	0.0553
Ni	mg/kg	0.08	0.16	0.07	0.39
	ton	0.014	0.112	0.0819	0.064

Table 5.9: Estimation of pollution on (dry basis) at ash pond for respective power plants at initial pH- 4

Metal	Unit	Bhatinda Fly ash	Dadri Fly ash	Nashik Fly ash	Suratgarh Fly ash
Fe	mg/kg	5.9	5.52	0.7	3.4
	ton	1.032	3.89	1.56	3.13
Mn	mg/kg	0.37	0.38	0.13	0.38
	ton	0.063	0.444	0.145	0.341
Zn	mg/kg	0.47	0.77	0.27	0.61
	ton	0.087	0.239	0.234	0.35
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	ton	0.00857	0.23	0.027	0.0784
Cu	mg/kg	0.08	0.23	0.027	0.032
	ton	0.013	0.051	0.022	0.1052
Ni	mg/kg	0.4	0.735	0.17	0.357
	ton	0.07	0.518	0.189	0.329

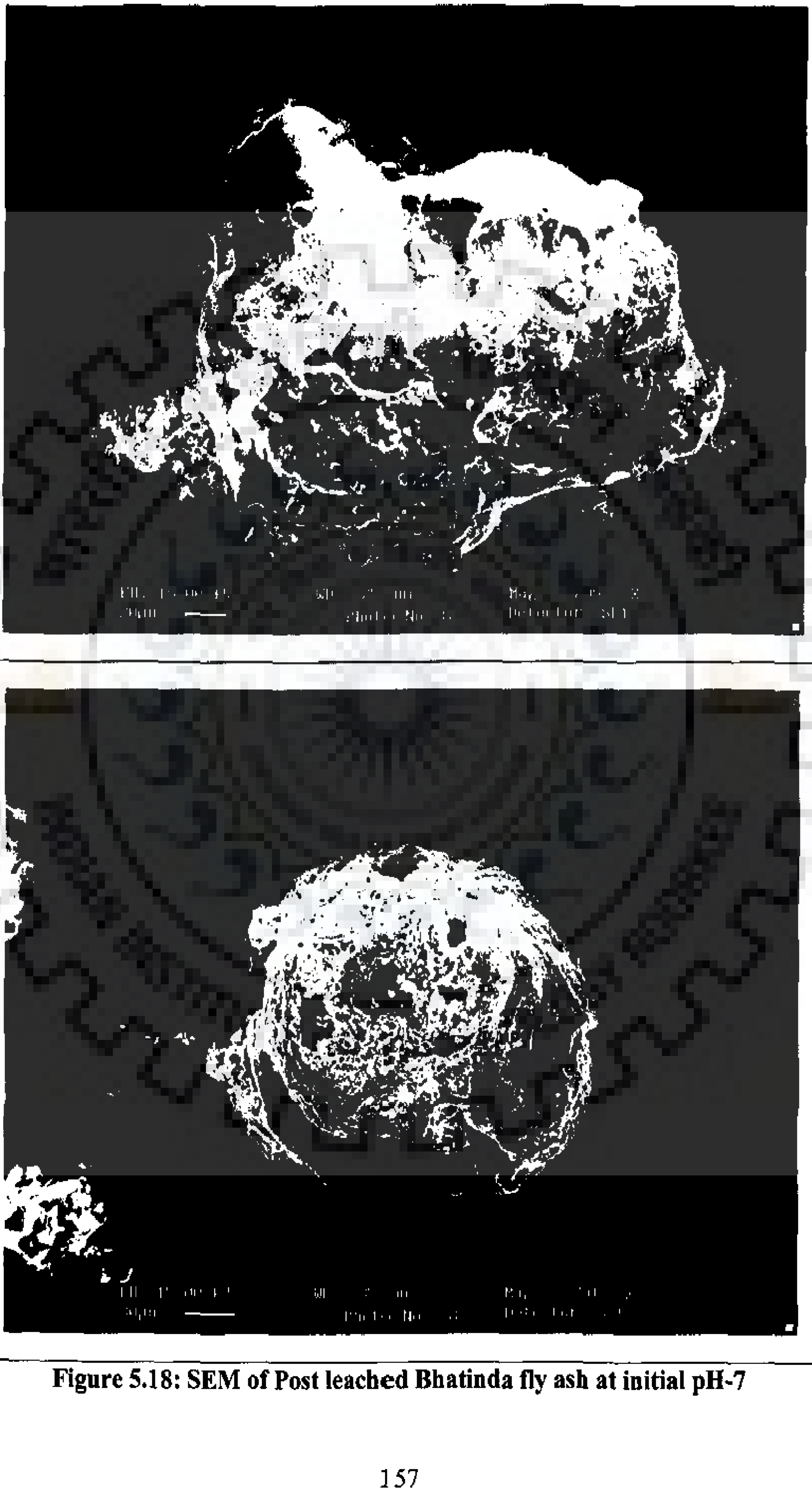

Figure 5.18: SEM of Post leached Bhatinda fly ash at initial pH-7

Figure 5.19: SEM of Post leached Dadri fly ash at initial pH-7

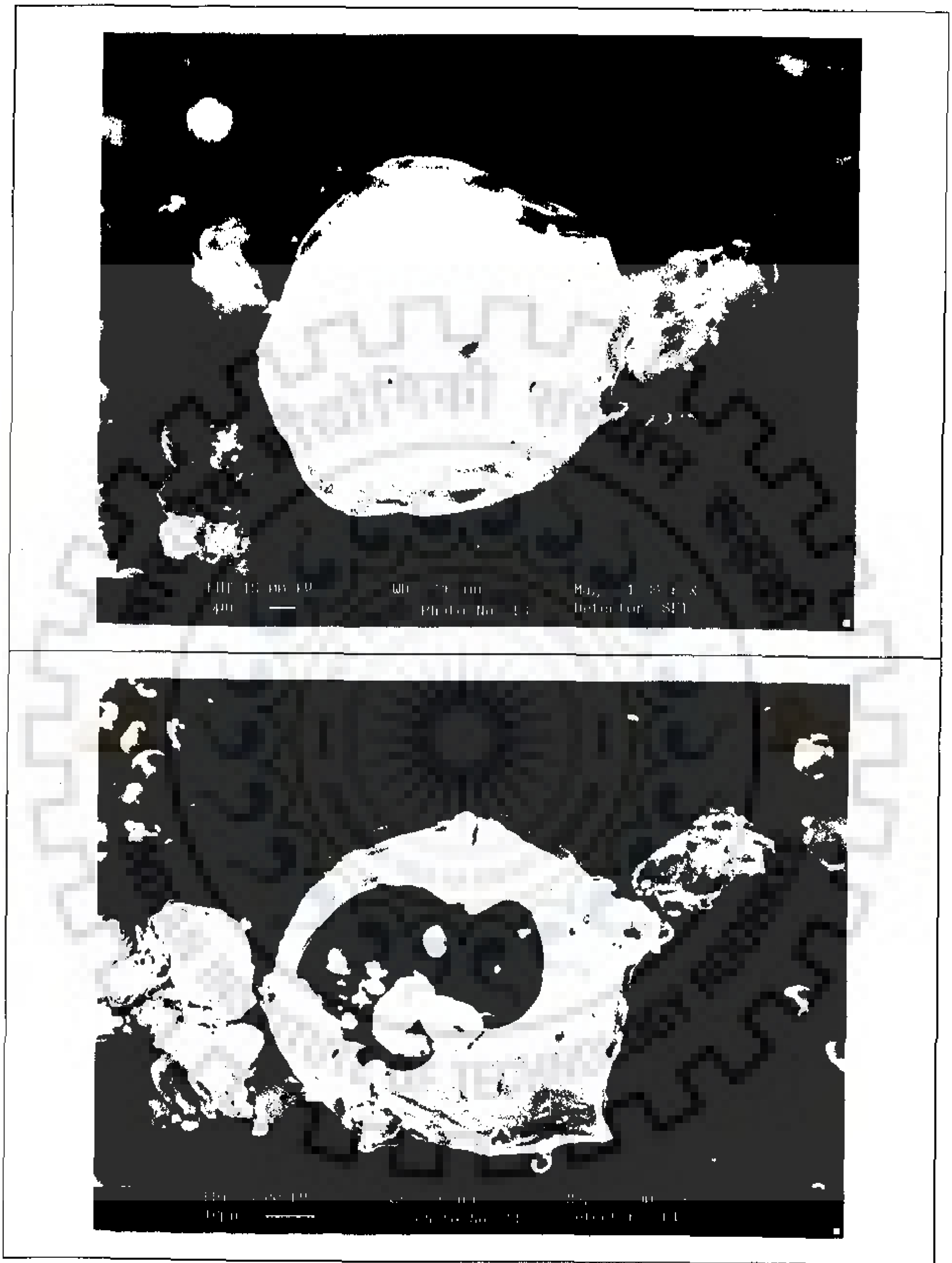

Figure 5.20: SEM of Post leached Nashik fly ash at initial pH-7

Figure 5.21:SEM of Post leached Suratgarh fly ash at initial pH-7

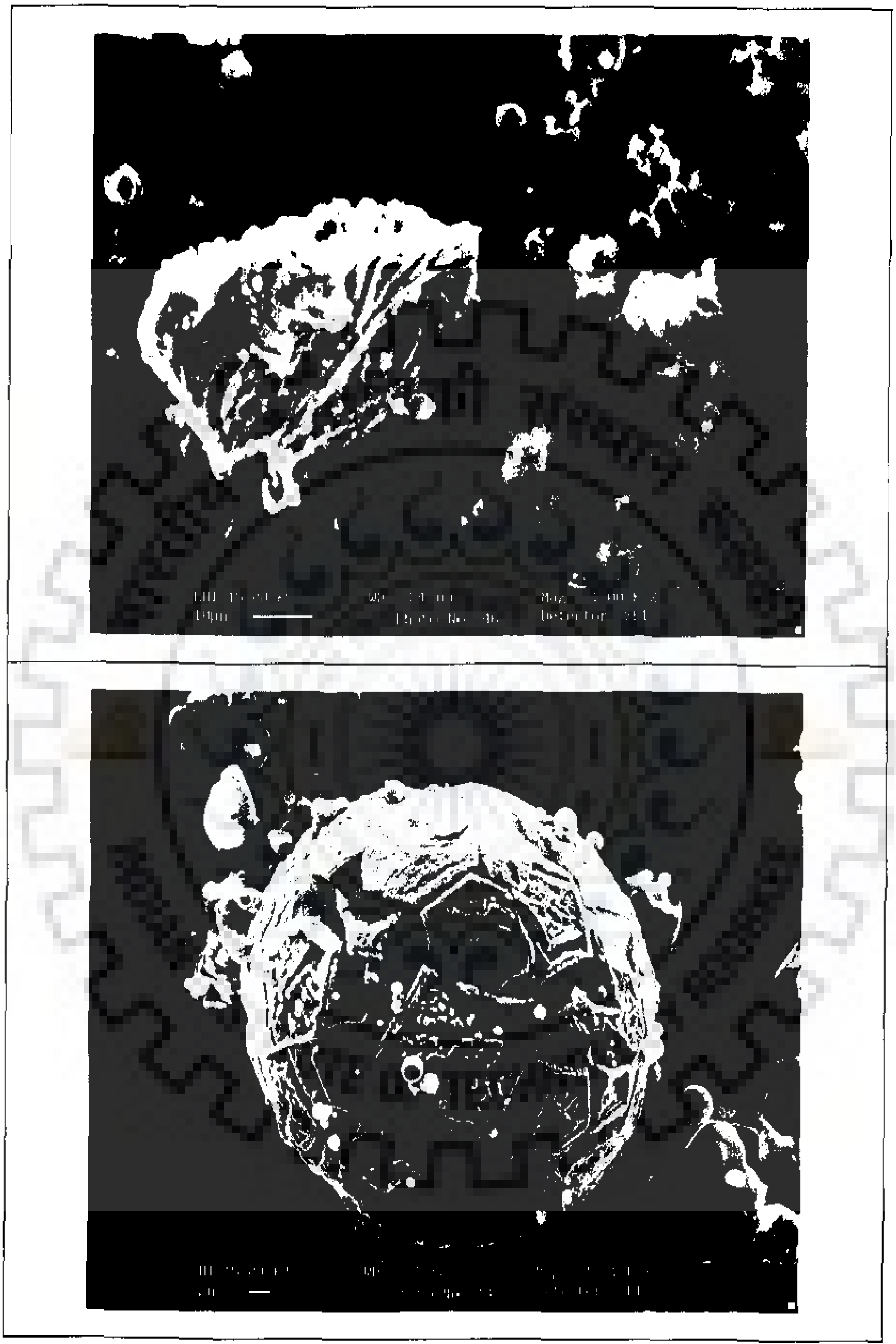

Figure 5.22: SEM of Post leached Bhatinda fly ash at initial pH- 4

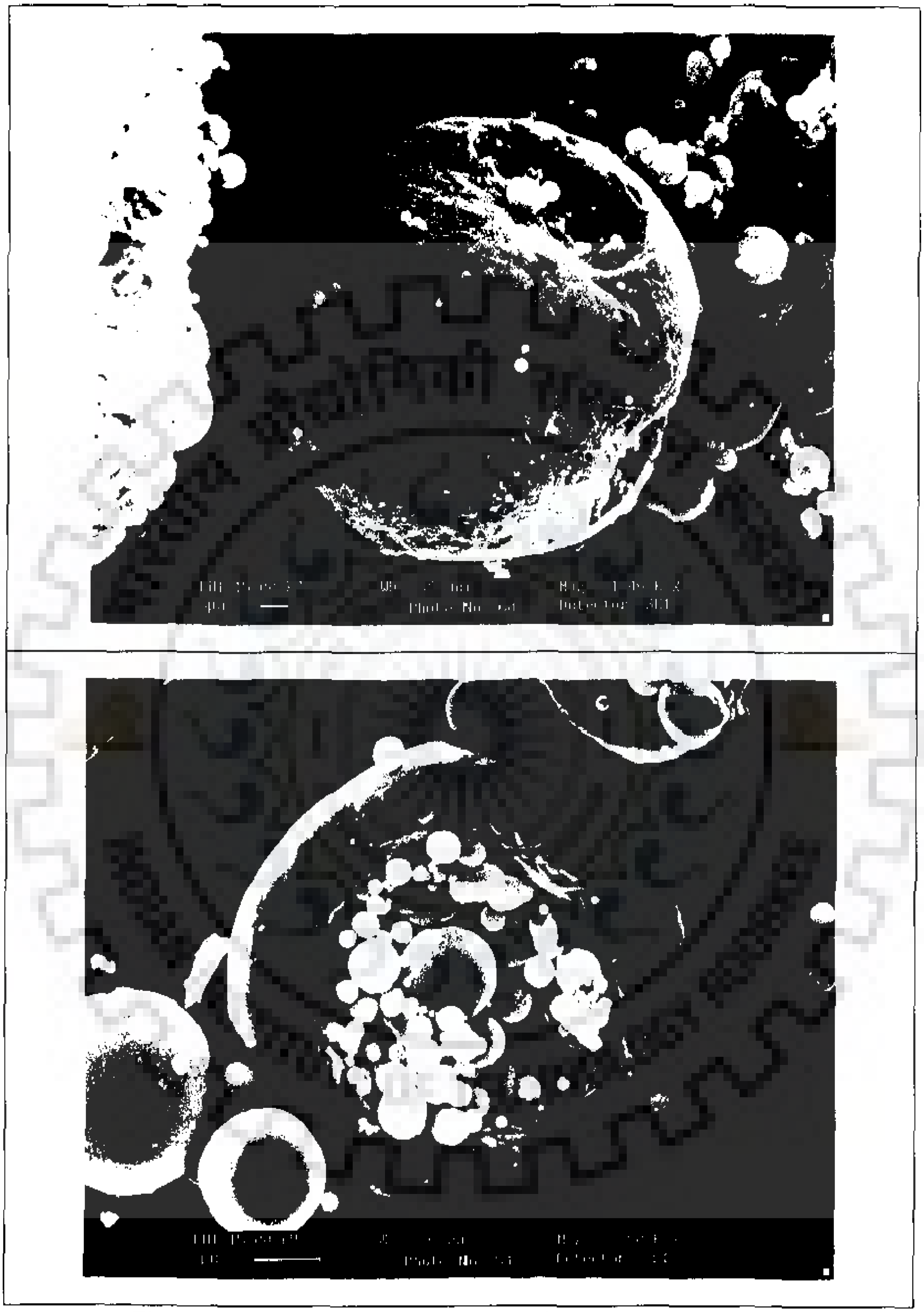

Figure 5.23: SEM of Post leached Dadri fly ash at initial pH- 4

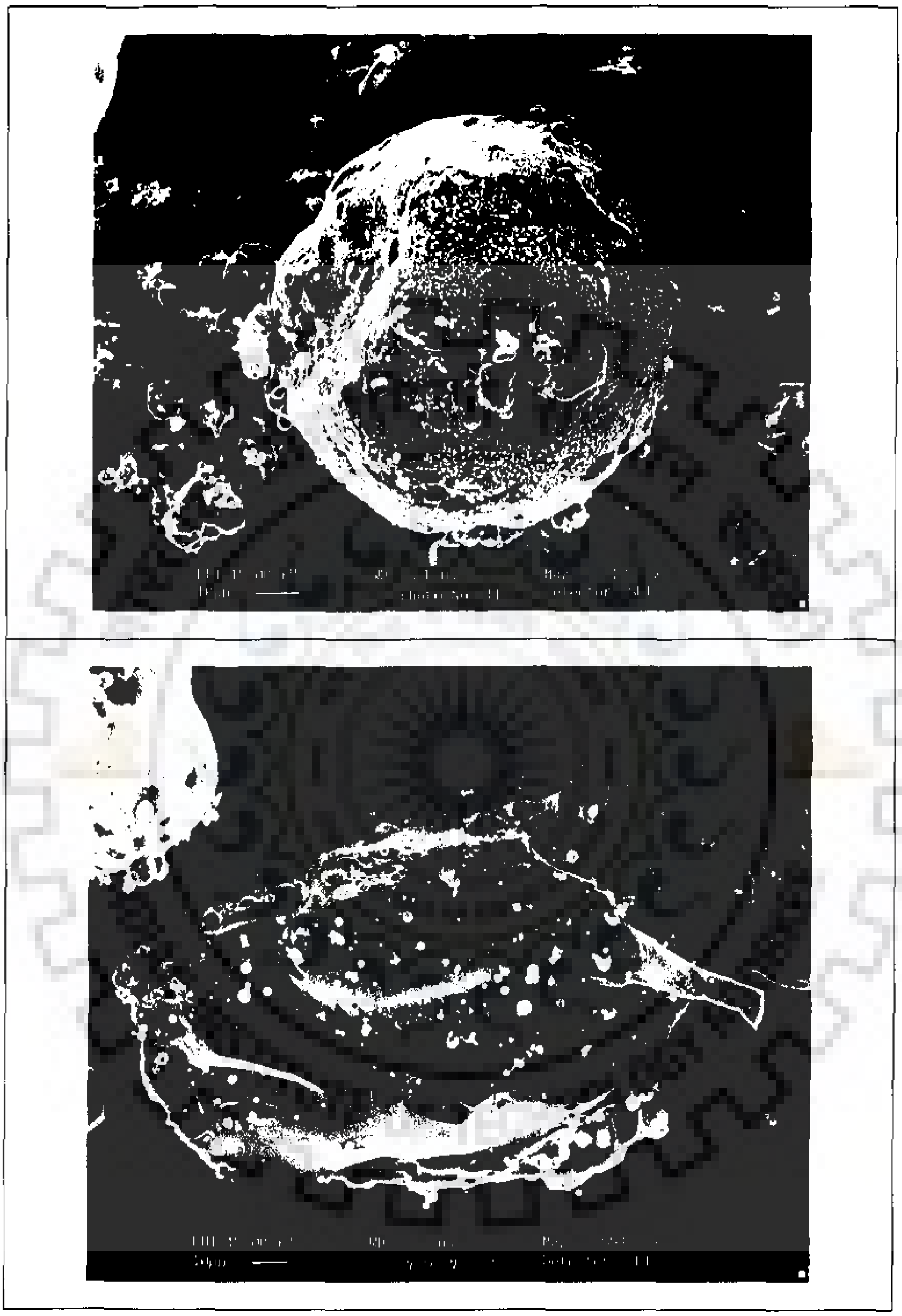

Figure 5.24: SEM of Post leached Nashik fly ash at initial pH-4

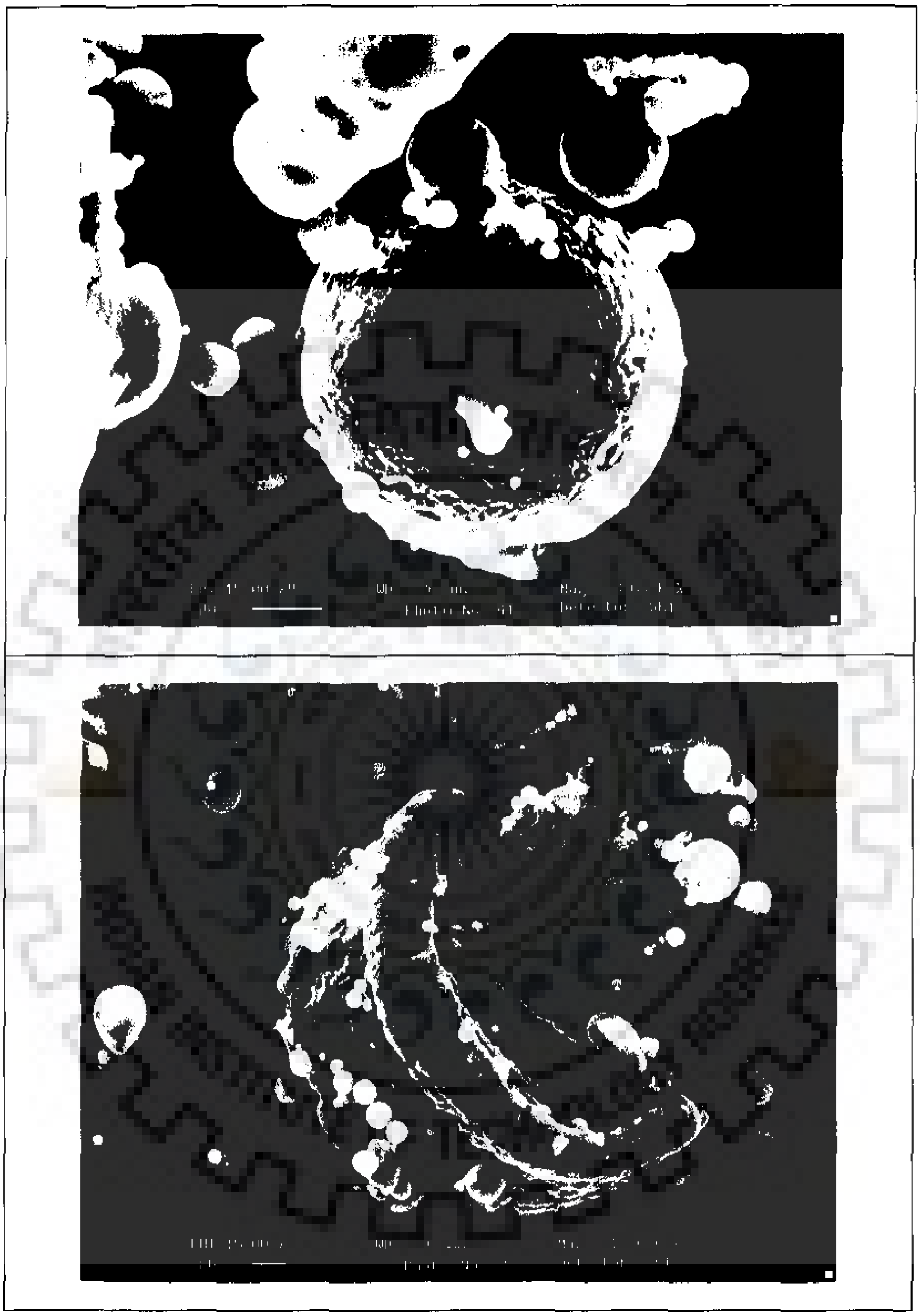

Figure 5.25: SEM of Post leached Suratgarh fly ash at initial pH- 4

5.9 CONCLUDING REMARKS

The cascade leaching test carried out in the present study truly represents natural leaching of ash in the ash pond or leaching of metals in fly ash transport water. The leaching trend observed was initial high concentration and decreasing to lower level. As the L/S ratio increases concentrations are decreased via dilution. The pH is the master variable which controls the mobility of metals or the leaching of metals. Among metals studied Cd is most easily water extractable element and this may pose problem in aquatic environment. Compared to neutral environment with acidified water good amount of metals are extracted. Cu and Ni show lowest mobility in neutral environment. Data obtained through cascade leaching test are closely matching with ash slurry water concentrations. In long term perspective leaching of iron is going to pose problem to surface water and perhaps groundwater. SEM of post leached samples indicates that surface of fly ash is leached. By observing post leached SEM, the severity of etched surface is more for SEM of acidified water leached ash compared to neutral environment leached ash.

CHAPTER 6

MODELING OF FLY ASH LEACHING

6.1 GENERAL

Whenever fly ash is disposed or deposited on land, leaching of toxic metals causes contamination of surface water as well as groundwater. A thorough understanding of leaching behavior and the transport of potential pollutants from existing fly ash disposal sites is essential for environmental impact assessment and protection. Many researchers have conducted the laboratory batch and column-leaching tests of fly ash from coal fired power plants (Kanungo and Mohapatra, 2000; Fytianos et al., 1998; Mudd et al., 2004; Singh et al., 2007). The purpose of experimental investigations has been to evaluate the leachate quantity, identify the type and concentration of potential contaminants in leachate, and examine the relationships of the residues with surrounding environments. These studies provide boundary input concentrations in the study of solute transport originating from an ash pond besides defining the distribution constant.

This chapter discusses single exponential decay models in vogue and composite exponential decay model. Using laboratory test data, the distribution coefficient has been estimated, and the relation of distribution coefficient with leachate concentration has been established.

6.2 LEACHING OF FLY ASH

Fly ash is a heterogeneous material and its chemical composition depends on the geological origin of coals. Leaching behavior of fly ash depends on the number of factors. The physical factors those influence leaching include particle size, mineralogy, contact time with leachant, flow rate of leachate, temperature during leaching, porosity of solid matrix and hydro-geological conditions (Van der Sloot, et al., 1997) . Apart from physical factors, the chemical factors such as pH of the solvent (water), redox conditions of the material, sorption process, potential leachability of constituents and complexation with inorganic or organic compounds also influence the leaching process. Therefore, it is not easy and practical to develop a methodology based on purely theoretical considerations to predict the long term behavior of leaching of fly ash. A simpler and more practical approach, which can be used to predict the long term leaching behavior without in depth understanding of the mechanism, is to use short term experimental result. The leaching of selected metals (Fe, Mn, Zn, Cd, Cu and Ni) can be ascertained using observed leaching trend from the experimental investigation. The leaching pattern that was observed by various investigators is an initial or early peak concentration of the metal in the leachate followed by an exponential decrease of concentration with time or liquid to solid ratio (L/S) or infiltrated pore volumes. L/S ratio is the most important parameter affecting the leachability of fly ash constituents (Zandi, M., et al., 2007). L/S ratio serves as a surrogate parameter for time. Generally, leaching of fly ash takes place from an ash pond due to infiltration or interflow consequent to a rainfall event. To simulate the field leaching, in the present study laboratory experiments were carried out and it was observed that metal concentrations in leachate decreases with increase in time. Envisaging that a fly ash layer is subjected to leaching during every rainfall event, and consequently the leachate which is generated outflows, and again the remaining fly ash is subjected to leaching at every successive rainfall event, experiments have been conducted at L/S ratio ranging from 2 to 10 using a neutral leachant with pH = 7 and at L/S ratio ranging from 5 to 100 using an acidic leachant having a pH = 4.

Leaching is normally expressed as a leaching rate or as the cumulative fraction leached (Cote and Constable, 1987). One of the main objectives of leaching rate measurements is to be able to predict the long term leaching characteristics of a stabilized waste based on short term measurement and to do this effectively, predictive mathematical models have been used (Bishop, 1986). Some of the mechanisms that have been considered when developing mathematical model for the leaching process are bulk diffusion, and bulk diffusion combined with chemical reactions. Empirical models have also been considered. Each time, a fixed mass of fly ash in consideration is subjected to a number of repetitive cycles of leaching. The schematic diagram of cascade leaching test pertaining to fly ash is given in Figure 6.1.

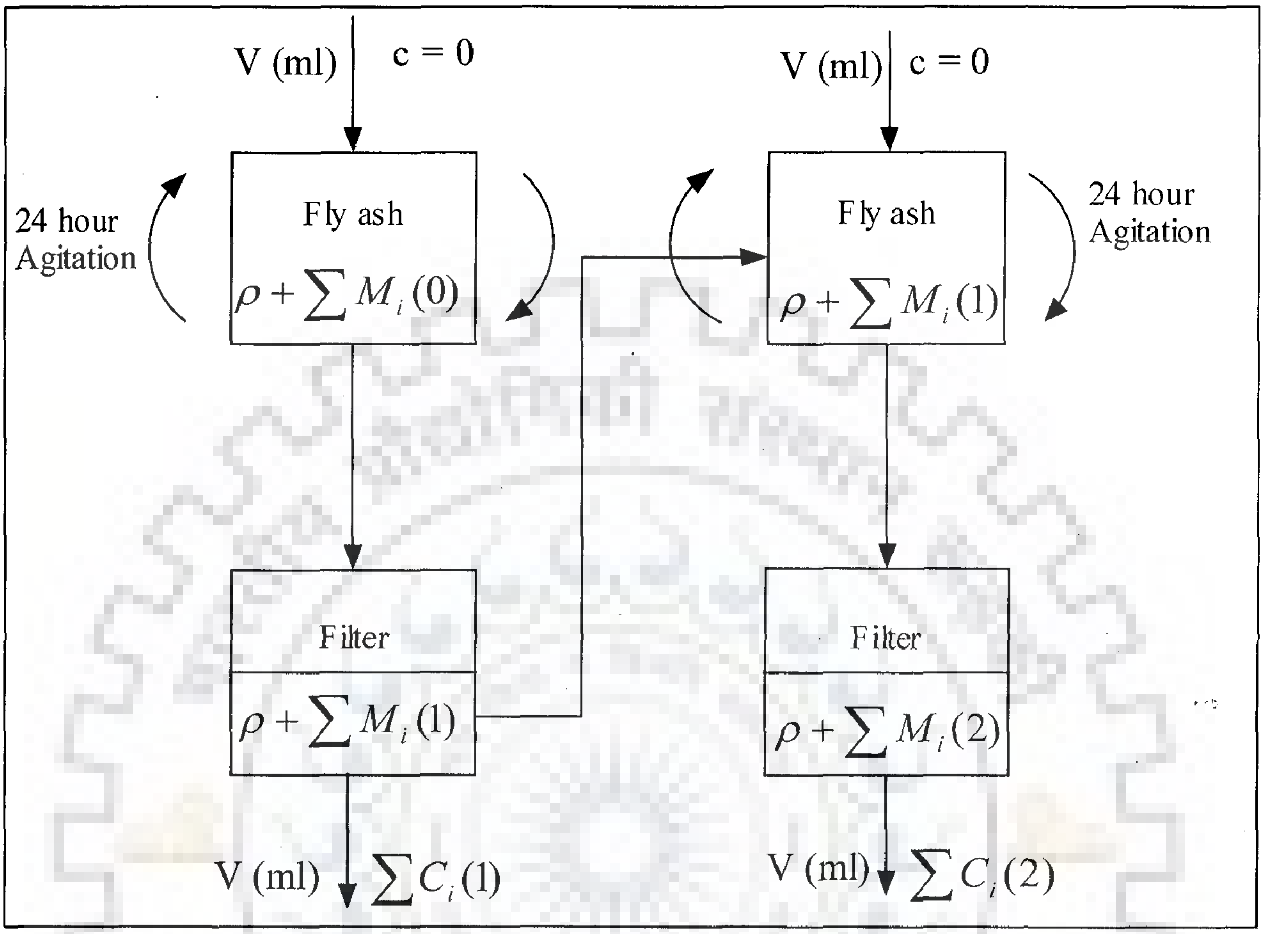

Figure 6.1 Schematic representation of Cascade Leaching test for coal fly ash

Assumptions

The exponential decay model derived by Muñoz (2006) is based on the following assumptions:

1. At each stage of leaching, the input influx volume is constant.
2. Equilibrium of desorption is assumed to reach in 24 hours.
3. The distribution constant is assumed to be a constant and independent of concentration of the element in the leachate.
4. Metal concentrations in leachate decreases exponentially with increase in time or L/S ratio or pore volume.

In the present study, leachate concentration has been derived considering variation in leachant volume during cascade leaching test; (ii) the distribution constant is not an invariant during different stages of leaching; (iii)the concentrations of metals in the influx leachant are below detection limit and are taken as zero (iv) equilibrium of desorption is assumed to reach in 24 hours.

Detailed derivation of the exponential decay model and prediction of metal concentrations are described below.

6.3 EXPONENTIAL LEACHATE CONCENTRATION DECAY MODEL

The behavior of trace metals associated with fly ash has been studied by many researchers. Theis and Wirth (1977) concluded that the mobilization of metal ions from the oxides surface is primarily a desorption phenomenon. Chapelle (1980) used desorption process for modeling the leaching of fly ash in aqueous phase and developed an exponential decay model assuming the rate of decrease in surface concentration of an element to be linearly proportional to the surface concentration of the element. Assuming that the rate of change in the dissolved contaminants is inversely proportional to the time when water flows through the most probable set of paths, Singh, et al., (2007) have developed empirical relations in the form of logarithmic equations for the prediction of trace metals in leachates generated from thermal power plants. Muñoz (2006) has developed a mathematical model relating leachate concentration with leaching stage assuming a constant distribution coefficient. In the present study, the model suggested by Muñoz (2006) has been extended considering variable distribution coefficient (desorption rate constant) and the relation between the distribution coefficient and concentration of the element in the leachate is established. The sequence of leaching in the leachate concentration decay model is as shown in Figure 6.2.

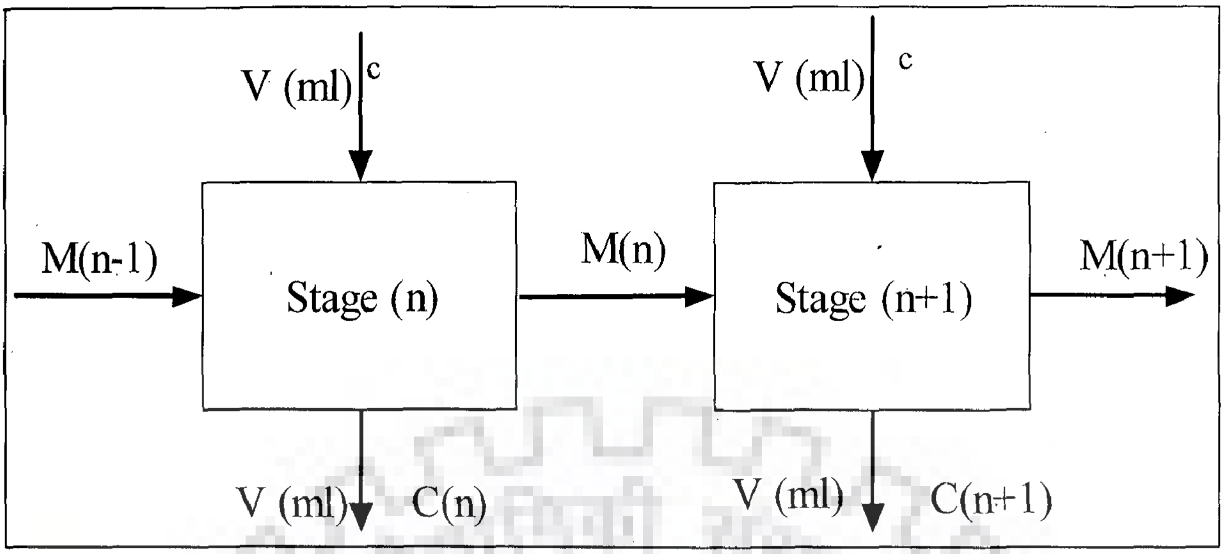

Figure 6.2 Schematic representations of sequence of leaching

Let us perform the mass balance for the i^{th} element during the $(n+1)^{th}$ unit application of influx leachant volume $V\ (ml)$. The concentration of the i^{th} element in the input influx volume is zero or undetectable. Prior to the application of $(n+1)^{th}$ unit influx, the mass of the i^{th} element present in the fly ash is $\rho M_i(n)$. Part of this gets leached to the influx V during 24 hours of agitation resulting in a leachate concentration $C_i(n+1)$, and the remaining unleached part $\rho M_i(n+1)$ remains along with the residual mass ρ. $M_i(n+1)$ is the unleached part per unit mass of residual fly-ash. The mass ρ is the mass of fly ash at each stage of leaching which is constant. Thus the mass balance equation is

$$\rho M_i(n) = \rho M_i(n+1) + VC_i(n+1) \tag{6.1}$$

Assuming that an equilibrium condition has been attained between $M_i(n+1)$ and $C_i(n+1)$ during the 24 hour agitation, the relation between $M_i(n+1)$ and $C_i(n+1)$ is given by:

$$C_i(n+1) = kM_i(n+1) \tag{6.2}$$

where k is the distribution constant specific for the i^{th} element.

Incorporating Eq. (6.2) in Eq. (6.1)

$$\rho M_i(n) = \rho M_i(n+1) + VkM_i(n+1) \tag{6.3}$$

$$M_i(n+1)(\rho + Vk) = \rho M_i(n) \tag{6.4}$$

$$M_i(n+1) = \frac{\rho}{\rho + Vk} M_i(n) = \frac{M_i(n)}{\left\{1 + \frac{Vk}{\rho}\right\}} = \frac{M_i(n)}{\{1+S\}} \tag{6.5}$$

where, $S = \frac{Vk}{\rho}$.

One can write equation (6.5) in differential form as:

$$M_i(n+\Delta n) = M_i(n) + \frac{dM_i(n)}{dn}\Delta n = \frac{M_i(n)}{\{1+S\}} \tag{6.6}$$

or

$$\frac{dM_i(n)}{dn}\Delta n = \frac{M_i(n)}{\{1+S\}} - M_i(n) \tag{6.7}$$

As $\Delta n = 1$

$$\frac{dM_i(n)}{dn} = \frac{M_i(n)}{\{1+S\}} - M_i(n) = -\frac{S}{\{1+S\}} M_i(n) \tag{6.8}$$

or

$$\frac{dM_i(n)}{M_i(n)} = -\frac{S}{\{1+S\}} dn \tag{6.9}$$

Integrating

$$\ln\{M_i(n)\} = -\frac{S}{1+S}n + A \tag{6.10}$$

For $n = 0, M_i(n) = M_i(0)$; hence , the integration constant $A = \ln\{M_i(0)\}$. Incorporating the constant A in Eq. 6.10 and simplifying

$$\ln\left\{\frac{M_i(n)}{M_i(0)}\right\} = -\frac{S}{1+S}n \tag{6.11}$$

or

$$2.302\log\left\{\frac{M_i(n)}{M_i(0)}\right\} = -\frac{S}{1+S}n \tag{6.12}$$

or

$$\log\left\{\frac{M_i(n)}{M_i(0)}\right\} = -\left(0.434\frac{S}{1+S}\right)n \tag{6.13}$$

or

$$\log\left\{\frac{C_i(n)}{kM_i(0)}\right\} = -\left(0.434\frac{S}{1+S}\right)n \tag{6.14}$$

Thus, the variation of $\log\left\{\frac{C_i(n)}{kM_i(0)}\right\}$ with n is a straight line. $M_i(0)$ and ρ are ascertained from acid digestion test data presented in Chapter 4 . The concentration $C_i(1)$ is measured. Therefore, k can be known from equation (6.14) following an iteration procedure. From Eq. (6.5)

$$M_i(n+1) = \frac{M_i(n)}{(1+S)} \tag{6.15}$$

For n = 0

$$M_i(1) = \frac{M_i(0)}{(1+S)} \tag{6.16}$$

For n = 1

$$M_i(2) = \frac{M_i(1)}{(1+S)} \quad ; \quad M_i(2) = \frac{M_i(0)}{(1+S)^2} \tag{6.17}$$

For n = 2

$$M_i(3) = \frac{M_i(2)}{(1+S)} \quad ; \quad M_i(3) = \frac{M_i(0)}{(1+S)^3} \tag{6.18}$$

Hence,

$$M_i(n) = M_i(0)\left[\frac{1}{1+S}\right]^n \tag{6.19}$$

Substituting $C_i(n) = kM_i(n)$ in Eq. 6.19, leachate concentration at any stage of leaching is obtained as

$$C_i(n) = kM_i(0)\left[\frac{1}{1+\frac{kV}{\rho}}\right]^n \tag{6.20}$$

Equation 6.20 gives leachate concentration at n^{th} stage of leaching. Equation 6.20 has been derived by Muñoz (2006) for a more generalized case, when the concentration of the element in the influx is not zero. Equation (6.20) can be rewritten as:

$$C_n = M(0)\left[\frac{k^{\frac{1}{n}}}{1+\frac{V}{\rho}k}\right]^n$$

or

$$\left[\frac{C_i(n)}{M_i(0)}\right]^{\frac{1}{n}} = \left[\frac{1}{\frac{1}{k^{\frac{1}{n}}}+\frac{Vk}{\rho k^{\frac{1}{n}}}}\right]$$

or

$$\left[\frac{C_i(n)}{M_i(0)}\right]^{\frac{1}{n}} = \left[\frac{1}{k^{-\frac{1}{n}} + \frac{V}{\rho}k^{\frac{n-1}{n}}}\right]$$

Cross multiplying

$$\left[\frac{C_i(n)}{M_i(0)}\right]^{\frac{1}{n}} k^{\frac{-1}{n}} + \left[\frac{C_i(n)}{M_i(0)}\right]^{\frac{1}{n}} \frac{V}{\rho} k^{\frac{n-1}{n}} - 1 = 0 \qquad (6.21)$$

For n=1

$$\left[\frac{C_i(1)}{M_i(0)}\right] k^{-1} + \left[\frac{C_i(1)}{M_i(0)}\right] \frac{V}{\rho} - 1 = 0 \qquad (6.22)$$

or

$$C_i(1)\left[\frac{1}{k} + \frac{V}{\rho}\right] = M_i(0) \qquad (6.23)$$

Solving for k

$$k = \frac{\rho C_i(1)}{\rho M_i(0) - VC_i(1)} \qquad (6.24)$$

$\rho M_i(0)$ is initial mass of ith element present in the fly ash, which is known from the acid digestion test. ρ is the residual mass after all elements have been leached away which can be computed from Table 4.3 given in Chapter 4. ρ = mass of fly ash used in acid digestion test- sum of mass of all elements present which have been estimated from acid digestion test. Thus k can be computed from the measured concentration $C_i(1)$. For $n \geq 1$, k can be computed from $C_i(n)$ as derived below following an iteration procedure.

$$Xk^{\alpha} + Yk^{\beta} - Z = 0 \qquad (6.25)$$

where $X = \left[\frac{C_i(n)}{M_i(0)}\right]^{\frac{1}{n}}$; $Y = \frac{XV}{\rho}$; $Z = 1$; α = -1/n; β =1+α .

For n = 1 α = -1, β = 0, n = 2, α = -0.5, β = 0.5 , n = 3 α = -0.33, β= 0.66
n= 4, α = -0.25, β = 0.75, n= 5, α =-0.2, β= 0.8.

6.3.1 A Composite Exponential Decay Model

The alternate form of Equation 6.11 is

$$M_i(n) = M_i(0)e^{-\frac{S}{1+S}n} \tag{6.26}$$

Multiplying both sides by k

$$C_i(n) = kM_i(0)e^{-\frac{S}{1+S}n} \tag{6.27}$$

$$C_i(n+1) = kM_i(0)e^{-(\frac{S}{1+S})(n+1)} \tag{6.28}$$

$$C_i(n+1) = kM_i(0)\left\{e^{-(\frac{S}{1+S})(n)} \times e^{-(\frac{S}{1+S})}\right\} = kM_i(n)e^{-(\frac{S}{1+S})} = C_i(n)e^{-(\frac{S}{1+S})} \tag{6.29}$$

$$\ln\frac{C_i(n+1)}{C_i(n)} = -\frac{S}{1+S} \tag{6.30}$$

Equation (6.30) is applicable for $n \geq 1$ as $C(0)$ is not defined.

The exponential decay model described by Equation (6.26) is valid provided i^{th} element is desorpted from only one compound of the element. The applicability of a single exponential decay model can be ascertained from the regression coefficient. If several compound of the i^{th} element are present, in that case a composite exponential decay model is applicable as the desorption rate from the different compound will be different and the initial masses each compound will also be different.

For attaining a regression coefficient close to 1, a composite exponential decay model is fitted between the metal concentration in leachate and number of successive leaching (or liquid to solid ratio), which takes the form as given below:

$$C_i(n) = a_i e^{-b_i n} + c_i e^{-d_i n}; \quad a_i > 0, \quad c_i > 0; \quad 0 < b_i < 1; \quad 0 < d_i < 1 \tag{6.31}$$

This model is applicable when one element is present in multiple compounds in the fly ash. The parameters a_i, b_i, c_i, d_i are to be positive constants specific for the i^{th} metal's compounds in the fly ash; $C_i(n) =$ concentration of i^{th} metal in the leachate in mg/lit in the n^{th} unit out flux volume; the n units of influxes are applied in succession; one unit of influx volume has a mass equal to an integer times that of the initial mass of fly ash; a_i, c_i have dimension as that of $C_i(n)$; b_i, d_i are dimensionless. Equation (6.31) is an empirical relation between concentration and surrogate time. The parameter n is the number of time the liquid volume V is applied. The volume V characterizes certain liquid to solid ratio. The parameters a_i, b_i, c_i, d_i are computed using MATLAB curve fitting tools for the selected i^{th} metal.

6.4 A LEACHATE MODEL WITH VARIABLE DISTRIBUTION COEFFICIENT k(n)

During $(n+1)^{th}$ stage of leaching, let the relation between concentration of the i^{th} element in the leachate and mass of the i^{th} element per unit mass of the constant fly ash mass that does not get leached be given by:

$$C_i(n+1) = k_i(n+1)M_i(n+1) \tag{6.32}$$

$k_i(n+1)$ is the distribution constant effective during $(n+1)^{th}$ stage of leaching specific for the i^{th} element.

Incorporating Equation (6.32) in Equation (6.1), the mass balance during $(n+1)^{th}$ stage of leaching is:

$$\rho M_i(n) = \rho M_i(n+1) + V(n+1)k_i(n+1)M_i(n+1) \tag{6.33}$$

$$M_i(n+1)\{\rho + V(n+1)k_i(n+1)\} = \rho M_i(n) \tag{6.34}$$

$$M_i(n+1) = \frac{\rho}{\rho + V(n+1)k(n+1)} M_i(n) = \frac{M_i(n)}{\left\{1 + \frac{V(n+1)k(n+1)}{\rho}\right\}} = \frac{M_i(n)}{\{1 + S(n+1)\}} \qquad (6.35)$$

where, $S(n+1) = \frac{V(n+1)k(n+1)}{\rho}$.

For n = 0

$$M_i(1) = \frac{M_i(0)}{1 + S(1)} \qquad (6.36)$$

For n = 1

$$M_i(2) = \frac{M_i(1)}{1 + S(2)} \quad ; \quad M_i(2) = \frac{M_i(0)}{\{1 + S(1)\}\{1 + S(2)\}} \qquad (6.37)$$

For n = 2

$$M_i(3) = \frac{M_i(2)}{1 + S(3)} \quad ; \quad M_i(3) = \frac{M_i(0)}{\{1 + S(1)\}\{1 + S(2)\}\{1 + S(3)\}} \qquad (6.38)$$

Hence,

$$M_i(n) = M_i(0)\left[\frac{1}{\{1 + S(1)\}\{1 + S(2)\}\{1 + S(3)\}.....\{1 + S(n)\}}\right] \qquad (6.39)$$

Multiplying both sides of Equation (6.39) by $k(n)$, and substituting $C_i(n) = k(n)M_i(n)$, the leachate concentration at any stage of leaching is expressed as

$$C_i(n) = k(n)M_i(0)\left[\frac{1}{\{1 + S(1)\}\{1 + S(2)\}\{1 + S(3)\}.....\{1 + S(n)\}}\right] \qquad (6.40)$$

$C_i(n)$, for $n = 1,2,3,...$ are measured. $M_i(0)$ is known from acid digestion test. Therefore, the distribution coefficients $k(n)$ can be computed from Equation (6.40) in succession starting from $n = 1$ following an iteration procedure. This model is also applicable when the influx leachant volume varies from stage to stage of leaching.

6.5 RESULTS AND DISCUSSIONS

$\rho M_i(0)$ is the mass of i^{th} element present in the mass of fly ash used in Cascade Leaching test. $\rho M_i(0)$ is measured from acid digestion test, ρ could be measured in the end when $C_i(n) \rightarrow 0$. In that case determination of ρ is time taking. The alternate method is to compute ρ from the following equation:

$$\sum_{i=1}^{n} \rho M_i(0) + \rho = M_f \tag{6.41}$$

where M_f = total mass of fly ash which contains all the components those would get leached and the mass that does not get leached and remains constant in all stages of leaching. $\rho M_i(0)$ is known from acid digestion test. Therefore,

$$\rho = M_f - \sum_{i=1}^{n} \rho M_i(0) \tag{6.42}$$

6.5.1 Fitting an Exponential Equation to Observed concentrations

On the basis of Equation 6.27, an exponential equation of the form $C_i(n) = a_i e^{-b_i n}$; $a_i > 0$, $0 < b_i < 1$, is fitted to the observed concentrations using the MATLAB curve fitting tool. A composite exponential equation of the form $C_i(n) = a_i e^{-b_i n} + c_i e^{-d_i n}$; $a_i > 0, c_i > 0; 0 < b_i < 1;$ $0 < d_i < 1$ has also been tried. Suitability of a single or a composite exponential equation has been chosen on the basis of higher regression coefficient approaching 1. The exponential equation in which a_i or b_i takes a negative value is rejected.

6.5.2 Fitting an Exponential Equation to Leachate Concentrations, Influx Leachant Neutral

Cascade Leaching tests have been conducted in a neutral environment with M_f=100 grams. The *pH* of the leachant is equal to 7. During each stage of leaching, a constant leachant volume of 200 *ml* has been used. The concentrations $C_i(n)$ (gm/l) are measured at the end of 24 hours in each stage of leaching. The variations of $C_i(n)$ with n are presented in Figure 6.3 through Figure 6.6. For most of the components, the variation of concentration with successive stage of leaching with a constant volume of neutral leachant is exponential in nature. The coefficients of the exponential equation and the regression coefficients are presented in Tables 6.1 through Table 6.4. There is exception for Fe. As seen from Figure 6.3, the single exponential equation very poorly simulates the observed concentration. The coefficients *a* and *b* are 0.001072 and 0.468 respectively, which are acceptable; but, the regression coefficient R = 0.7714. When a composite exponential function is fitted the corresponding regression coefficient is 0.998. The coefficients *a, b, c, d* are 0.02591, 3.852, 0.0002754, 0.09889 respectively. Though the regression coefficient is very near to 1, the composite exponential function is not acceptable as the parameter b is greater than 1. Parameter *b* is analogous to the ratio $\frac{S}{1+S}$; therefore, theoretically b is not greater than 1.

Table 6.1 Exponential decay model for Bhatinda fly ash leached at initial pH = 7

Metal	Exponential Decay Model	R^2
Fe	$C(n) = 0.001072e^{-0.468*n}$	0.7714
Mn	$C(n) = (9.335E-05)e^{-0.4608*n}$	0.9216
Zn	$C(n) = (7.493E-05)e^{-0.3943*n}$	0.8142
Cd	$C(n) = (7.909E-06)e^{-0.9006*n} + (7.66E-06)e^{-0.3445*n}$	0.9346

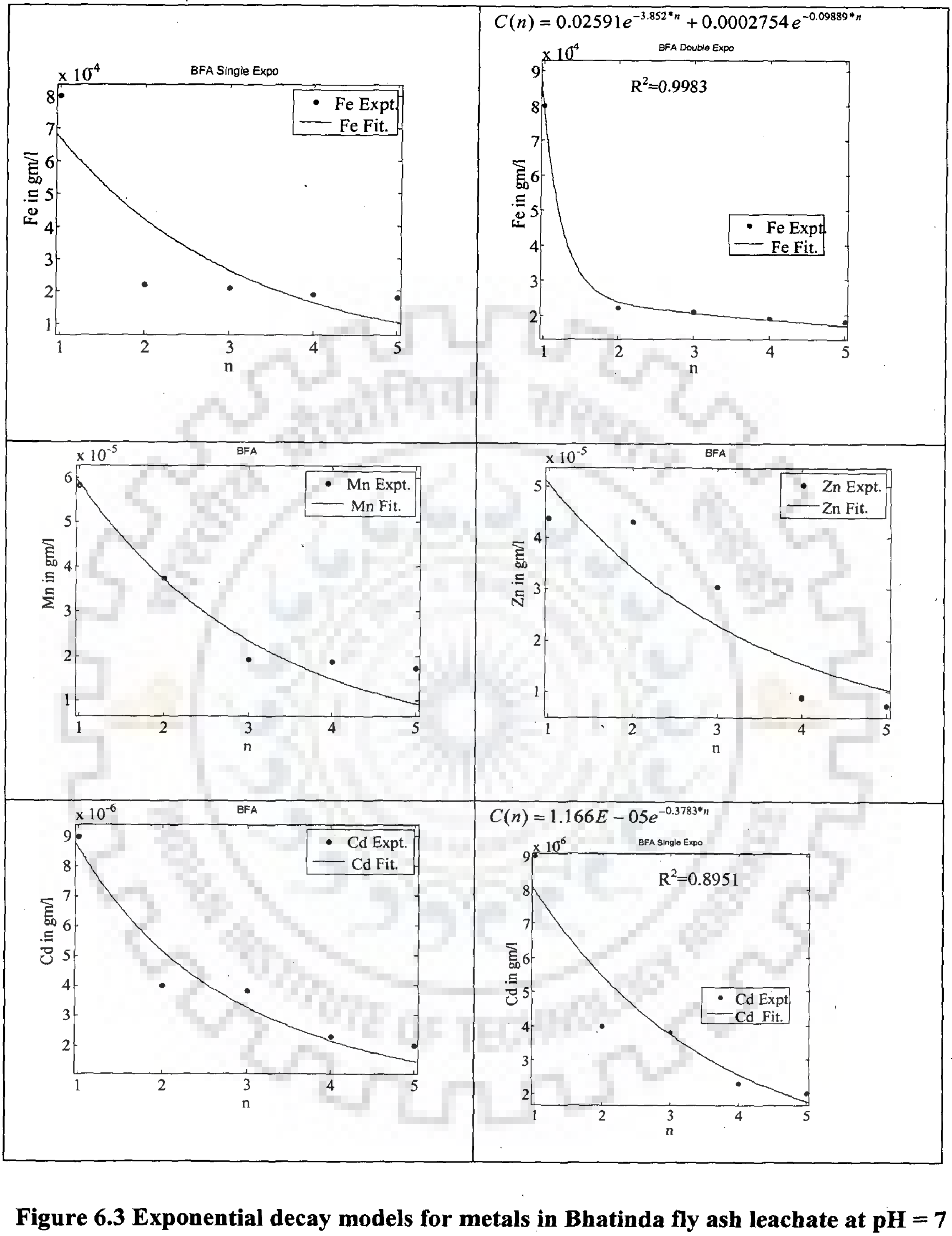

Figure 6.3 Exponential decay models for metals in Bhatinda fly ash leachate at pH = 7

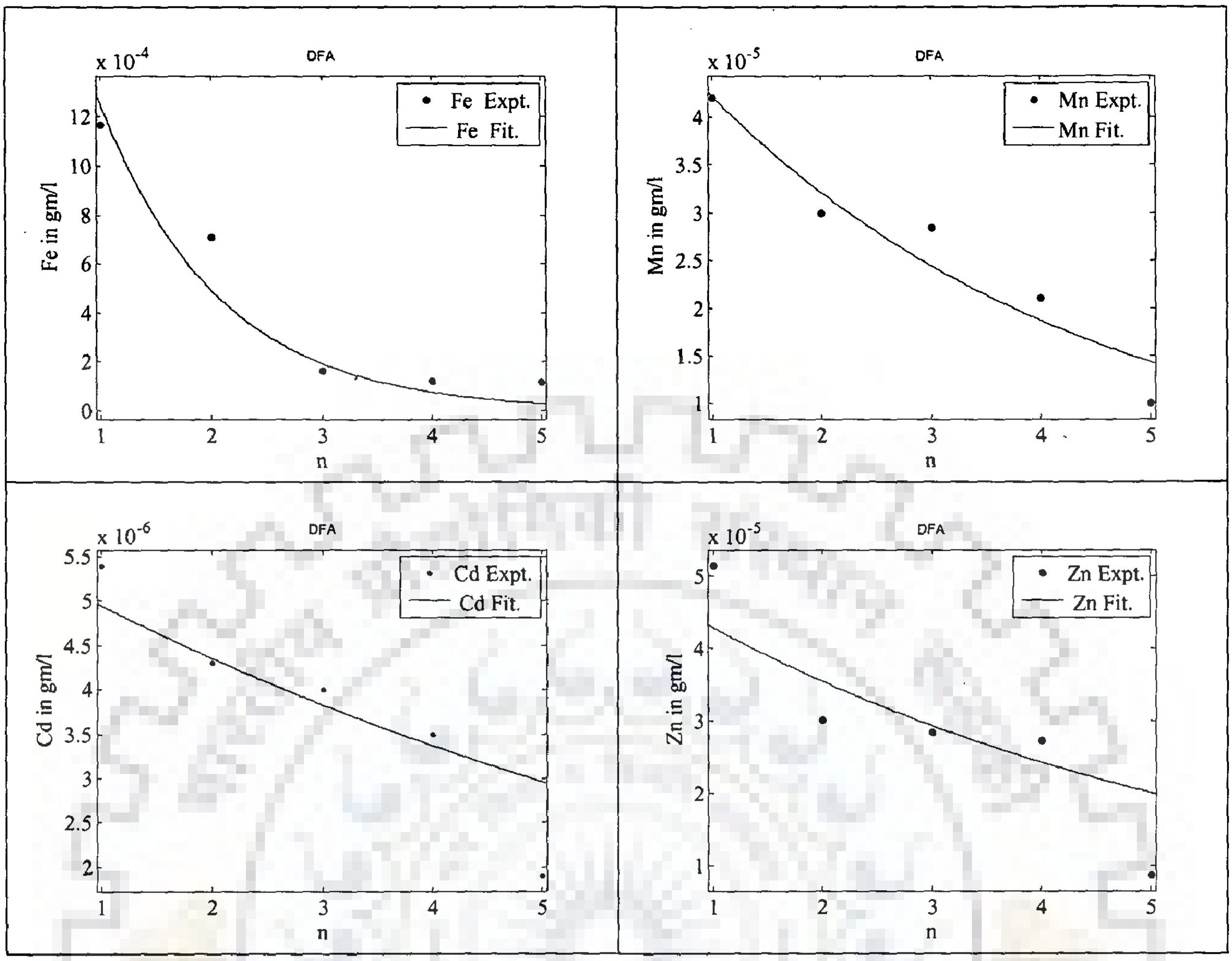

Figure 6.4 Exponential decay models for metals in Dadri fly ash leachate at pH = 7

Table 6.2 Exponential decay model for Dadri fly ash leached at initial pH = 7

Metal	Exponential Decay Model	R^2
Fe	$C(n) = 0.003202e^{-0.9361*n}$	0.9247
Mn	$C(n) = (4.394E-05)e^{-0.3022*n} + (1.717E-05)e^{-0.1862*n}$	0.9199
Zn	$C(n) = (5.175E-05)e^{-0.1894*n}$	0.7372
Cd	$C(n) = (5.628E-06)e^{-0.1286*n}$	0.79

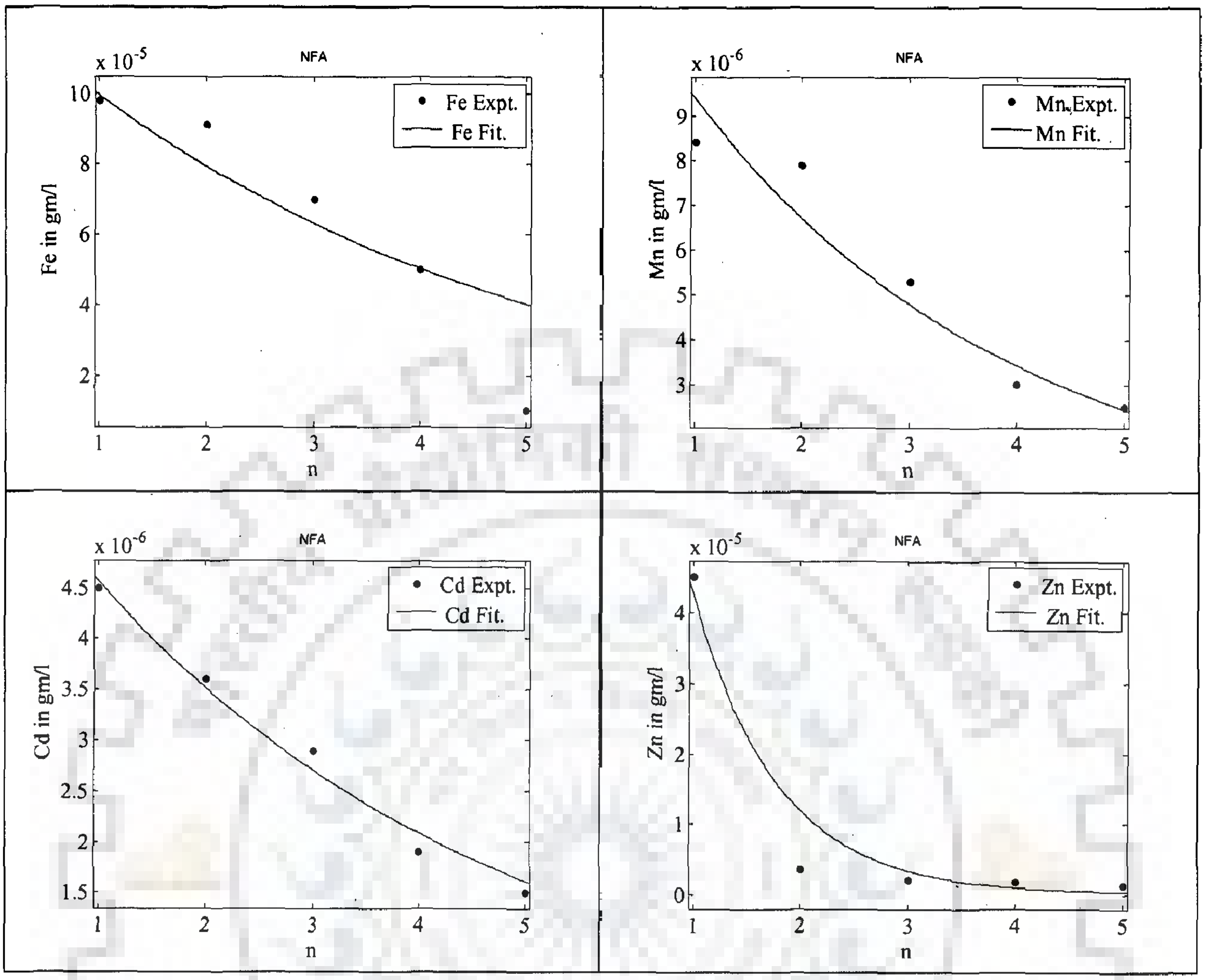

Figure 6.5 Exponential decay models for metals in Nashik fly ash leachate at pH = 7

Table 6.3 Exponential decay model for Nashik fly ash leached at initial pH = 7

Metal	Exponential Decay Model	R^2
Fe	$C(n) = 0.0001248e^{-0.2271*n}$	0.7828
Mn	$C(n) = (1.316E - 05)e^{-0..3375*n}$	0.9028
Zn	$C(n) = 0.0001528e^{-1.275*n}$	0.9463
Cd	$C(n) = (5.928E - 06)e^{-0.2616*n}$	0.9844

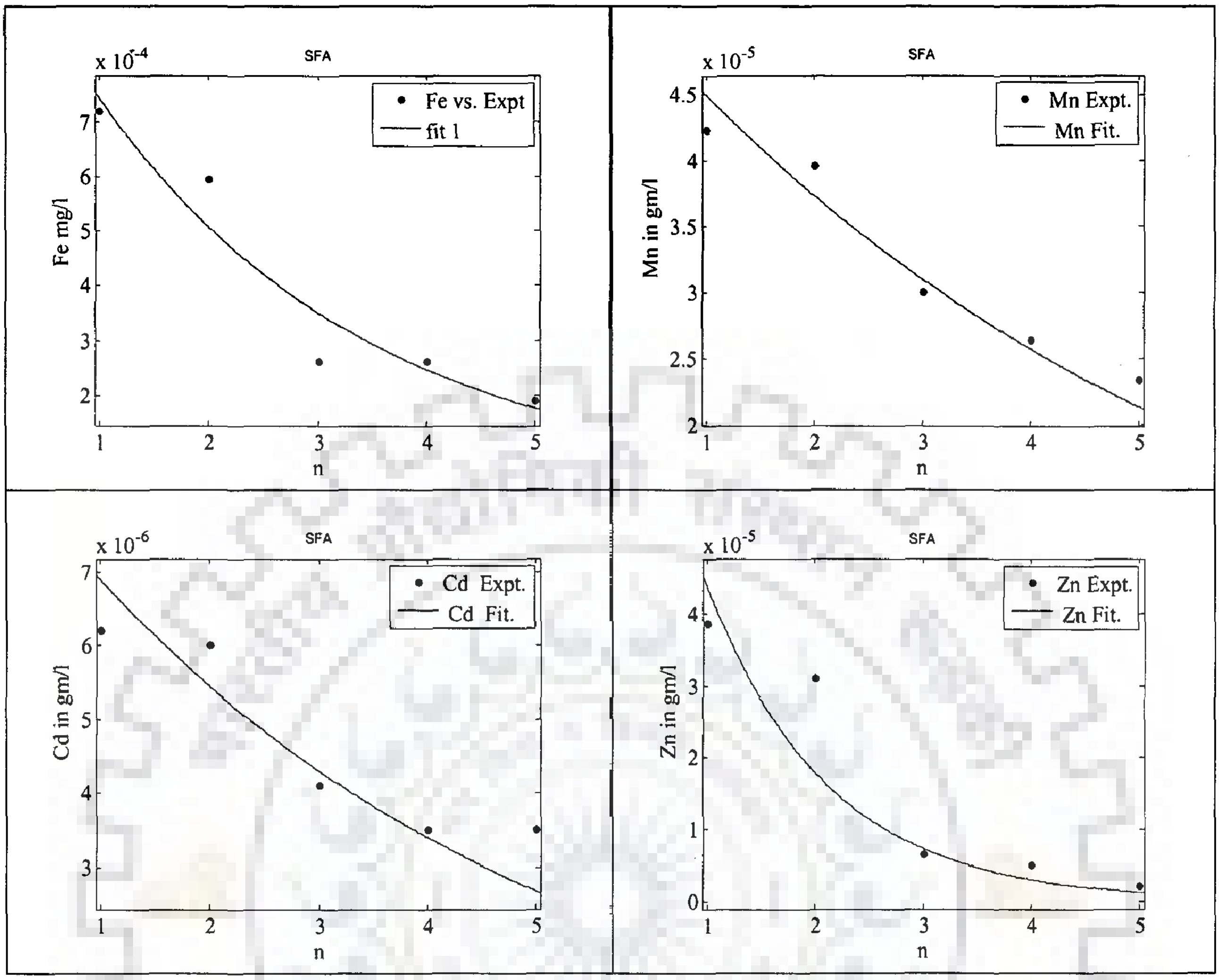

Figure 6.6 Exponential decay models for metals in Surathgarh fly ash leachate at pH =7

Table 6.4 Exponential decay model for Surathgarh fly ash leached at initial pH = 7

Metal	Exponential Decay Model	R^2
Fe	$C(n) = 0.0008786e^{-0.459*n} + 0.0002292e^{-0.1923*n}$	0.924
Mn	$C(n) = (5.416E-05)e^{-0.1865*n}$	0.9337
Zn	$C(n) = 0.0001082e^{-0.9031*n}$	0.8175
Cd	$C(n) = (8.735E-06)e^{-0.2366*n}$	0.7875

6.5.3 Fitting an Exponential Equation to Leachate Concentrations, Influx Leachant Acidic

There are several ways to study long term leaching behavior of fly ash in the laboratory. One method is to simply extract columns of ash with an aqueous solution over an extended period of time to observe the variation in concentration with time. A second method for studying the long term leaching characteristics of fly ash is to use moderately acidic leaching reagent to cause accelerated solubilization of the ash over a short period of time and third method involves simulation modeling (El Mogazi et al.,1988). In the present study, cascade leaching tests have been carried using a leachant having a pH = 4 , the cumulative L/S ratio varying from 5 to100. The initial mass of fly ash taken M_f=50 grams. The influx leachant volume has been changed after 4th stage of leaching from 250 *ml* to 500*ml*. As S changes after 4th stage of leaching, the exponential decay curve is not differentiable at *n=4*. A jump is likely to occur in the concentration variation when the change in leachant volume is significant. Therefore, different exponential curves have been fitted for the two sets of data, one set considering $C_i(n)$ up to *n=4*, and the other set considering $C_i(n)$ for *n=4* to *12*.

The variations of $C_i(n)$ with *n*, *n* varying from 1 to 4 are presented in Figures. 6.7 through 6.10 for Bhatinda, Dadri, Nashik and Surathgarh respectively. The coefficients of exponential function fitted to the observed concentration using a MATLAB for six metals (Fe, Mn, Zn Cd Cu and Ni) are presented in Table 6.5.

The variations of $C_i(n)$ with *n*, *n* varying from 4 to 12 are presented in Figures. 6.11 through 6.14 for Bhatinda, Dadri, Nashik and Surathgarh respectively. The coefficients of exponential function fitted to the observed concentration using a MATLAB for the six metals (Fe, Mn, Zn Cd Cu and Ni) are presented in Table 6.6.

It is observed that the variation of concentration with *n*, the stage of leaching, with a constant leachant volume in each stage of leaching, is mostly exponential in nature; an exponential function can be fitted to predict the leachate concentration at a higher value of 'n'.

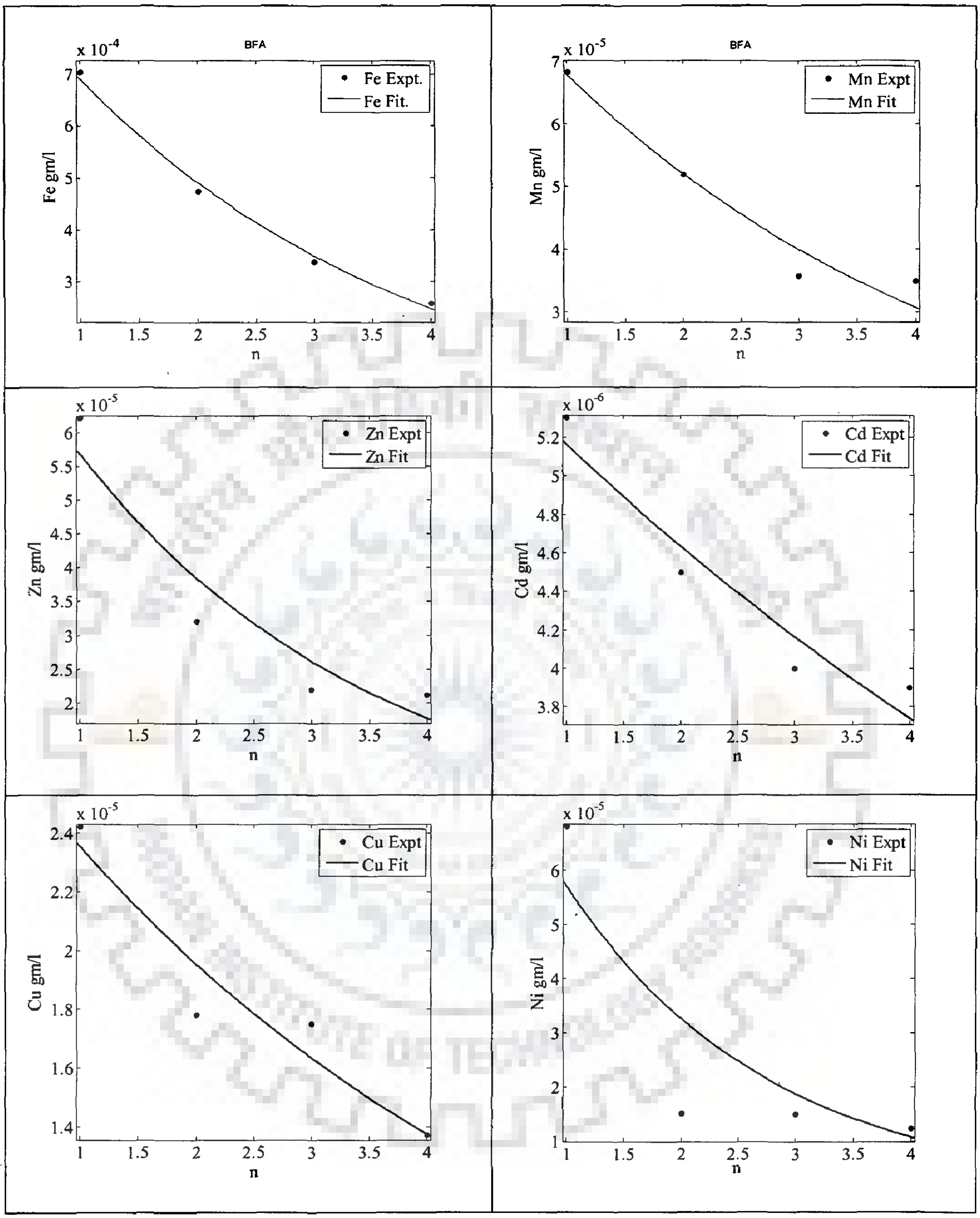

Figure 6.7 Exponential decay models for metals in Bhatinda fly ash leachate at pH= 4 for n=1 to 4

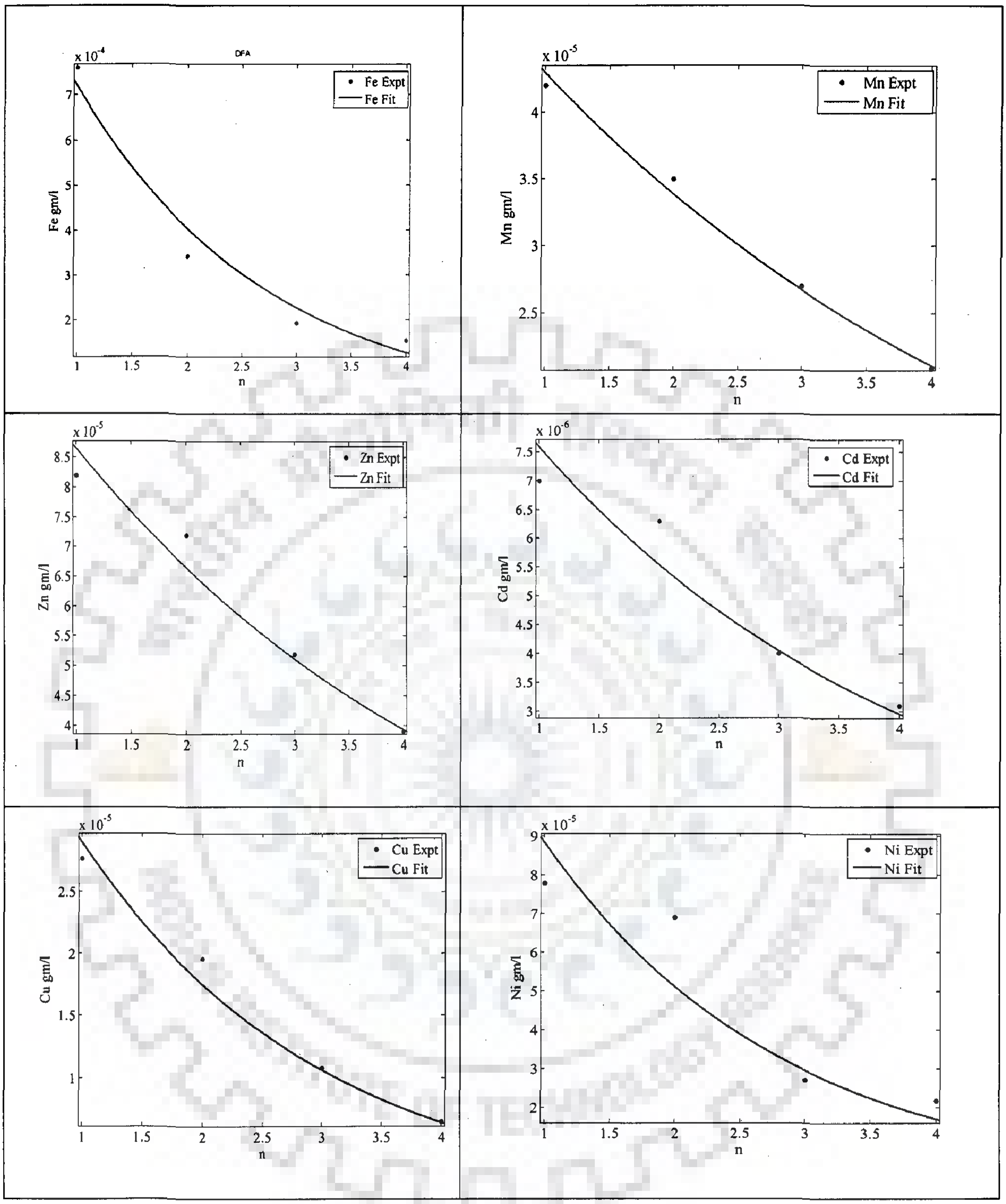

Figure 6.8 Exponential decay models for metals in Dadri fly ash leachate at pH= 4 for n=1 to 4

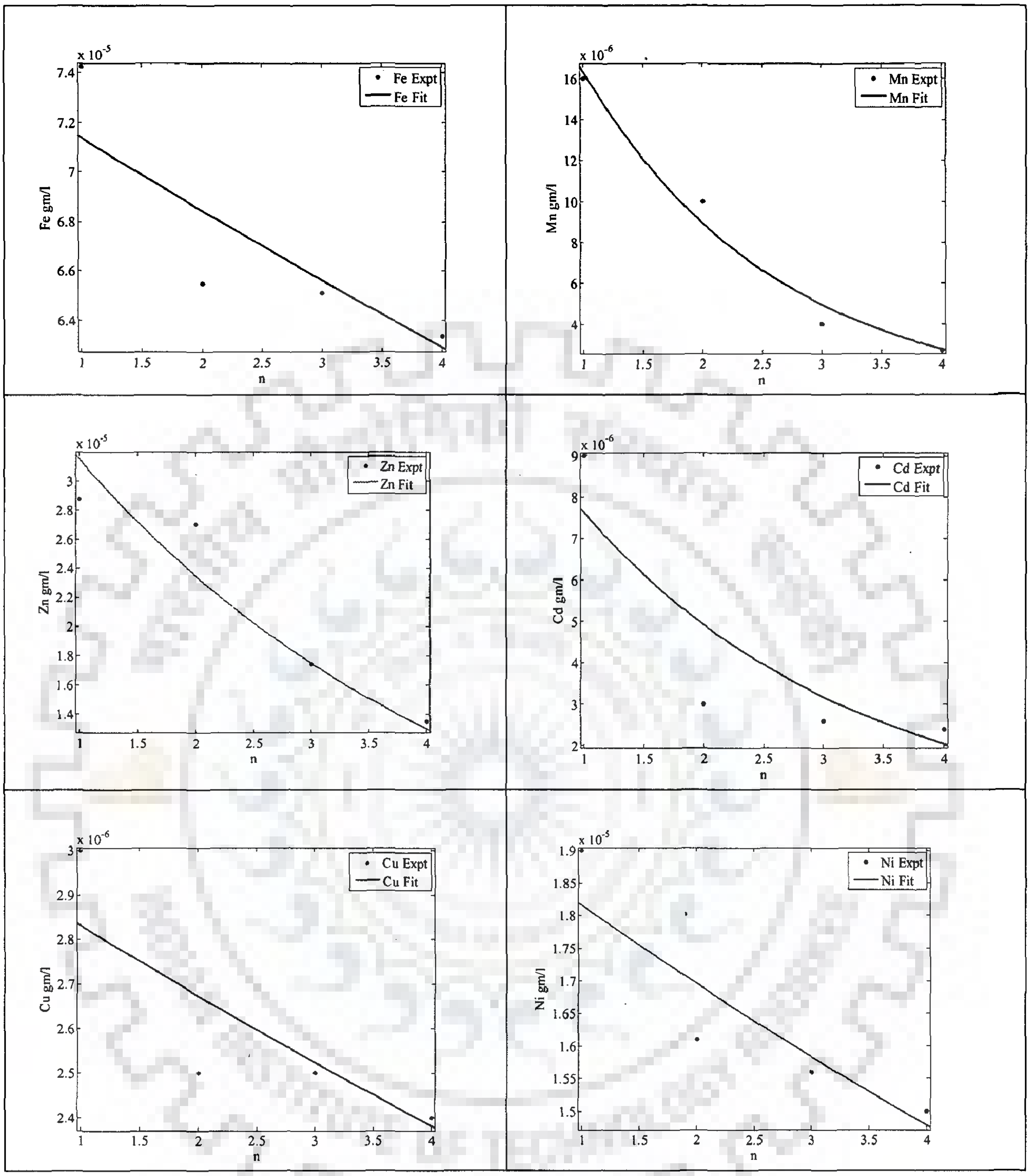

Figure 6.9 Exponential decay models for metals in Nashik fly ash leachate at pH= 4 for n=1 to 4

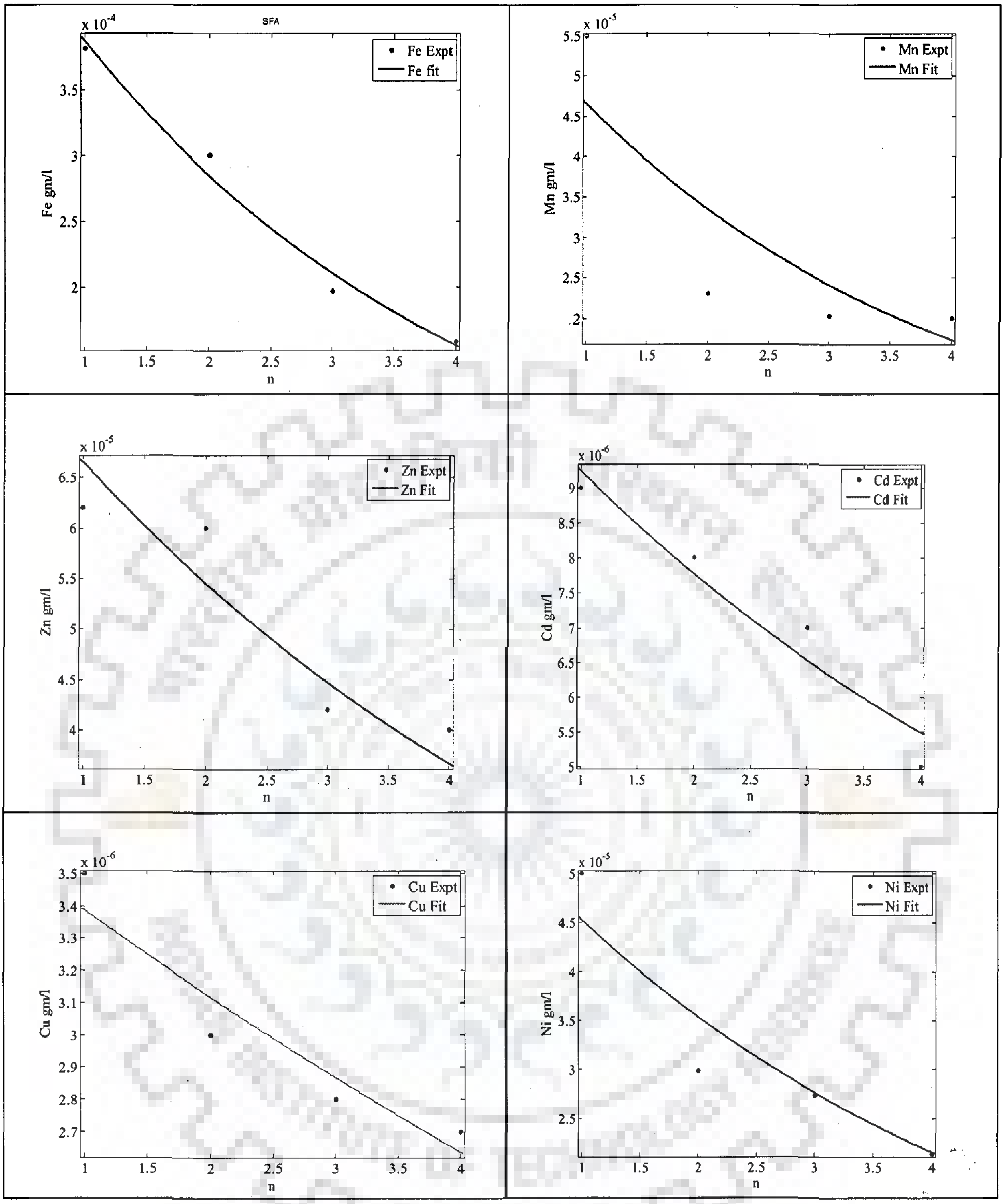

Figure 6.10 Exponential decay models for metals in Suratgarh fly ash leachate at pH= 4 for n=1 to 4

Table 6.5 Coefficients of exponential decay model for fly ash leached with leachant at pH = 4 for case, n =1 to 4

Fly ash	Metal	Exponential Decay Model	R^2
Bhatinda Fly ash	Fe	$C(n) = 0.0009702e^{-0.341*n}$	0.9944
	Mn	$C(n) = (8.826E-05)e^{-0.2649*n}$	0.9524
	Zn	$C(n) = (8.37E-05)e^{-0.3887*n}$	0.9101
	Cd	$C(n) = (5.751E-06)e^{-0.1078*n}$	0.9267
	Cu	$C(n) = (6.49E-06)e^{-0.3906*n} + (2.216E-05)e^{-0.1456*n}$	0.9155
	Ni	$C(n) = (9.97E-05)e^{-0.5584*n}$	0.7965
Dadri	Fe	$C(n) = 0.001285e^{-0.5778*n}$	0.969
	Mn	$C(n) = (5.447E-05)e^{-0.2373*n}$	0.9911
	Zn	$C(n) = 0.0001126e^{-0.263*n}$	0.9543
	Cd	$C(n) = (1.038E-05)e^{-0.3138*n}$	0.9084
	Cu	$C(n) = (4.799E-05)e^{-0.5029*n}$	0.9776
	Ni	$C(n) = 0.0001529e^{-0.5473*n}$	0.8133
Nashik Fly ash	Fe	$C(n) = (7.445E-05)e^{-0.04216*n}$	0.7588
	Mn	$C(n) = (1.825E-05)e^{-0.6731*n} + (1.167E-05)e^{-0.5125*n}$	0.9813
	Zn	$C(n) = (4.229E-05)e^{-0.2946*n}$	0.8735
	Cd	$C(n) = (1.18E-05)e^{-0.4377*n}$	0.80
	Cu	$C(n) = (3E-06)e^{-0.05776*n}$	0.7316
	Ni	$C(n) = (1.945E-05)e^{-0.0686*n}$	0.8371
Surathgarh Fly ash	Fe	$C(n) = 0.0004313e^{-0.3261*n} + (9.456E-05)e^{-0.2272*n}$	0.9855
	Mn	$C(n) = (6.461E-05)e^{-0.3295*n}$	0.7668
	Zn	$C(n) = (8.13E-05)e^{-0.1987*n}$	0.8296
	Cd	$C(n) = (1.1E-05)e^{-0.1742*n}$	0.9346
	Cu	$C(n) = (3.682E-06)e^{-0.08353*n}$	0.9091
	Ni	$C(n) = (5.8E-05)e^{-0.2469*n}$	0.8846

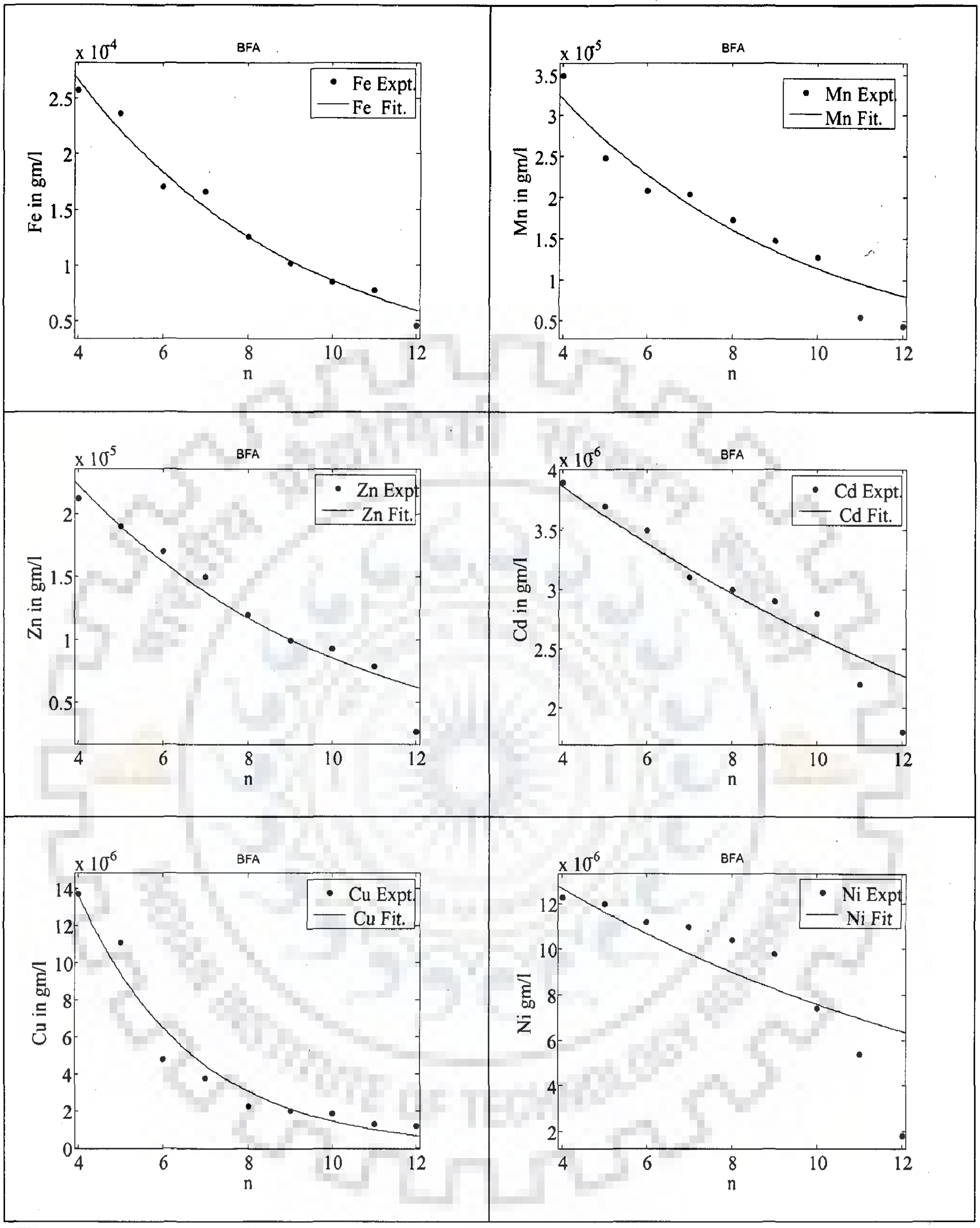

Figure 6.11 Exponential decay models for metals in Bhatinda fly ash, leachant pH= 4 , n=4 to 12

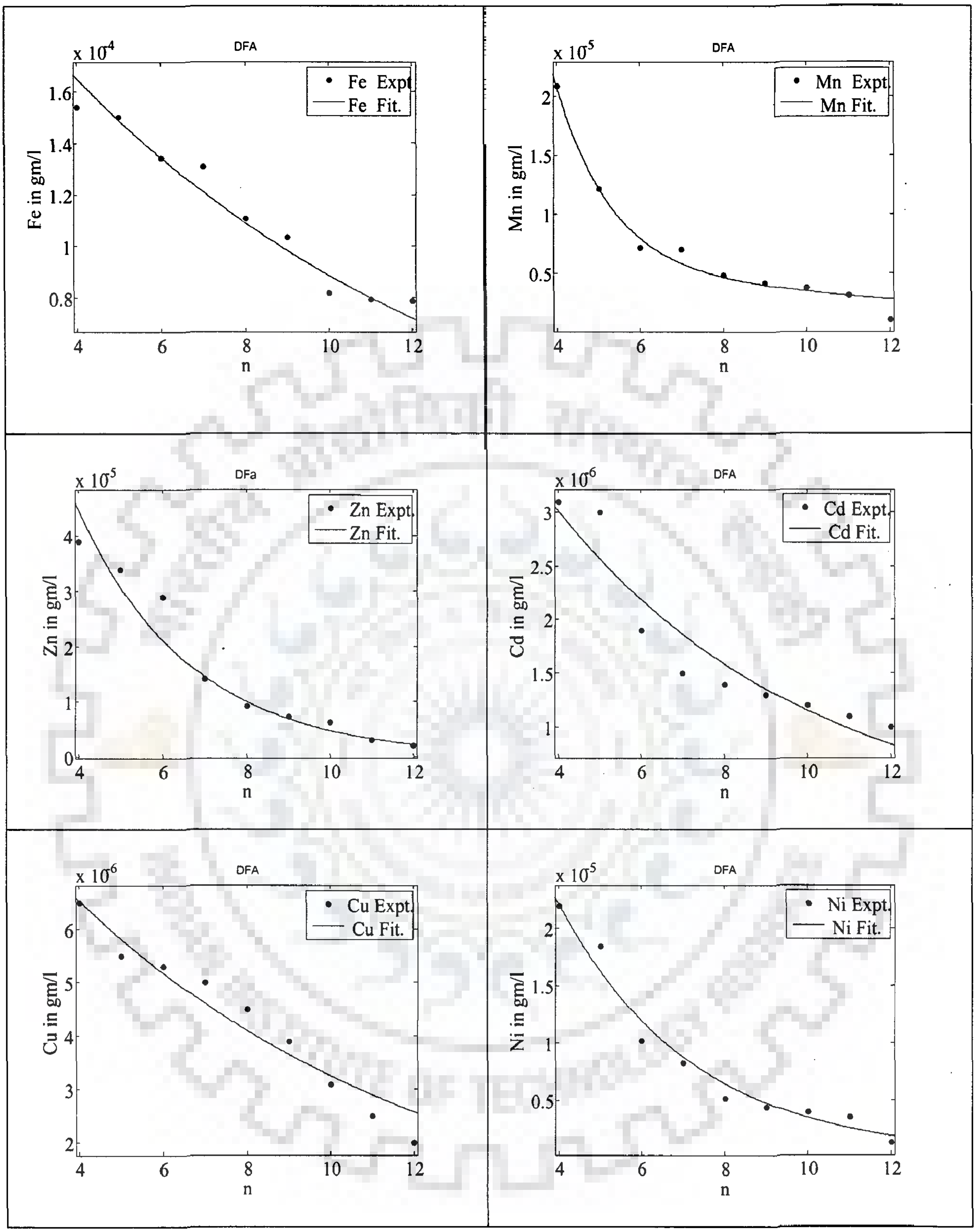

Figure 6.12 Exponential decay models for metals in Dadri fly ash, leachant pH= 4 , n=4 to 12

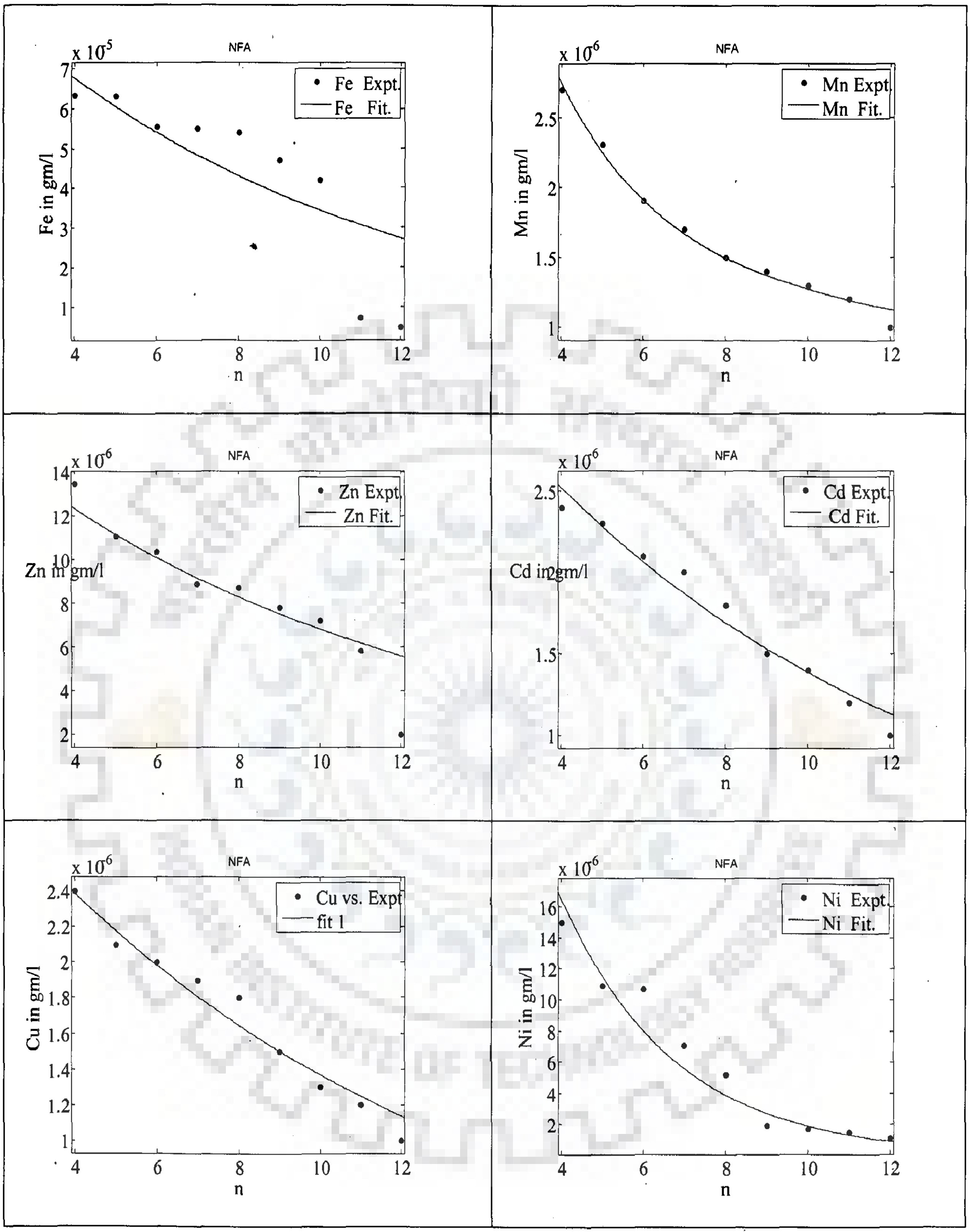

Figure 6.13 Exponential decay models for metals in Nashik fly ash, leachant pH= 4, n=4 to 12

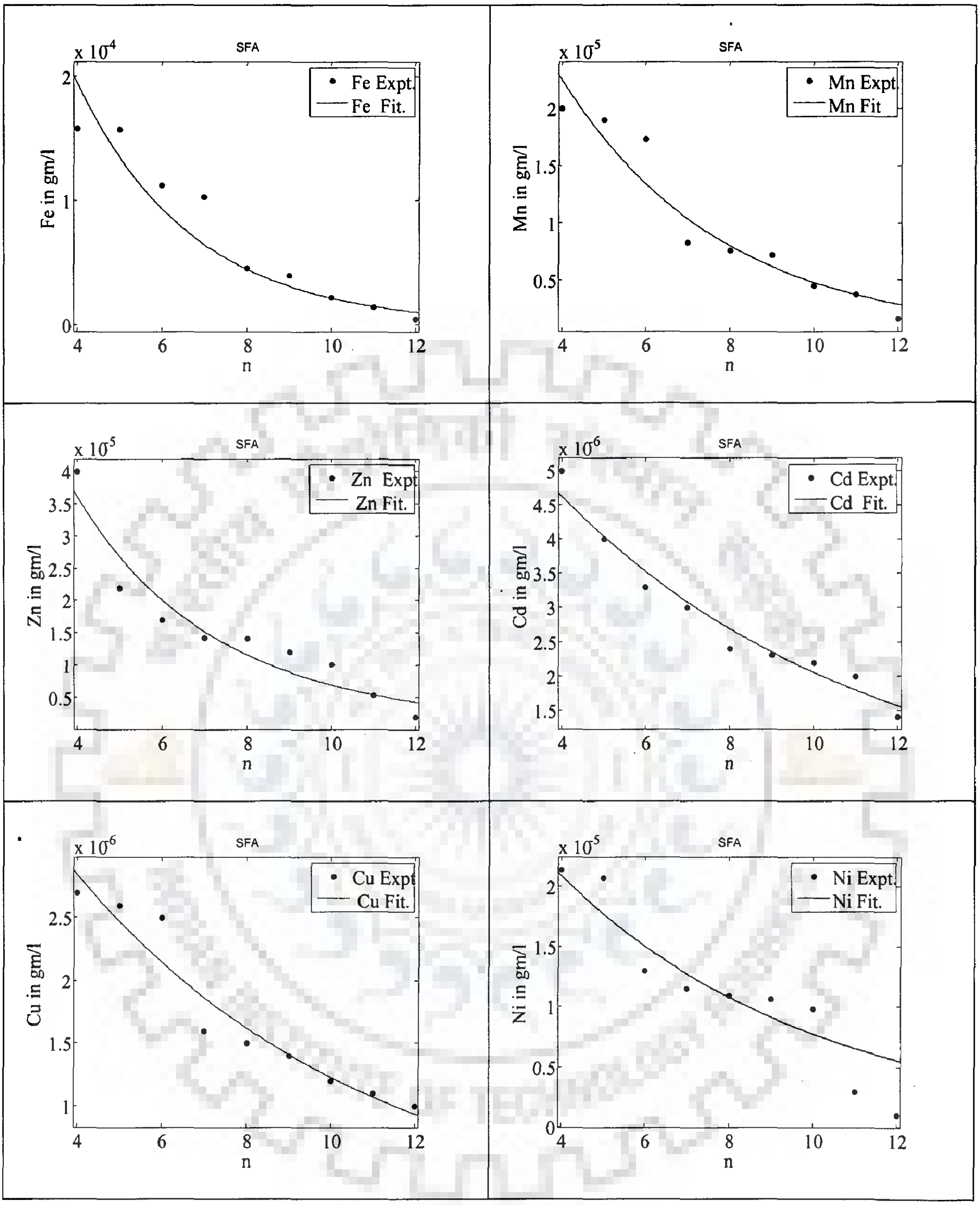

Figure 6.14 Exponential decay models for metals in Suratgarh fly ash, leachant pH= 4. n=4 to 12

Table 6.6 Coefficient of exponential decay model for fly ash leached in leachant with pH = 4, case n=4 to 12

Fly ash	Metal	Exponential Decay Model	R^2
Bhatinda Fly ash	Fe	$C(n) = 0.0005677e^{-0.1885*n}$	0.9779
	Mn	$C(n) = (6.428E - 05)e^{-0.1735*n}$	0.9268
	Zn	$C(n) = (3.635E - 05)e^{-0.1532*n} + (6.115E - 06)e^{-0.2184*n}$	0.9396
	Cd	$C(n) = (5.029E - 06)e^{-0.06612*n}$	0.9012
	Cu	$C(n) = (6.108E - 05)e^{-0.3734*n}$	0.9567
	Ni	$C(n) = (1.788E - 05)e^{-0.08574*n}$	0.698
Dadri	Fe	$C(n) = 0.0002501e^{-0.1036*n} +$	0.9515
	Mn	$C(n) = 0.0003319e^{-0.7715*n} + (8.142E - 06)e^{-0.08931*n}$	0.9816
	Zn	$C(n) = 0.000202e^{-0.3762*n}$	0.9315
	Cd	$C(n) = (5.73E - 06)e^{-0.1603*n}$	0.9035
	Cu	$C(n) = (1.04E - 05)e^{-0.1164*n}$	0.9443
	Ni	$C(n) = (7.606E - 05)e^{-0.3082*n}$	0.9714
Nashik Fly ash	Fe	$C(n) = 0.0001065e^{-0.1133*n}$	0.6552
	Mn	$C(n) = (7.179E - 06)e^{-0.4392*n} + (1.771E - 06)e^{-0.04047*n}$	0.99
	Zn	$C(n) = (1.837E - 05)e^{-0.09938*n}$	0.8302
	Cd	$C(n) = (3.761E - 06)e^{-0.099*n}$	0.9657
	Cu	$C(n) = (3.457E - 06)e^{-0.09259*n}$	0.963
	Ni	$C(n) = (7.019E - 05)e^{-0.3613*n}$	0.9298
Suratgarh Fly ash	Fe	$C(n) = 0.0008573e^{-0.3689*n}$	0.8671
	Mn	$C(n) = (6.322E - 05)e^{-0.2582*n}$	0.9207
	Zn	$C(n) = (9.661E - 05)e^{-0.3971*n} + (3.558E - 05)e^{-0.1927*n}$	0.9179
	Cd	$C(n) = (7.955E - 06)e^{-0.1355*n}$	0.9617
	Cu	$C(n) = (4.932E - 06)e^{-0.1479*n} + (1.341E - 07)e^{-0.02448*n}$	0.9309
	Ni	$C(n) = (4.06E - 05)e^{-0.1659*n}$	0.8535

6.5.4 Estimation of Distribution Constant from Observed Concentration

Determining the distribution constant from observed concentrations of an element in the leachate is an inverse problem. An inverse problem can not be solved unless the direct problem has been solved a priori. Solution of the inverse problem reveals regarding the solution of the direct problem that is used for solving the inverse problem. The leachate concentration given by Equation (6.25) has been derived with an assumption that the distribution constant *k* does not change during different stages of leaching. The distribution coefficient corresponding to each stage of leaching is determined from Equation (6.25) using an iteration procedure for all the elements and for all the fly ash samples collected from four fly ash disposal sites. The variations of distribution coefficient *k(n)* with *n*, and with metal concentrations $C_i(n)$ are shown in Figures 6.15 through Figures 6.20 for fly ash desorped in neutral environment. As seen from the graphs, the distribution coefficient for any element is not invariant; it decreases exponentially with *n* approximately. The distribution coefficient is linearly proportional to the leachate concentration; it decreases with decrease in leachate concentration.

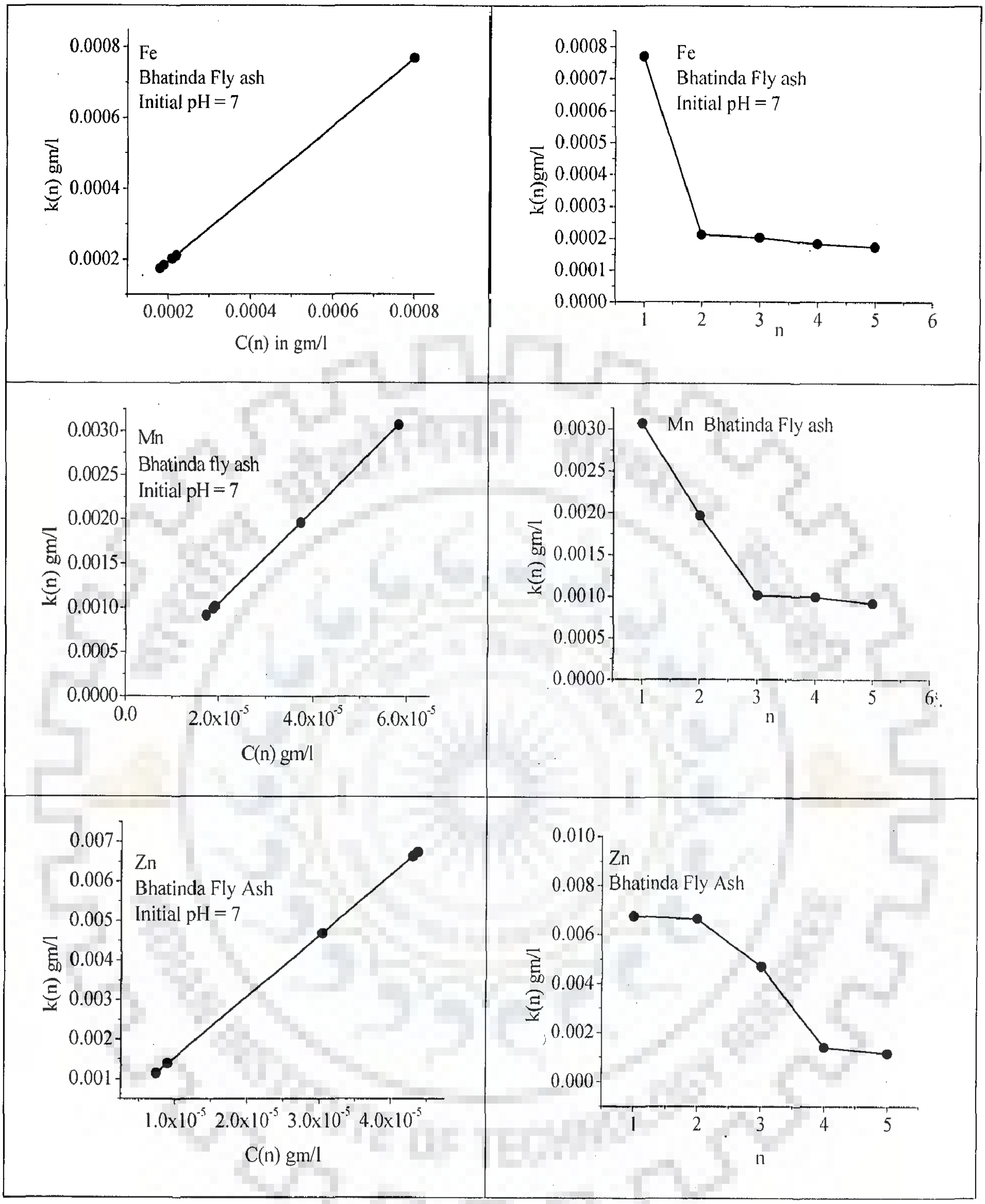

Figure 6.15 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metals Fe, Mn and Zn of Bhatinda fly ash at initial pH=7

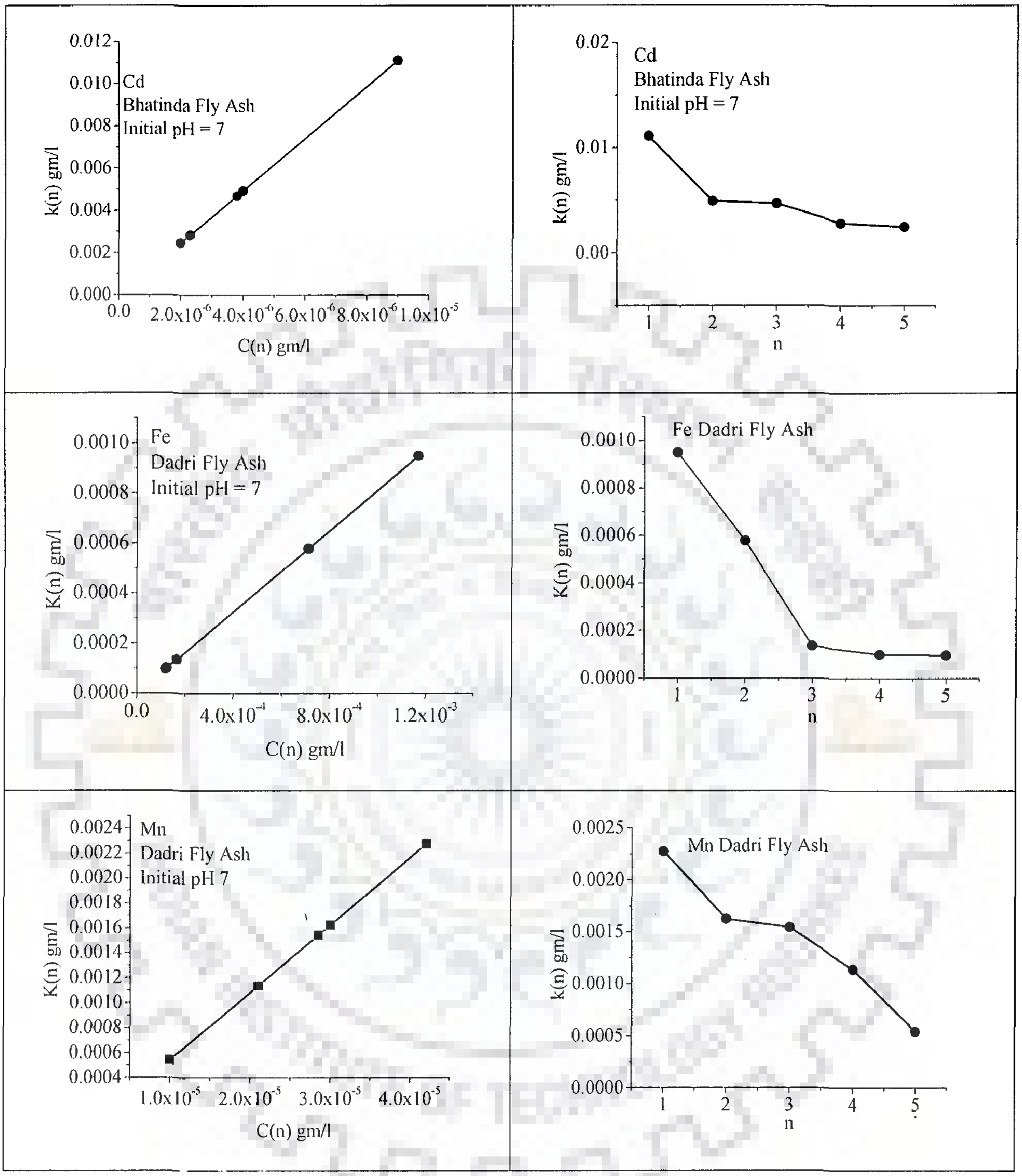

Figure 6.16 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metals Cd of Bhatinda fly ash and Fe and Mn of Dadri fly ash at initial pH=7

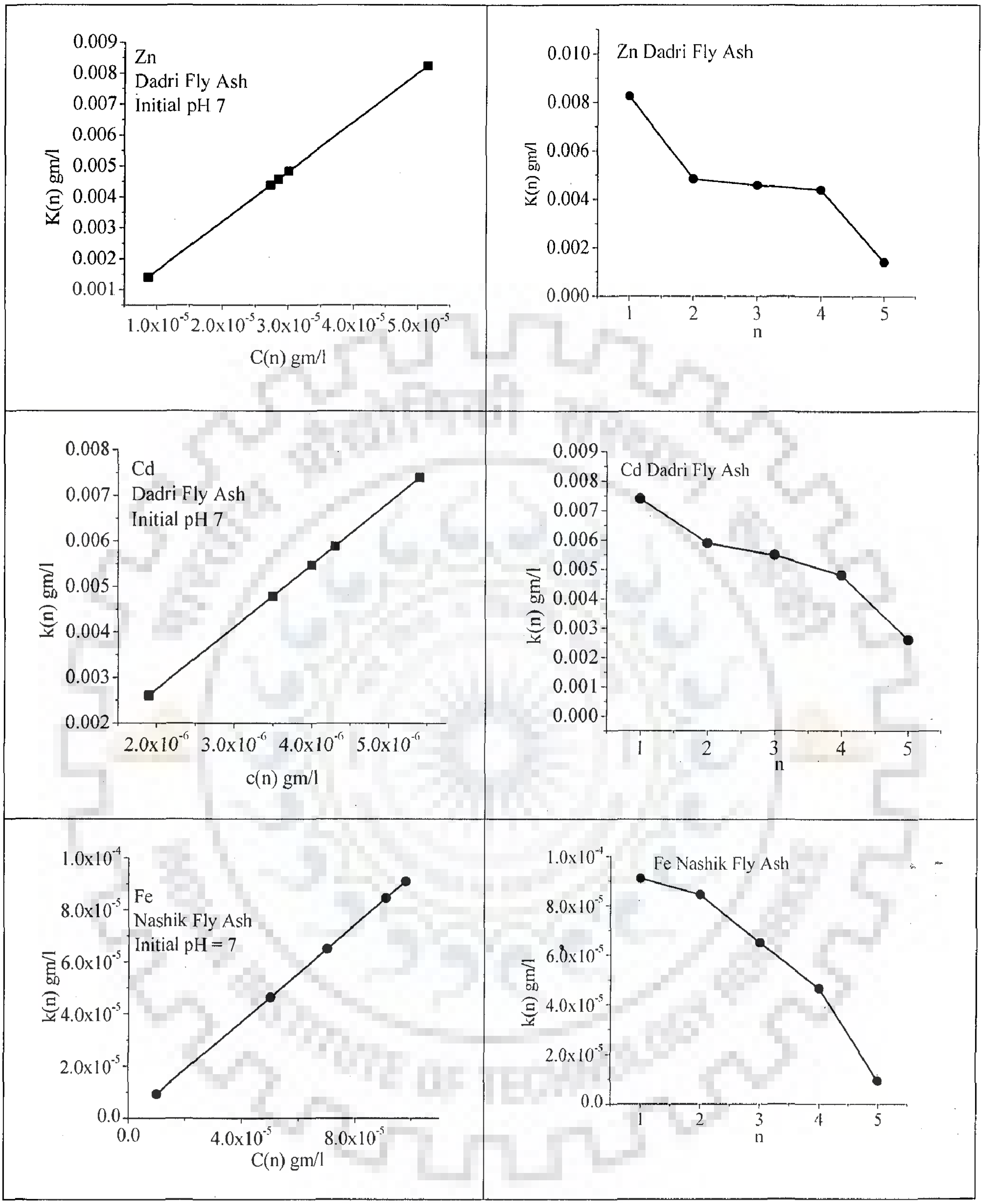

Figure 6.17 Variation of Concentration with ‘k’ and variation of ‘k’ with the stage of leaching for metals Zn and Cd of Dadri fly ash and Fe of Nashik fly ash at initial pH=7

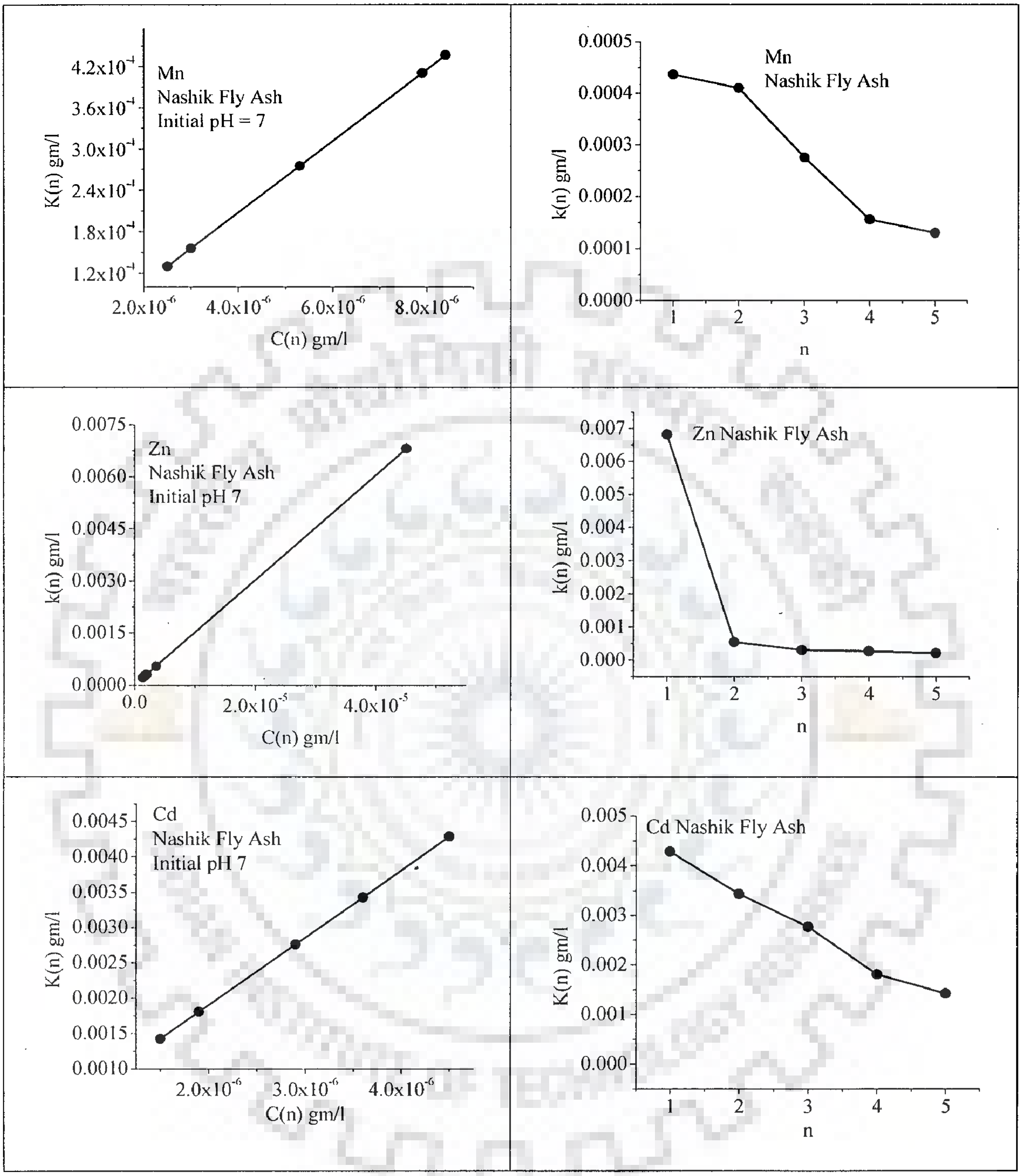

Figure 6.18 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metals in Mn Zn and Cd of Nashik fly ash at initial pH=7

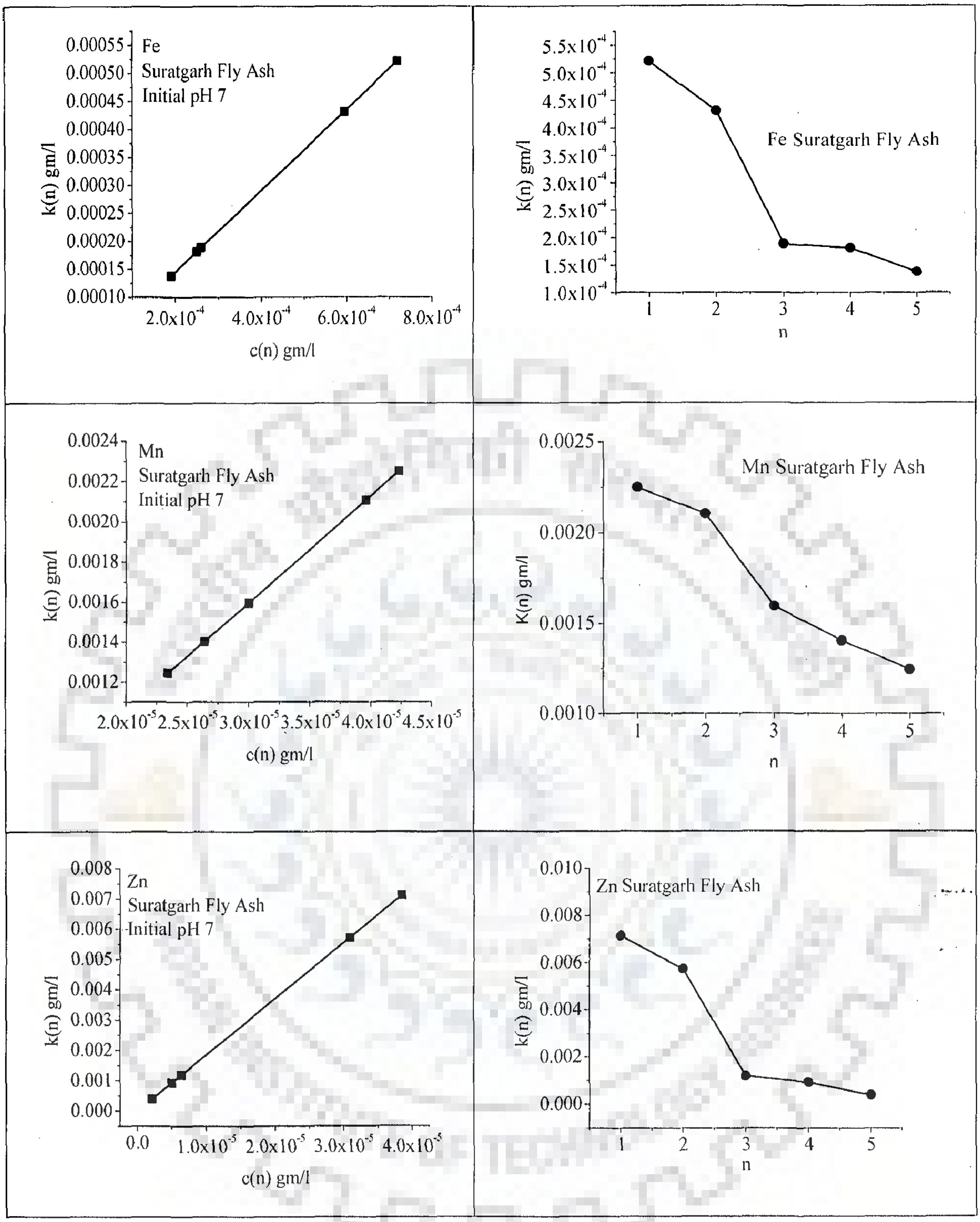

Figure 6.19 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metals Fe ,Mn and Zn of Suratgarh fly ash at initial pH=7

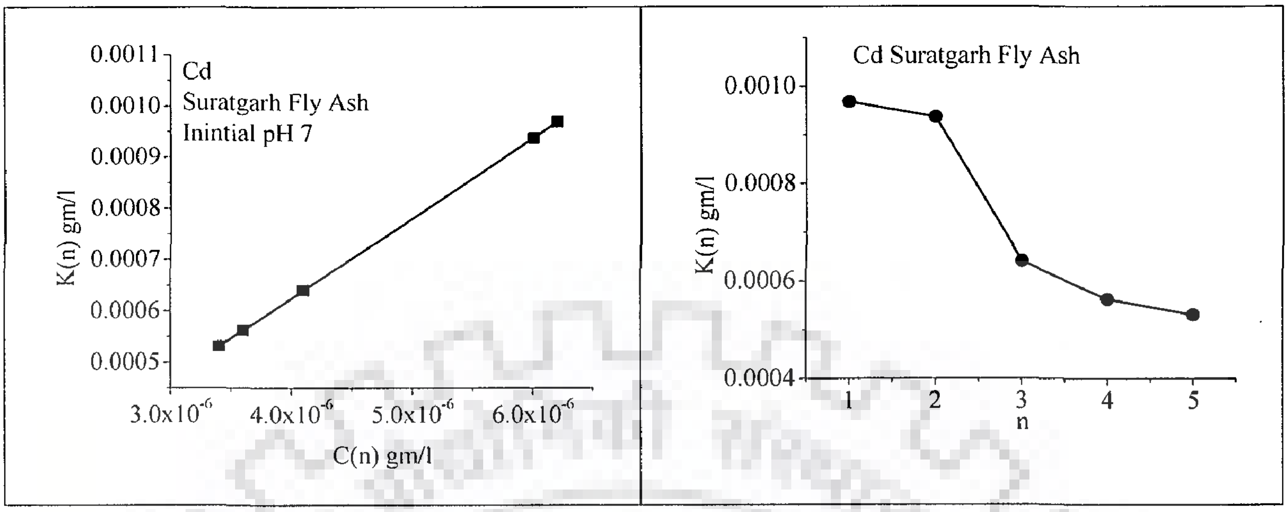

Figure 6.20 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metal Cd of Suratgarh fly ash at initial pH=7

The variations of distribution coefficient *k(n)* with *n*, and with metal concentrations $C_i(n)$ are shown in Figures 6.21 through Figures 6.26 for fly ash desorped in acidic environment. As seen in these figures, the distribution constant does not remain invariant, it changes from stage to stage. At n= four, the distribution constant decreases significantly because of change in leachant volume. The variation of *k(n)* with C*(n)* is linear. Thus whether it is neutral environment or acidic environment the variation of the distribution coefficient with C*(n)* is linear. As the concentration decreases with stage of leaching, the distribution constant being linearly dependent on concentration of an element in the leachate, would not remain invariant.

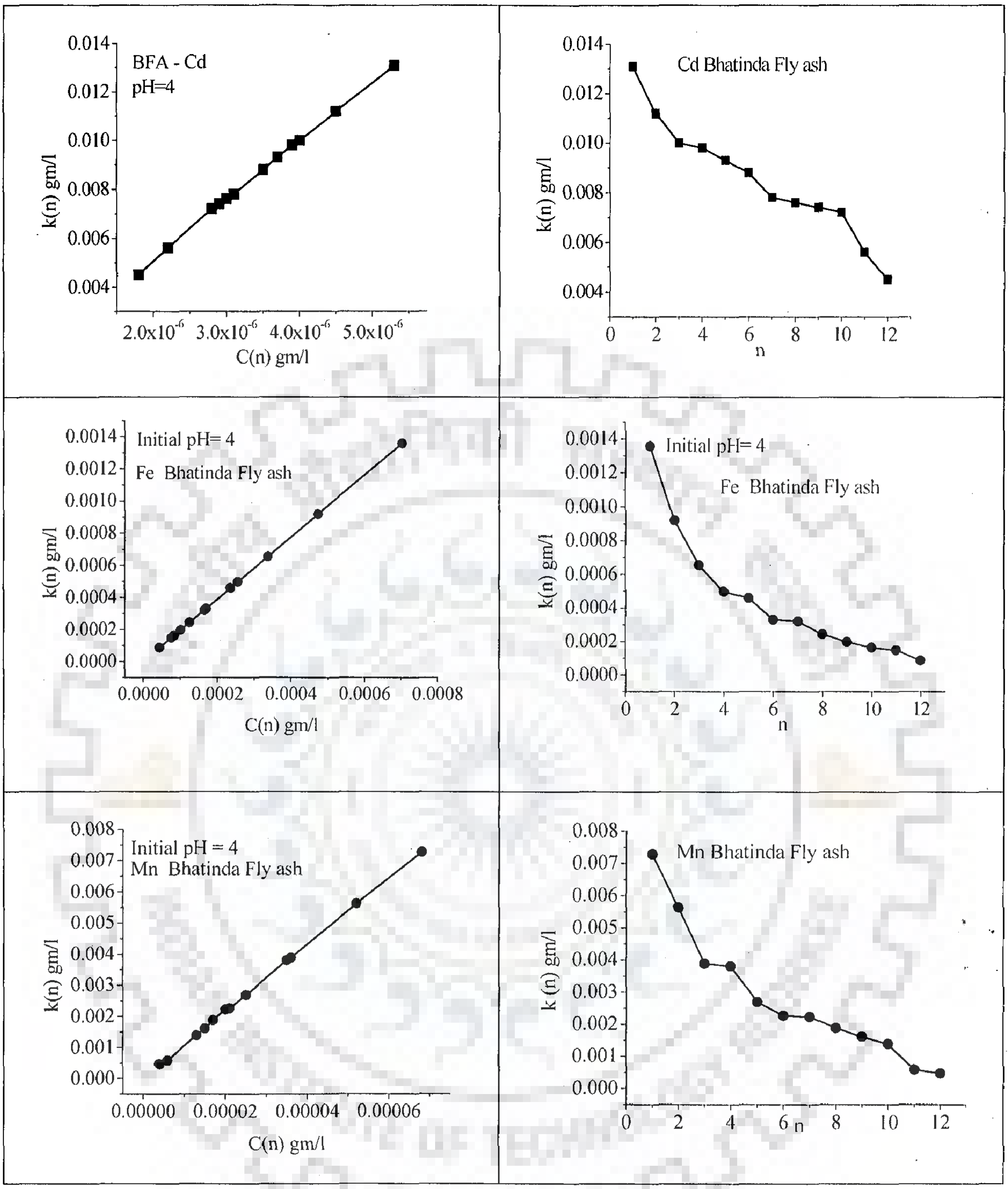

Figure 6.21 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metal Cd, Fe and Mn of Bhatinda fly ash at initial pH = 4

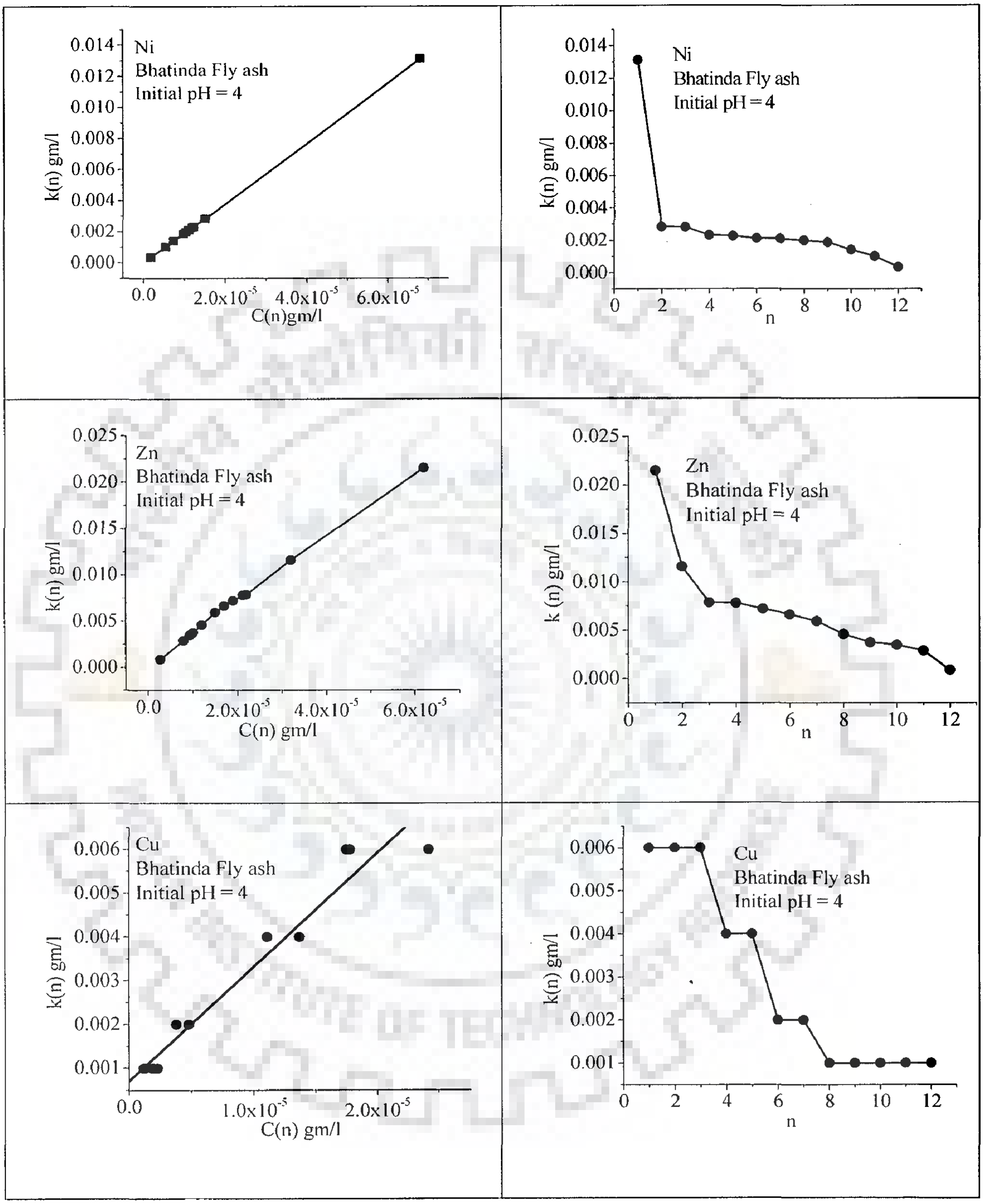

Figure 6.22 Variation of Concentration with ‘k’ and variation of ‘k’ with the stage of leaching for metal Ni, Zn and Cu of Bhatinda fly ash at initial pH= 4

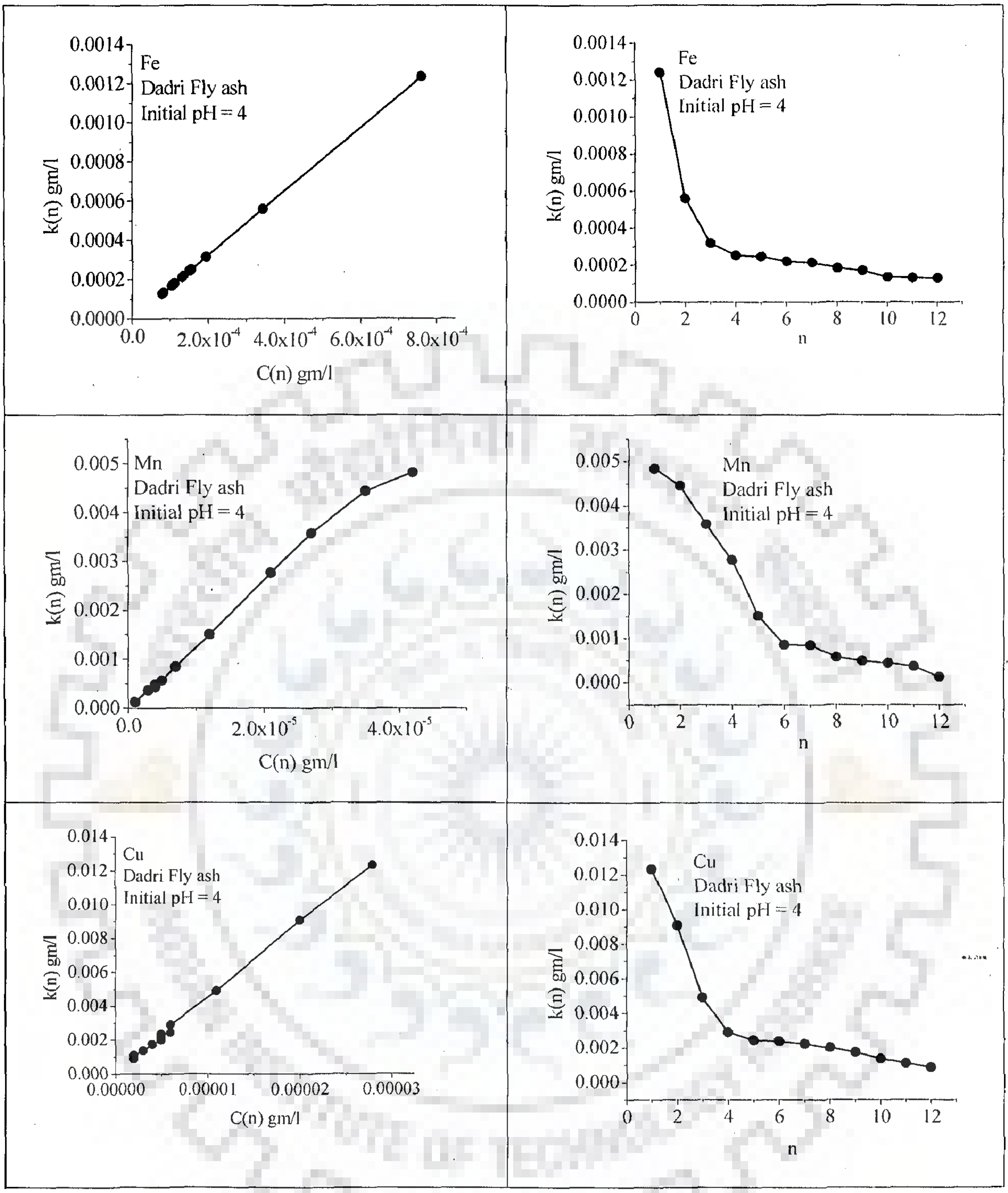

Figure 6.23 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metal Fe, Mn and Cu of Dadri fly ash at initial pH=4

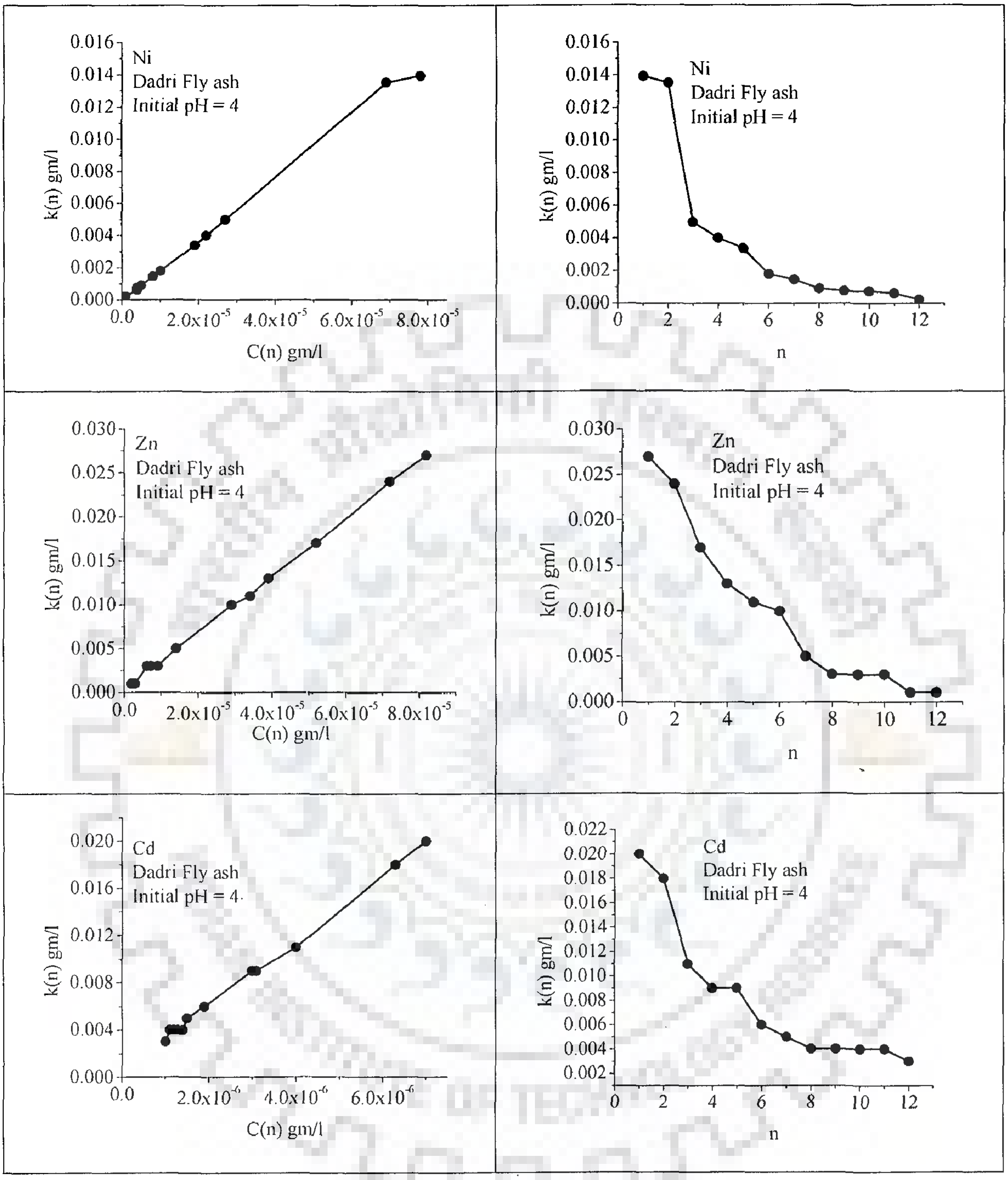

Figure 6.24 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metal Ni, Zn and Cd of Dadri fly ash at initial pH= 4

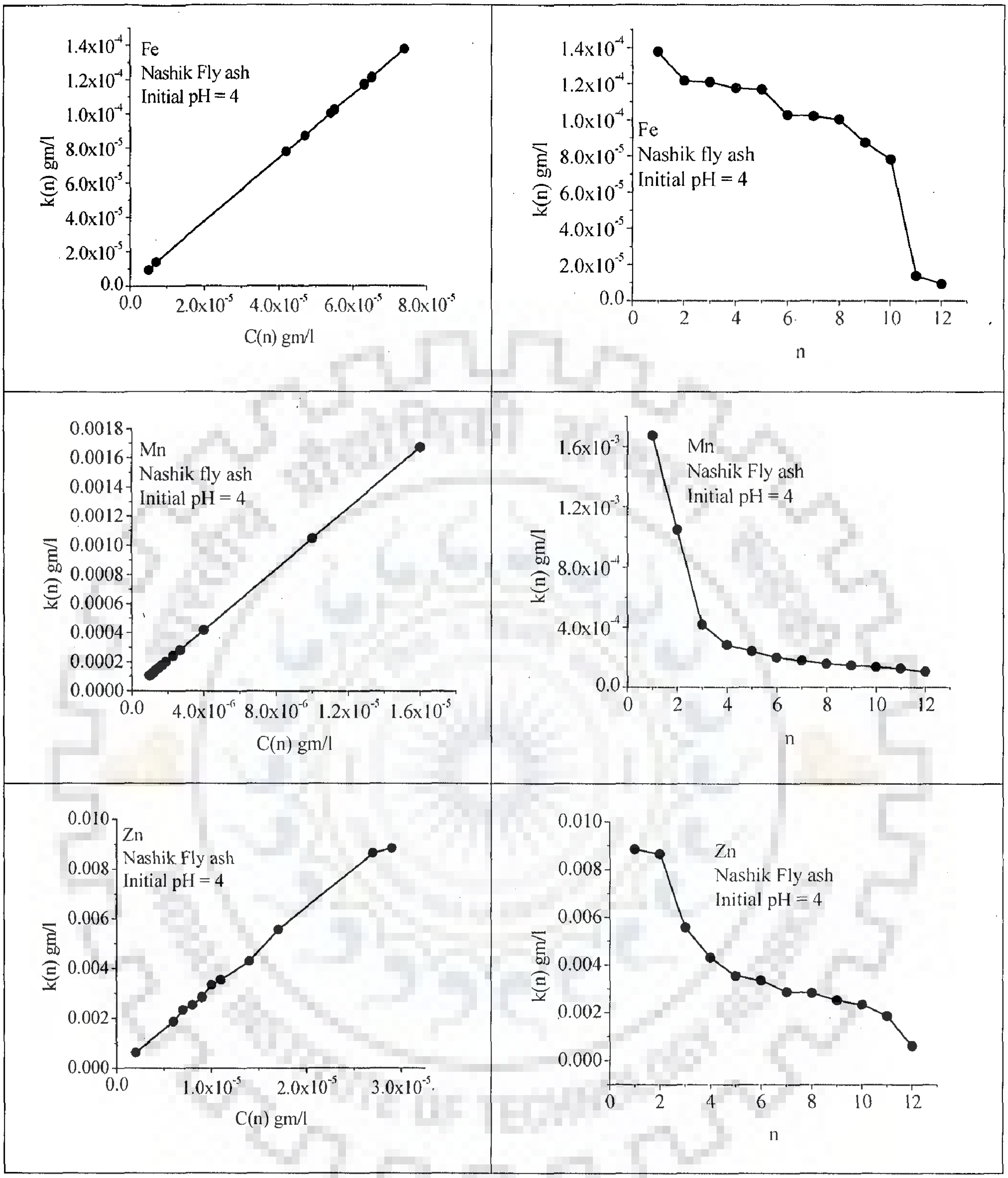

Figure 6.25 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metals Fe, Mn and Zn of Nashik fly ash at initial pH=4

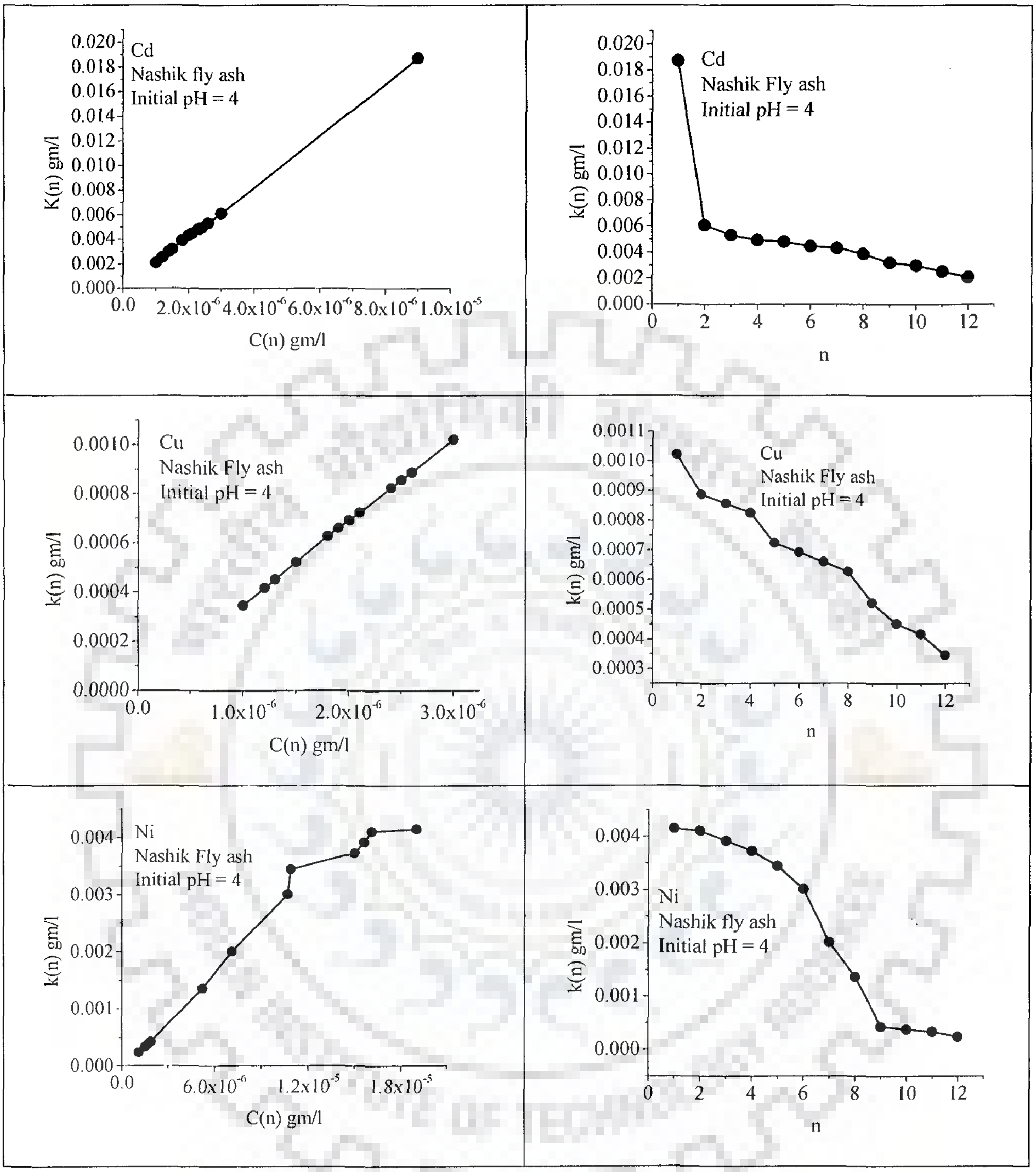

Figure 6.26 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metal Cd, Cu and Ni of Nashik fly ash at initial pH = 4

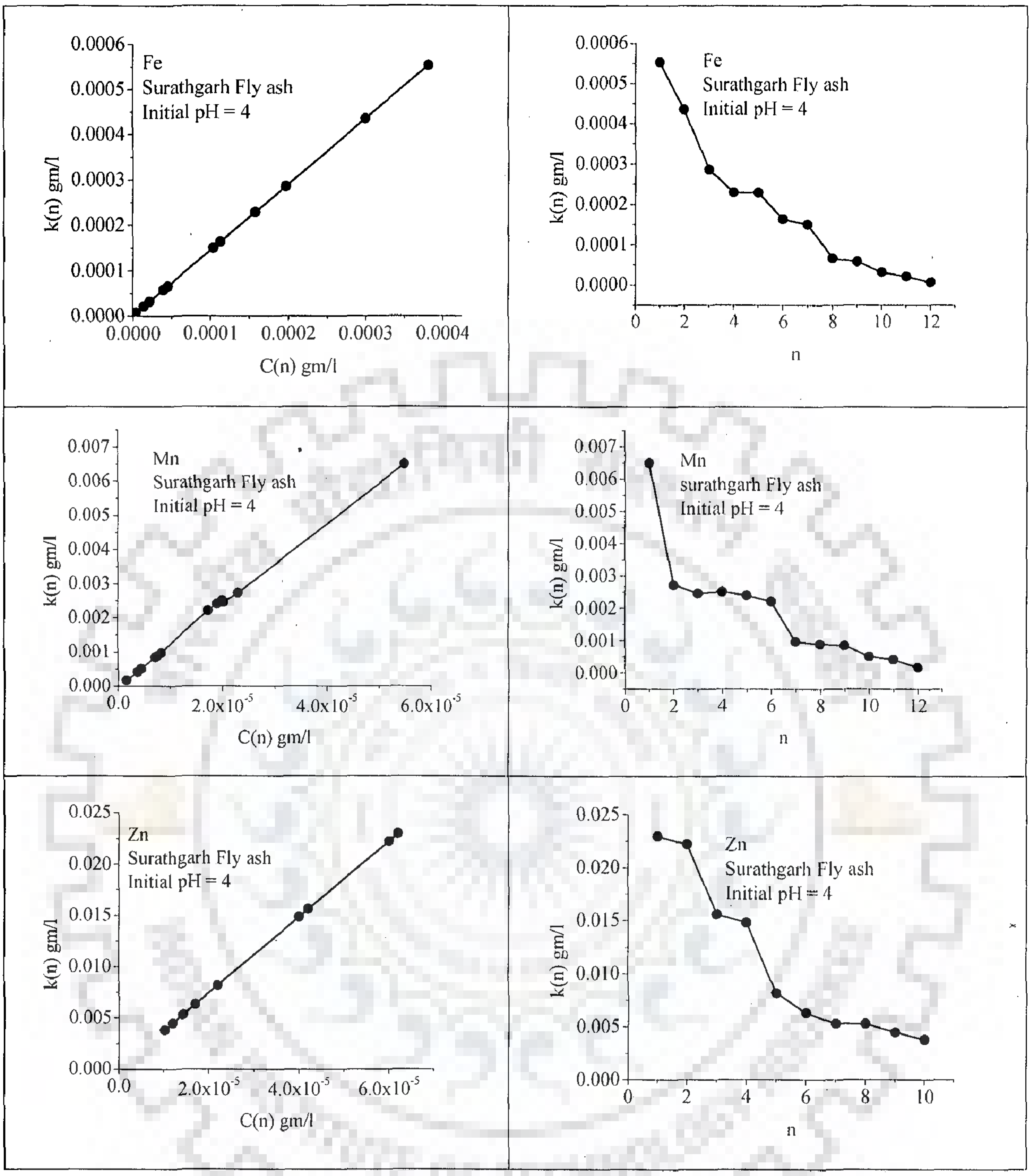

Figure 6.27 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metal Fe, Mn and Zn of Suratgarh fly ash at initial pH = 4

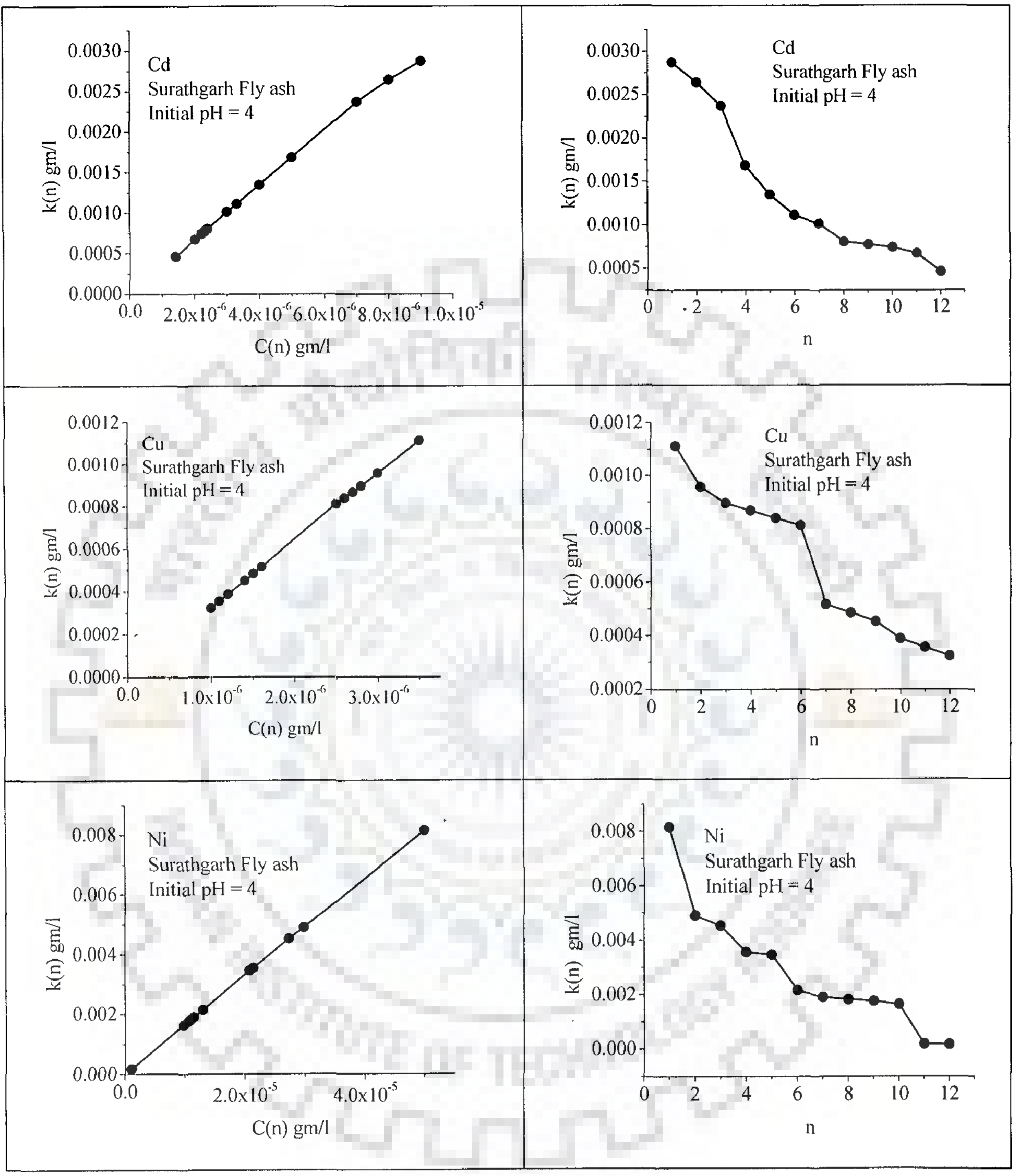

Figure 6.28 Variation of Concentration with 'k' and variation of 'k' with the stage of leaching for metal Cd, Cu and Ni of Suratgarh fly ash at initial pH = 4

Results using Equation 6.40, which has been derived considering the variation in distribution coefficient in each stage of leaching, are presented in Tables 6.7 through 6.10 for Bhatinda, Dadri, Nashik and Suratgarh fly ash leachates respectively. Results using Equation 6.20, which has been derived presuming constant distribution coefficient during each stage of leaching, are compared in the Table 6.11. It could be seen that either of the two models estimates very equal values. The reason for this is as follows:

Equation 6.20 is

$$C_i(n) = kM_i(0)\left[\frac{1}{1+\frac{kV}{\rho}}\right]^n = kM_i(0)\frac{1}{(1+S)^n}$$

Equation 6.40 is

$$C_i(n) = k(n)M_i(0)\left[\frac{1}{\{1+S(1)\}\{1+S(2)\}\{1+S(3)\}.....\{1+S(n)\}}\right]$$

In the present case S is very small and is of the order of 10^{-6}. Therefore, there is no appreciable difference between the numerical values of $\frac{1}{(1+S)^n}$ and $\left[\frac{1}{\{1+S(1)\}\{1+S(2)\}\{1+S(3)\}.....\{1+S(n)\}}\right]$.

Table 6.7 Distribution coefficient of metals in Bhatinda Fly ash leachate at each stage of leaching for which initial pH= 4

n	Fe gm/l	Mn gm/l	Zn gm/l	Cd gm/l	Cu gm/l	Ni gm/l
1	0.00136	0.00728	0.02151	0.0131	0.006	0.01311
2	9.19E-04	0.00563	0.01159	0.0112	0.006	0.00284
3	6.55E-04	0.00388	0.00786	0.01	0.006	0.00282
4	4.98E-04	0.00381	0.00781	0.0098	0.004	0.00232
5	4.59E-04	0.00269	0.00718	0.0093	0.004	0.00227
6	3.30E-04	0.00226	0.00663	0.0088	0.002	0.00212
7	3.21E-04	0.00223	0.00592	0.0078	0.002	0.00209
8	2.43E-04	0.00188	0.00459	0.0076	1.00E-03	0.00198
9	1.97E-04	0.00161	0.00373	0.0074	1.00E-03	0.00187
10	1.64E-04	0.00139	0.00347	0.0072	1.00E-03	0.0014
11	1.49E-04	5.80E-04	0.00288	0.0056	1.00E-03	0.00101
12	8.71E-05	4.64E-04	8.70E-04	4.50E-03	1.00E-03	3.33E-04

Table 6.8 Distribution coefficient of metals in Dadri Fly ash leachate at each stage of leaching for which initial pH = 4

n	Fe gm/l	Mn gm/l	Zn gm/l	Cd gm/l	Cu gm/l	Ni gm/l
1	0.00124	4.83E-03	2.70E-02	2.00E-02	0.01232	0.01394
2	5.58E-04	0.00445	0.024	0.018	0.00907	0.01353
3	3.15E-04	0.00357	0.017	0.011	0.0049	0.00499
4	2.50E-04	0.00276	0.013	0.009	0.00289	0.00401
5	2.44E-04	0.00151	0.011	0.009	0.00244	0.00337
6	2.18E-04	8.48E-04	0.01	0.006	0.00237	0.0018
7	2.13E-04	8.41E-04	0.005	0.005	0.00224	0.00146
8	1.80E-04	5.66E-04	0.003	0.004	0.00201	9.00E-04
9	1.68E-04	4.82E-04	0.003	0.004	0.00174	7.60E-04
10	1.33E-04	4.34E-04	0.003	0.004	0.00137	7.60E-04
11	1.29E-04	3.63E-04	1.00E-03	0.004	0.0011	6.20E-04
12	1.28E-04	1.21E-04	1.00E-03	0.003	8.70E-04	2.22E-04

Table 6.9 Variation in distribution coefficient of metals in Nashik Fly ash leachate at each stage of leaching for which initial pH = 4

n	Fe gm/l	Mn gm/l	Zn gm/l	Cd gm/l	Cu gm/l	Ni gm/l
1	1.38E-04	1.67E-03	8.84E-03	1.87E-02	0.00102	0.00415
2	1.22E-04	0.00105	0.00864	0.00611	8.88E-04	0.00411
3	1.21E-04	4.18E-04	0.00556	0.00533	8.57E-04	0.00392
4	1.18E-04	2.81E-04	0.0043	0.00496	8.25E-04	0.00373
5	1.17E-04	2.40E-04	0.00354	0.00483	7.24E-04	0.00345
6	1.03E-04	1.98E-04	0.00334	0.00447	6.92E-04	0.00301
7	1.02E-04	1.77E-04	0.00286	0.00432	6.60E-04	0.00201
8	1.00E-04	1.56E-04	0.00282	0.0039	6.27E-04	0.00136
9	8.73E-05	1.46E-04	0.00252	0.00322	5.22E-04	4.25E-04
10	7.80E-05	1.35E-04	0.00233	0.00301	4.52E-04	3.77E-04
11	1.38E-05	1.25E-04	0.00186	0.00255	4.17E-04	3.30E-04
12	9.29E-06	1.04E-04	6.10E-04	0.00209	3.46E-04	2.38E-04

Table 6.10 Variation in distribution coefficient of metals in Suratgarh Fly ash leachate at each stage of leaching for which initial pH = 4

n	Fe gm/l	Mn gm/l	Zn gm/l	Cd gm/l	Cu gm/l	Ni gm/l
1	5.53E-04	6.50E-03	2.30E-02	2.87E-03	0.00111	0.00816
2	4.35E-04	0.00273	0.02224	0.00264	9.58E-04	0.00491
3	2.85E-04	0.00246	0.0156	0.00237	8.97E-04	0.00453
4	2.29E-04	0.00251	0.01483	0.00168	8.68E-04	0.00355
5	2.28E-04	0.0024	0.00817	0.00135	8.40E-04	0.00346
6	1.63E-04	0.00221	0.0063	0.00111	8.13E-04	0.00215
7	1.50E-04	9.72E-04	0.0053	0.00102	5.17E-04	0.0019
8	6.57E-05	8.90E-04	0.00528	8.05E-04	4.85E-04	0.00181
9	5.77E-05	8.46E-04	0.00446	7.74E-04	4.53E-04	0.00176
10	3.18E-05	5.10E-04	0.0038	7.42E-04	3.88E-04	0.00163
11	2.11E-05	4.15E-04	**	6.73E-04	3.55E-04	1.77E-04
12	6.40E-06	1.74E-04	**	4.61E-04	3.23E-04	1.61E-04

** *Iteration does not yield*

Table 6.11 Comparison of k(n) with C(n) at stage of leaching as obtained from Equation 6.40 and Equation 6.20

Sr no.	C(n) (gm/l)	k(n) from Equation 6.40. (variable k) (gm/l)	k(n) from Equation 6.20. (constant k) (gm/l)
1	0.8E-03	0.7690020E-03	0.7687121E-03
2	0.22E-03	0.2114020E-03	0.2113960E-03
3	0.21E-03	0.2017920E-03	0.2017870E-03
4	0.19E-03	0.1825720E-03	0.1825691E-03
5	0.18E-03	0.1730020E-03	0.1729602E-03

6.5 CONCLUDING REMARKS

With constant influx leachant volume, whether the leachant is acidic or neutral, the concentration of an element, $C_i(n)$, in the leachate decreases exponentially with *n*, the stage of leaching. An exponential function can be fitted to predict the leachate concentration at a higher value of n. The distribution constant $k(n)$ specific for an element is linearly proportional to $C_i(n)$, the concentration of the i^{th} element in the leachate. Therefore, as during leaching the concentration of the element in the leachate would change, the distribution constant is not invariant. An assumption of a constant distribution coefficient during process of leaching is not applicable.

CHAPTER 7

FLY ASH SLURRY INFILTRATION IN SOIL COLUMN

7.1 PRELUDE

Understanding of the transport and attenuation of chemicals in the subsurface is essential for effective management of risks posed by chemicals and their possible impact on groundwater resources. In actual practice fly ash is disposed in the slurry form in the ash pond by wet disposal scheme. Leaching of heavy metals in aqueous phase due to land disposal of fly ash is a major environmental concern. Application of fly ash over the soil generally increases trace element concentration to a degree that depends on fly ash properties, rate of application and soil physicochemical characteristics. Laboratory leaching tests are used to determine the leachability of metals from the coal fly ash. To evaluate the potential of pollutant movement through the soil profile after surface application of fly ash slurry, column experiment was conducted. Adsorption and exchange properties in combination make up pollution abatement capacity of soil.

To determine the feasibility of land disposal of fly ash, it is necessary to study the mechanisms by which pollutants, both organic and inorganic, are attenuated in soil. In the present study soil column experiments are conducted to make the assessment of the transport of metals The present study is limited to determine the presence of metals Fe, Mn, Zn, Ni, Cu and Cd. Purpose of this experiment is to verify that after application of slurry in soil column, which elements are recovered in the percolate water as pore water concentrations.

7.2 PROPERTIES OF FLY ASH AND SOIL USED IN COLUMN STUDY

For the experiment the soil samples were oven dried and sieve analysis was carried out. The pH of the soil was measured by mixing it with 1:1 solid water suspension. The soil was thoroughly cleaned prior to use with de ionized water. Then organic impurities, if present, were removed by soaking the soil in hydrogen peroxide (5% H_2O_2) for 3 hrs, followed by washing with double distilled water. The soil was then washed thoroughly with distilled water and it was oven dried at 105°C for 24 hrs. The properties of fly ash, and soil used in the column test are given in Table 7.1. The total concentrations of Fe, Mn, Zn, Cd, Cu and Ni were given in the soil compared to total concentrations of fly ash and are within their ranges of world averages.

Table 7.1: Properties of fly ash and soil used in this study

Soil/ fly ash parameter	Bhatinda Fly ash	Nashik Fly ash	Bhatinda Soil	Nashik Soil
pH	6.7	8.7	6.9	7.2
% Silt	79.8	79.2	13.6	13.4
% Sand	20.2	20.8	86.4	86.6
Fe	2685	2630	977	798
Mn	129.7	132.5	117	108
Zn	64.85	66.2	58.9	52.2
Cd	8.1	10.5	1.1	1.0
Cu	69.3	58.9	38.35	54
Ni	108.3	117.5	39.85	48

All metals concentrations are in mg/kg

The fly ash slurry at L/S ratio 10 (250 ml: 25 gm, Fly ash and deionized water with initial pH-4) is allowed to leach for 24 hours and on the next day (again pH was adjusted to 4), it is poured in to the soil column from the top and leachates were collected at the bottom of the column. The concentrations of metals leached at L/S ratio 10 used in soil column experiment before application into the soil column are given in Table 7.2.

Table 7.2: Concentrations of fly ash slurry used in column test

Metal Concentrations	Bhatinda Fly ash mg/lit	Nashik Fly ash mg/lit
Fe	0.65	0.15
Zn	0.09	0.03
Mn	0.09	0.025
Cd	0.005	0.0035
Cu	0.02	0.003
Ni	0.03	0.015

7.3 SOIL FLY ASH SLURRY COLUMN STUDY

The schematic diagram of an open percolation column used for leaching experiment is shown in Figure 7.1 was made of Acrylic pipe, circular in cross section diameter 4.3 cm and total depth 1 m, out of which depth 30 cm, is filled by soil. At the bottom filter paper was placed. Soil was packed in column in 5 cm lift and tamped with wooden compactor which occupied 0.75 kg of soil and top was kept unpacked for fly ash slurry application. Leachate was collected in 500 ml polyethylene beakers. Column is saturated with the deionized water before the start of the experiment and excess water was allowed to drain for 24 hours.

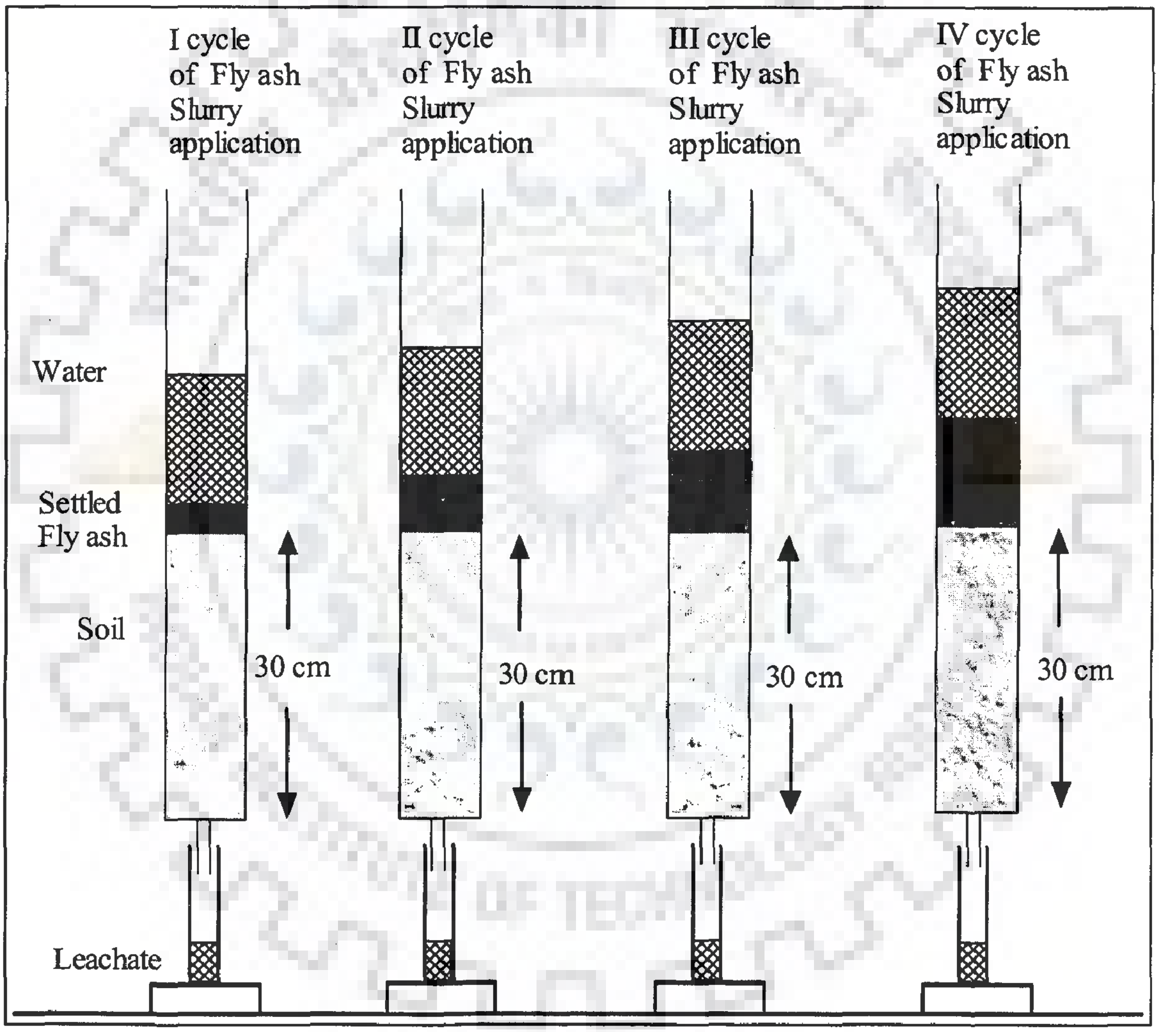

Figure 7.1: Schematic representation of fly ash slurry application to soil column

Fly ash slurry was poured from top and leachates were collected at the bottom of the column. Second layer of slurry is poured only after the first percolate is completely collected as leachate at the bottom of the column. Leachtes were tested for pH, TDS and EC and then acidified to prevent precipitation. On the same line successively total 16 layers of fly ash slurry were applied from the top of the column. Once the slurry application to soil column is stopped i.e. from 17th cycle onwards column is washed with deionized water for 6 days with 350 ml of water at each cycle. The soil column test was conducted for total 44 days. Collected leachate were tested for Fe, Mn, Cd, Cu, Ni and Zn.

7.3.1 EFFECT ON pH, TDS AND EC

The pH value of the leachate were consistently observed in the range of 7- 8.5 which is shown in Figure 7.2. Oxides on the ash surfaces supply hydroxyl ions responsible for the elevated pH. Similar findings are reported by Fulekar, M. H., et al., (1992); Hajarnavis, M. R., et al., (2003). Bin Shafique, M. S., et al., (2006) observed through the soil and fly ash mixed column study that the pH of the pore fluid is persistent for at least 30 pore volumes of flow, which corresponds to at least 30 years of the flow in the field. In the present investigation pH is likely to remain alkaline throughout the operating life of ash pond. In the alkaline environment the leaching metals is less.

Variation of total dissolved solids as a function of number of cycles of application of is shown in Figure 7.3, it can be seen that the TDS value is high in early cycles and after 6th cycle it almost gets stabilized. It is observed from the Figure 7.2 and Figure 7.3 that after 6th cycle and in the stability field ranges most of the metals are below range for drinking water standard limit. Twardowska, I., et al., (2003), observed after analyzing water quality within and outside the ash pond of Chandrapura thermal power plant located at Maharashtra, India that pH of the water is in the range of 7.4 – 8.3 as stability field and most of the metals are below detection limit in this range. Of the 6 metals examined in this experiment only Fe, Mn and Zn were detected on consistent basis through soil column. Since the mobility of Cd and Ni in soils is limited as the clay fraction of the soil has high affinity for these heavy metals Thakare R., (1996) and therefore Cd, Cu and Ni were not detected in leachate.

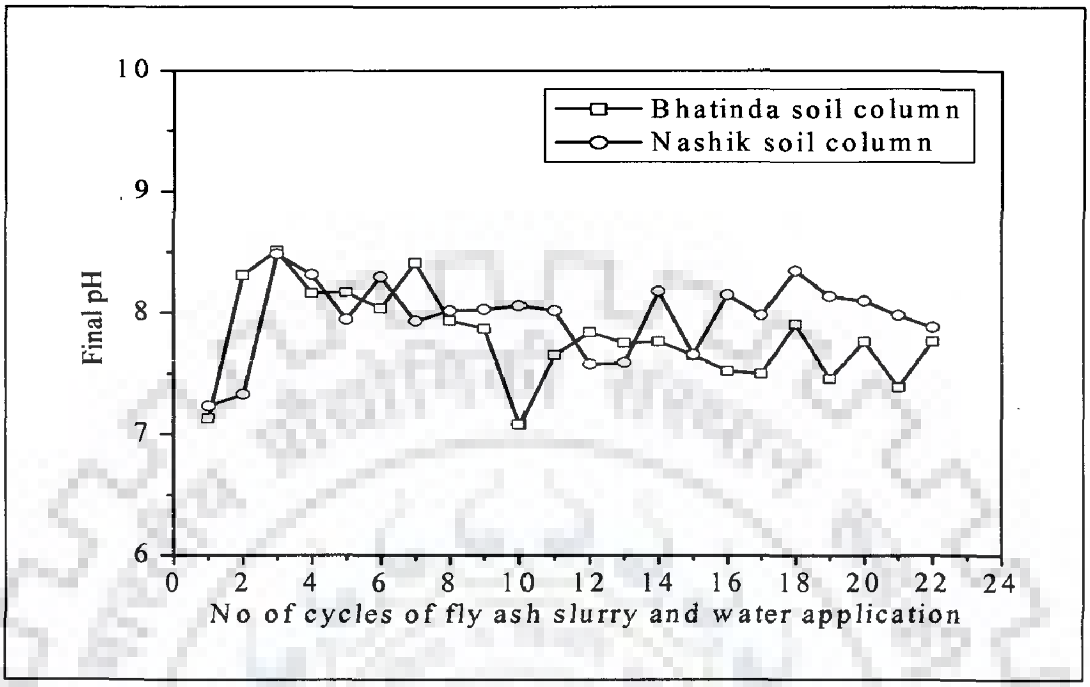

Figure 7.2 Variation of pH to fly ash slurry application in to soil column

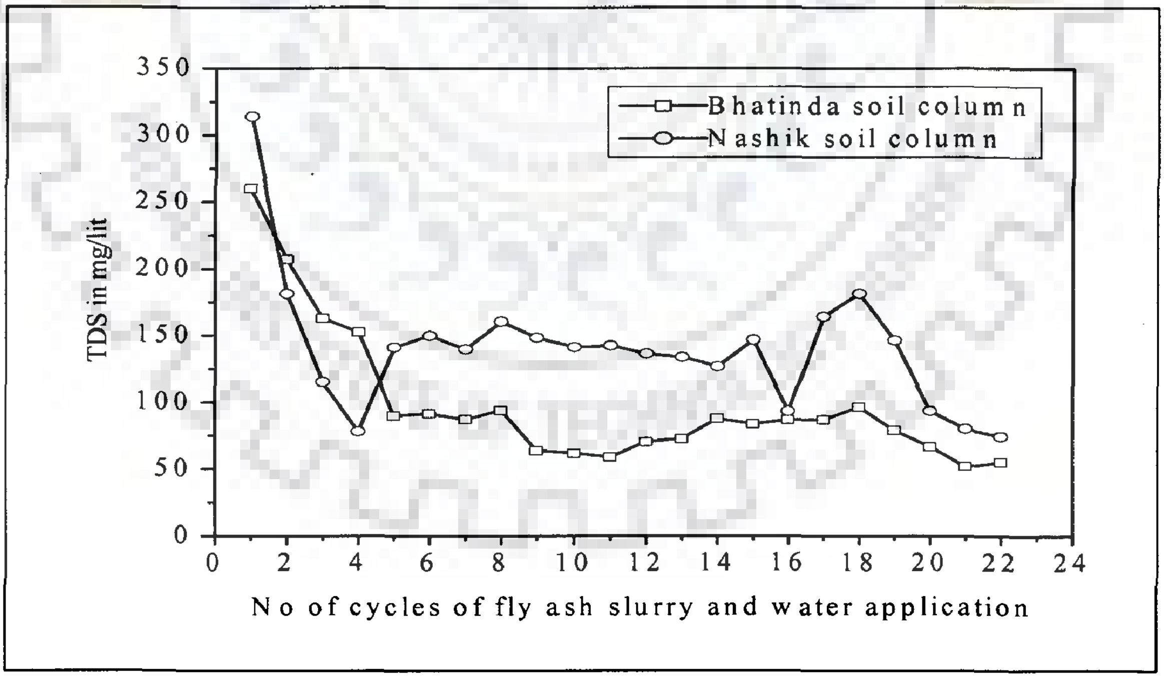

Figure 7.3 Variation of TDS to fly ash slurry application in to soil column

7.3.2 Mobility of Metals through Soil Column with Fly Ash Slurry Application

Recovery of metals in leachates is consistent only for Fe, Mn and Zn, rest of the metals are get adsorbed in the soil or their influent concentration might be less. No Cd was detected in the leachate which may be due to less concentrations of Cd in the soil and coal fly ash used in this soil column study. Mukherjee S., et al., (1984) observed that Cd has higher sorption value than Zn. In another study Williams, D. E., (1980) reported that Cu was considered to be closely associated with the humic acid fraction and strongly complexed and therefore is considered least mobile among the tested pool of metals. Bilski, J. J., et al., (1995) observed that recovery of metals in leachate increased with an increase in the rate of fly ash application except Cu.

In the present investigation the variation of metal concentration in the soil column prepared from samples from Bhatinda fly ash is presented in Figure 7.4. It can be seen that leaching of iron is lower with values ranging from 0.049 mg/l to 0.13 mg/l up to 10th cycle and again it increases from 11th cycle onwards. Later it remains in the stability zone of 0.24 mg/l. For Mn leaching is between 1st cycle to 9th cycle and from 10th cycle onwards upto 16th cycle it remains in the range of 0.0079 to 0.029 mg/lit. Similarly for Zn leaching is more in initial stages of leaching from 1st cycle to 9th cycle and then onwards it remains almost in the range of 0.029-0.042 mg/l. From 17th cycle onwards it is washed with deionized water up to 22nd cycle. Again it shows leaching of Fe, Mn and Zn and again it drops at 22nd cycle as shown in Figure 7.4.

Similarly experiments have been conducted for the samples collcted from Nashik power plant and the variation of metal concentration in leachate for Nashik soil column is presented in Figure 7.5. In this case leaching of iron is lower i.e. of 0.016 mg/lit in 1st cycle to 0.026 mg/l up to 10th cycle and again it increses 11th cycle onwards and later it remains in the stability zone of 0.037 mg/l. For Mn, leaching is between 1st cycles to 5th cycle, from 6th cycle to 8th cycle it drops down. From 9th cycle onwards upto 16th cycle it remains in 0.014 to 0.033 mg/l. Similarly for Zn leaching is more in initial stages of leaching from 1st cycle to 10th cycle and then onwards it remains almost in the range of 0.017-0.033 mg/l. From 17th cycle onwards it is also washed with deionized water up to 22nd cycle. Again it shows leaching of Fe, Mn and Zn and later it drops at 22nd cycle as shown in Figure 7.5. Sandy texture and low organic carbon content are the probable main factors for high mobility of Zn in the soil column (Li, Yuncong., et al., 2003).

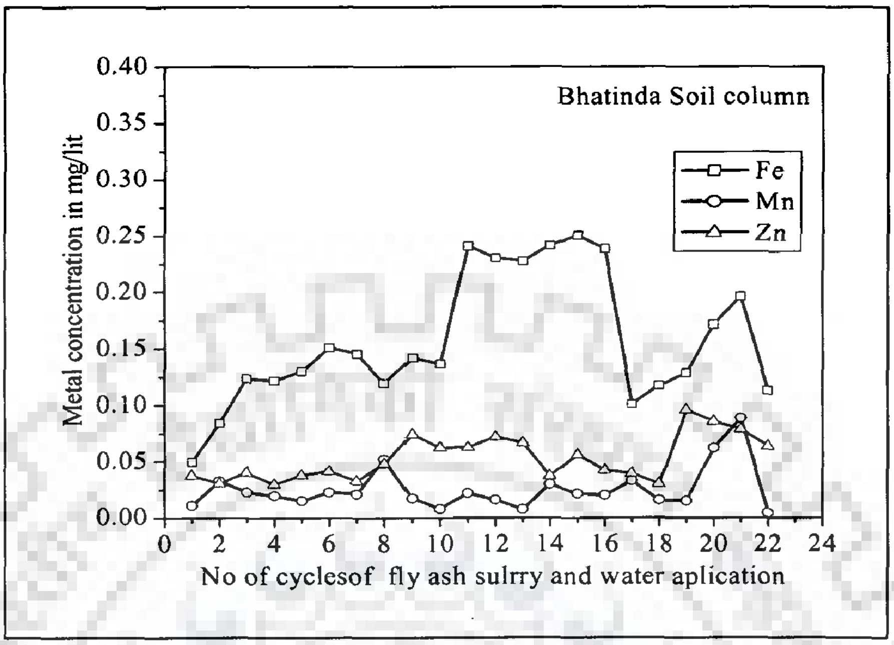

Figure 7.4 Variation of metal concentrations in leachates for Bhatinda soil column

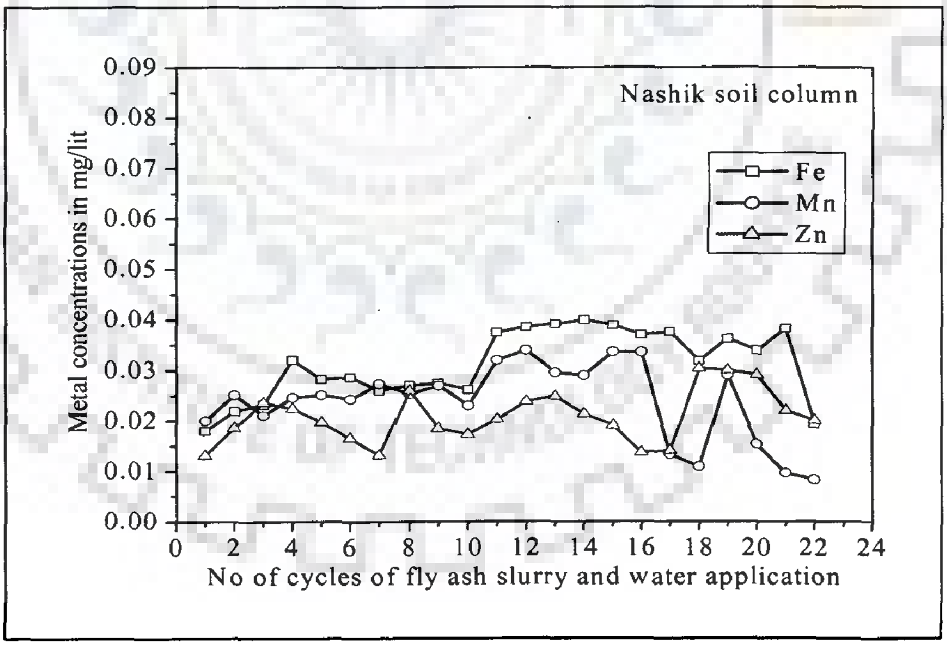

Figure 7.5 Variation of metal concentrations in leachates for Nashik soil column

7.4 NEED FOR PROVISION OF LINER

In the present investigation studies carried out are limited to the determination of Fe, Mn, and trace metals such as Zn, Ni, Cu, Cd, which suggest that it is likely to pollute the unsaturated zone first and not likely to pollute the groundwater. But depending upon chemical composition of ash, field conditions and hydro-geological conditions and pore water velocity, in longer run it may pollute groundwater. The seasonal variation plays important role in downward percolation of the leachate. During dry season the only part of slurry water contributes to leachate but in rainy season the quantity of the leachate will be more and it move at faster rate compared to dry season percolation rate and which will enhance the possibility of groundwater contamination. As the height of ash deposit increases, fresh ash at the top of the deposit contributes to the downward movement of trace element. In addition long term weathering of ash may also result in the release of trace elements from the older ash at the bottom of the ash pond (Sivakumar D. S., 1996).

Sen, P. K., et al., (1996) concluded that the presence of contaminants in both the season are high and there is every possibility, that the leachate generated in the bottom layer of the ash ponds had began to reach down gradient water resource. This suggests that down gradient groundwater had not reached steady state concentration conditions with respect to the movement and mixing of leachate to the down gradient location. With every slurry disposal cycle, this steady state concentration condition will change and it is likely to increase in down gradient groundwater over next several years. Sandhu S. S., et al., (1993) reported that older ash disposal basins are potential source of groundwater contamination even though ash deposition has ceased. Sinha R., et al (2000), observed increased trace metal concentration in the two boreholes in side the ash pond of Feroze Gandhi Unchaahar Thermal Power Plant, Unchahar, Uttarpradesh, India and exceeded WHO drinking water standards. Twardowska, I., et al., (2003), reported that in India, the significant water quality of wells is altered due to trace metals in the ash pond and down gradient of ash pond at Chandrapur ash pond, Maharashtra due to wet disposal of fly ash.

Use of dry ash handling system or installed lining materials in the ash pond to reduce seepage or infiltration of leachate is probable solution to avoid the contamination of water bodies. Conventional technologies for the removal and recovery of heavy metals from waste water include chemical precipitation, ion exchange, membrane separation, adsorption on activated carbon and electrolytic methods. The addition of appropriate chemicals directly to ash sluice water can effectively control metal release by forming insoluble compounds which precipitate in ash pond. Lime, CaO is the chemical of choice and is effective in promoting the formation of insoluble hydroxide. Since ash pond water is generally low in dissolved carbonate, the addition of soda ash, Na_2Co_3, may prove more effective by forming metal carbonates which are generally more insoluble than respective hydroxide.

To reduce seepage losses from ponds or waste impoundments for water conservation and environmental protection, the liners are used. Choice of lining material is important factor, because at least 100 Ha of ash pond area is to be covered; therefore local availability is most important consideration for selection of material. Various materials such as clay, wooden charcoal, rice husk, bioactive material (water hyacinth), plays important role. Low permeability clay liners are easily available and cheap. Kharkhanis M., et al., (2005) used rhizofiltration technique for the treatment of coal ash leachate. Bioactive materials such as (water hyacinth) was employed for the treatment of fly ash leachate by Mahakur, D., et al., (1998). Lecahate can be collected and taken to the sump well and then pumped for further treatment. The pollutant from leachate can be removed by chemical treatment followed by activated carbon treatment before its disposal. Since this treatment is quite costly the alternate approach of storage of the leachate in lined solar evaporation pond in which duckweed or water hyacinth is grown to remove the chemical pollutants (Hajarnavis, et al., 2003).

Low permeability clay liners are easily available and economically viable and they are also known to retain the heavy metals due to their surface characteristics (Cherry 1987; Fetter, 1990). Chemical liners are expensive and sometimes subject to degradation. Therefore provision of liner is must in order to prevent the contamination of groundwater through ash pond leachate via trace metal enriched seepage of leachate. As per Pollution Control Board of India norms, an impervious membrane has to be provided to prevent pollution of the ground water (Gandhi, S. R., 2005). World Bank (1998) has given guideline to monitor and treat leachates and overflows from settling ponds in addition to their disposal in lined places to avoid contamination of water bodies. It is also kept in mind that, proper hydro-geological investigation for ash pond area are necessary, in order to decide the requirement of liner i.e. it should be site specific, and which will save the cost of lining material.

7.5 CONCLUDING REMARKS

The pH of the leachate is persistent for the period of test and due to this pH the mobility of metals is less because it is in the range of 7.1- 8.5, which is found to be a stability zone. Concentrations of metals used in the study were less particularly of Cd, Cu and Ni. Application of fly ash increases the concentrations of metals in leachates and onwards it gets stabilized. The release of metals appears to be adsorption controlled, due to which attenuation of heavy metals took place. Attenuated heavy metals, however, are not biodegradable. They are stored in the soil and may be remobilised and migrate into groundwater when the soil's adsorption capacity is exceeded or its properties change. The presence of organic compounds such as, phenols and fatty acids in the leachate, might also result in increased heavy metal mobility. Ultimately it contributes to contamination of soil, surface water and groundwater. To protect unsaturated zone and groundwater provision of liners is essential.

CHAPTER 8

FIELD INVESTIGATIONS AT NASHIK ASH POND

8.1 PRELUDE

Land disposal of fly ash is a major concern due to its effect on local air quality, soil and terrestrial vegetation, also on groundwater and surface water. In the present study detailed field investigations were made at Nashik ash pond. Area under investigation consists of basic ash pond, neighbourhood area of ash pond and two ash pond effluent channel namely Eastern side and Southern side. The purpose of this study was to investigate in detail the entire fly ash pond, Eastern side ponded ash pond, and two ash pond effluent channel namely East side as well as South side for transport of the selected metals for surface water and Darna river water contamination. Groundwater samples were also collected from two villages namely Kotamgaon and Hinganvedhe and investigated for migration of trace metals in to groundwater from natural pond seepage.

8.2 ASH POND DESCRIPTION

The Nashik ash pond is situated near village Eklahare, 7 km from Nashik Road railway station, Maharashtra, India. The location map of Nashik thermal power plant is shown in Figure 8.1. The water requirement of the power station is met by pumping water from the river Godavari by means of four river water pumps of capacity 3050 m^3 per hour, out of which normally two pumps are running, the other two are kept standby. The ash disposal area is within the range of 1 km from the power station and total area of ash pond is 389 Ha. Usually fly ash is disposed in ash pond in an alternate fashion. When one primary pond is filled, the other is allowed to dry for the removal operation. Pond water overflow is recycled during ash sluicing process. Each pond cycle has duration of 4-5 months.

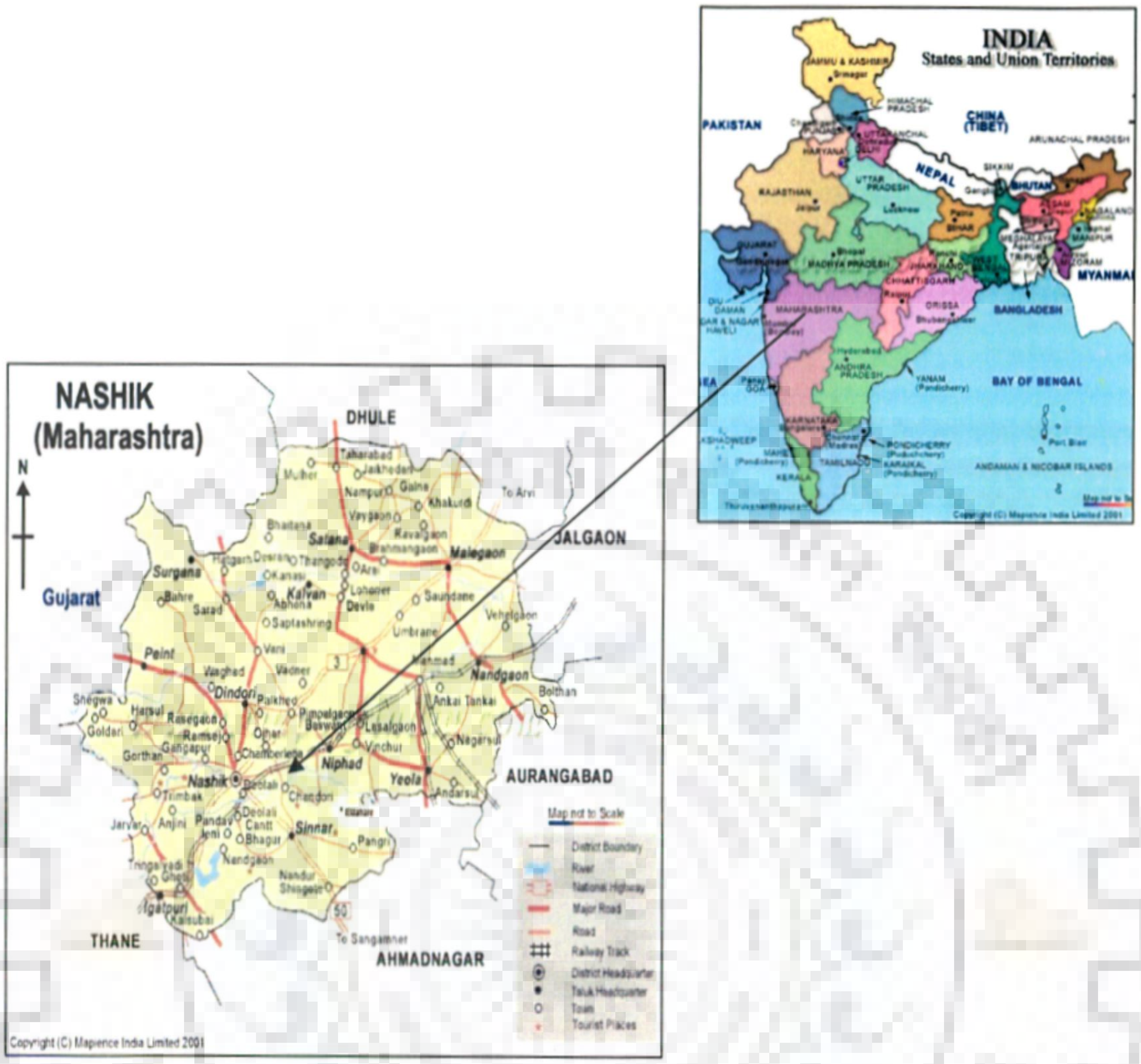

Figure 8.1 Location map of Nashik Thermal power plant at Eklahre Village.

The Great Trap region of the Deccan covers the whole district, which is entirely of volcanic formation. The volcanic portion consists of compact, stratified basalt, and an earthy trap. The basalts are the most conspicuous geological feature. To the west they lie in flat-topped ranges, separated by valleys, trending from west to east. In some flows the-basalt is columnar and then it weathers into the fantastic shapes. The formation at the base of the traps is chiefly amygdaloidal, containing quartz in vertical veins, crystals and zeolitic minerals, especially apophyllite weathering into a gray soil. The absence of laterite, which caps the summits of the hills to the south, is a curious feature in the geology of the area. The basalt is either fine textured or it is coarse and nodular. Sheet jointed amygdaloidal basalt below the overburden roughly up to 1 to 1.5 m thick underlain by compact basalt broadly jointed. In short there is a flow of compact basalt belonging to Deccan trap formation, the top of which became vesicular amygdaloidal basalt which is typical characteristics of compact basalt flow is occurring in Maharashtra state of India. There is every possibility of conversion of this top vesicular amygdaloidal basalt part into sheet jointed amygdaloidal basalt which is locally referred as murum. Water table is at 9- 10 m.

8.3. EFFECTS OF FLY ASH DISPOSAL ON SOIL AROUND POWER PLANT

Dry fly ash easily becomes windborne due to minute size particles during transportation, dumping and even in idle conditions due to its less cohesive forces in fly ash particles. Possible pollution pathways are shown in Figure 8.2 for an ash mound. Particle size analysis shows that more than 90% of fly ash particles in Nashik fly ash are in the range of 0.1μm-65μm making them susceptible to air pollution. The climate in the major part of India is dry tropical with temperature varying from 30-50°C almost for 8-9 months throughout the year. Under such temperature condition there is every possibility that upper surface of ash pond may remain dry due to evaporation losses. Air pollution from such ash pond is never ending problem, usually provoking the people lying adjacent to ash pond and this is serious problem during summer season.

Earlier studies indicated that long term deposition of fly ash led to considerable changes in soil characteristics, plant available nutrients, and trace element concentration around plants. These changes are attributed to disposal of fly ash in the form of slurry and emission and atmospheric fallout of fly ash. (Singh, J., et al.1994, Praharaj, T., et al., 2003, Gulec, N., et al., 2000). The contamination is more pronounced in the soils within or close to the predominant wind direction (Mandal, A., et al., 2006, Singh, J., et al. 1994). The physicochemical and mineralogical properties of the profile soil in the predominant wind direction are found to be modified compared to the background and other soil profile (Mandal, A., et al., 2006, Praharaj, T., et al., 2003.).

After assessment of radioactive contamination around Yatagan (Mugla, Turkey) coal fired power plant waste disposal site was found to be enriched with radium (Baba, A., 2002). Studies of Kolaghat Thermal power station reveals that Radionuclides (U, Th) show enrichment of 3-5 times in coal ash compared to their crustal average and are much higher than in the pond ashes of other thermal power plants of India (Mandal, A., 2005).

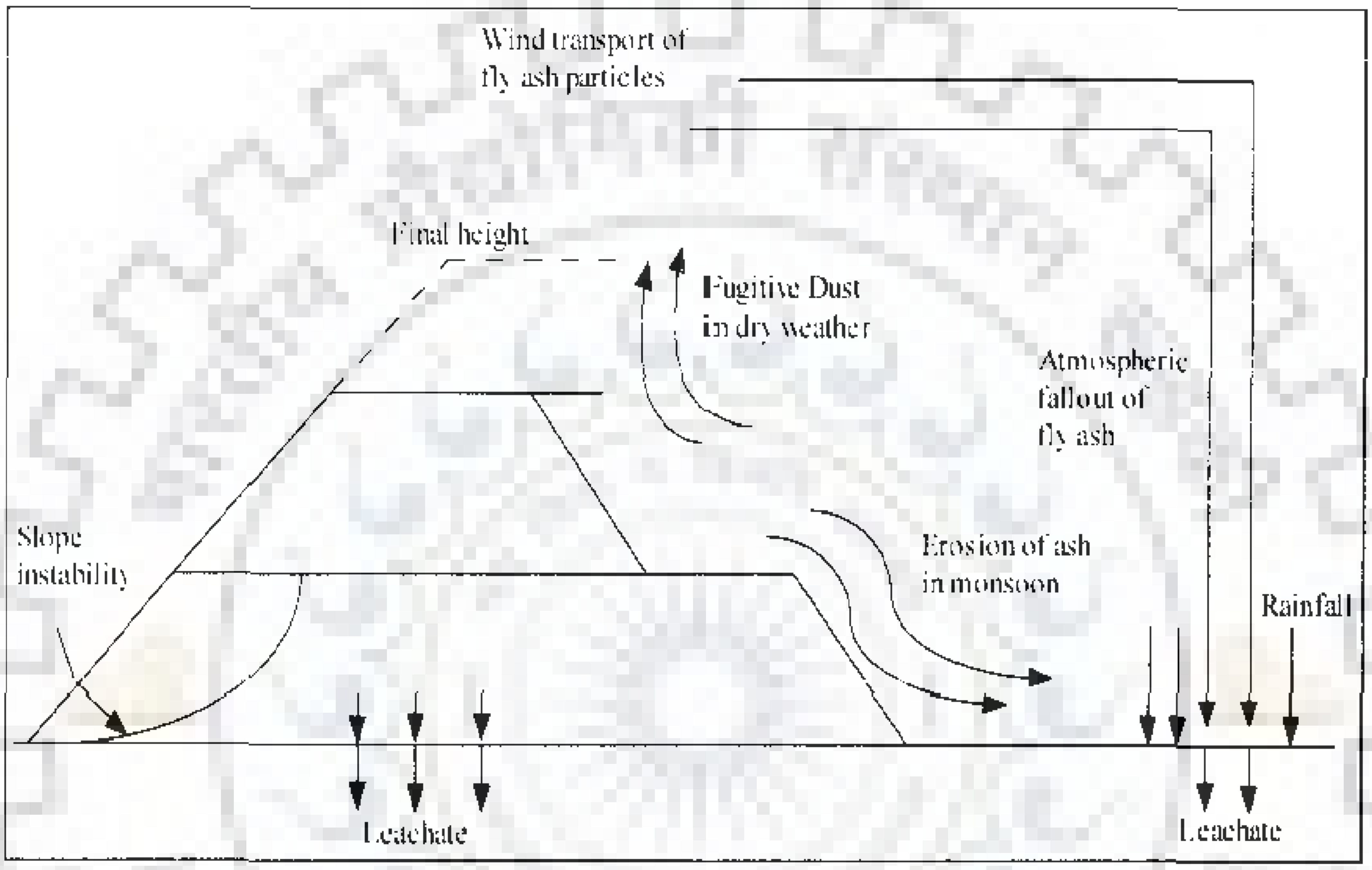

Figure 8.2 Possible polluting pathways in an ash mound

On the basis of the site visits around the power plant, it is found that the top portion of soil is overlaid by these fly ash particles in predominant wind direction which can be observed through Figure 8.3. The increase in the concentration of heavy metals in the soil around ash pond increase the leaching of contaminated soil during runoff and these metals travel laterally away from the pond. The best way to prevent the dust emission from ash pond, by way of keeping the surface wet throughout the year, but in actual practices it is not possible. However during summer season, wind transport of fly ash particles is eternal problem.

Figure 8.3 Top of the soil around plant is polluted due to fly ash fall out in predominant wind direction

8.4 EFFECT ON GROUNDWATER

Groundwater is contaminated due to trace metal and radionuclide due to fly ash disposal in the wet form (Baba, A., 2002, Gulec, N., et al., 2000, Mandal, A., 2005). Migration of trace metal takes place into groundwater from natural pond seepage (Theis, T. L., et al., 1978, Mandal, A., 2005). Groundwater quality near the ash pond is changed due to leaching of soluble ions present in fly ash (Choi, S. K., et al., 2002, Suresh, I. V., et al., 1998 Praharaj, T., et al., 2002). Leachate from ash pond passes through an intermediate zone of soil beneath the ash pond and groundwater table level. The soil in this zone adsorbs the trace elements in the leachate and prevents them from reaching the groundwater table. Once the attenuation capacity of the soil is exhausted the trace elements will reach the groundwater zone. The schematic diagram of possible leachate transport from fly ash slurry pond via unsaturated zone to groundwater table is shown in Figure 8.4.

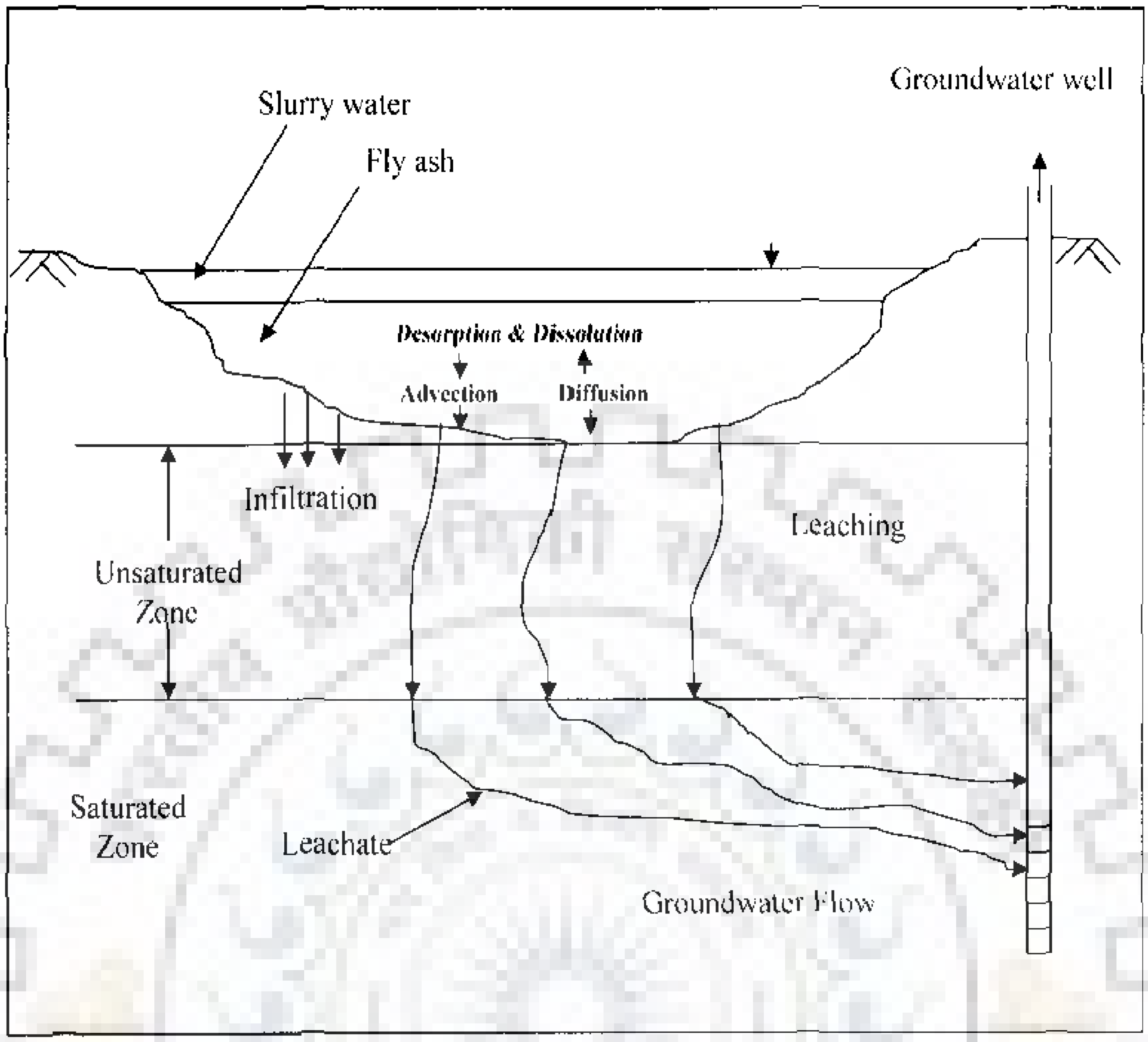

Figure 8.4 Contamination of groundwater from leachate transport from ash pond

8.5. FIELD INVESTIGATION AT NASHIK ASH POND

In the present study several samples were collected in and around Nashik ash pond consisting of slurry water from effluent channel, ground water samples etc. These various samples include: immediately disposed fly ash slurry water (collection date- 23rd January 2007), ash pond decant water (collection date- 24rd January 2007), Eastern ash pond effluent channel later joining to Darna river (collection date- 25th January 2008), groundwater of open dug wells from Hinganvedehe village (collection date- 26th January 2008), Southern ash pond effluent channel later joining to Darna river (collection date- 18th April 2009), groundwater of open dug wells from Kotamgaom village (collection date- 19th April 2009). The parameters such as pH, TDS, EC were determined in situ immediately after filtration of the sample and samples are immediately acidified to pH-2 to prevent oxidation of ferrous iron. Samples were analyzed at I IC I I T Roorkee. Figure 8.5 gives aerial view of Nashik ash pond which is obtained from Google Earth.

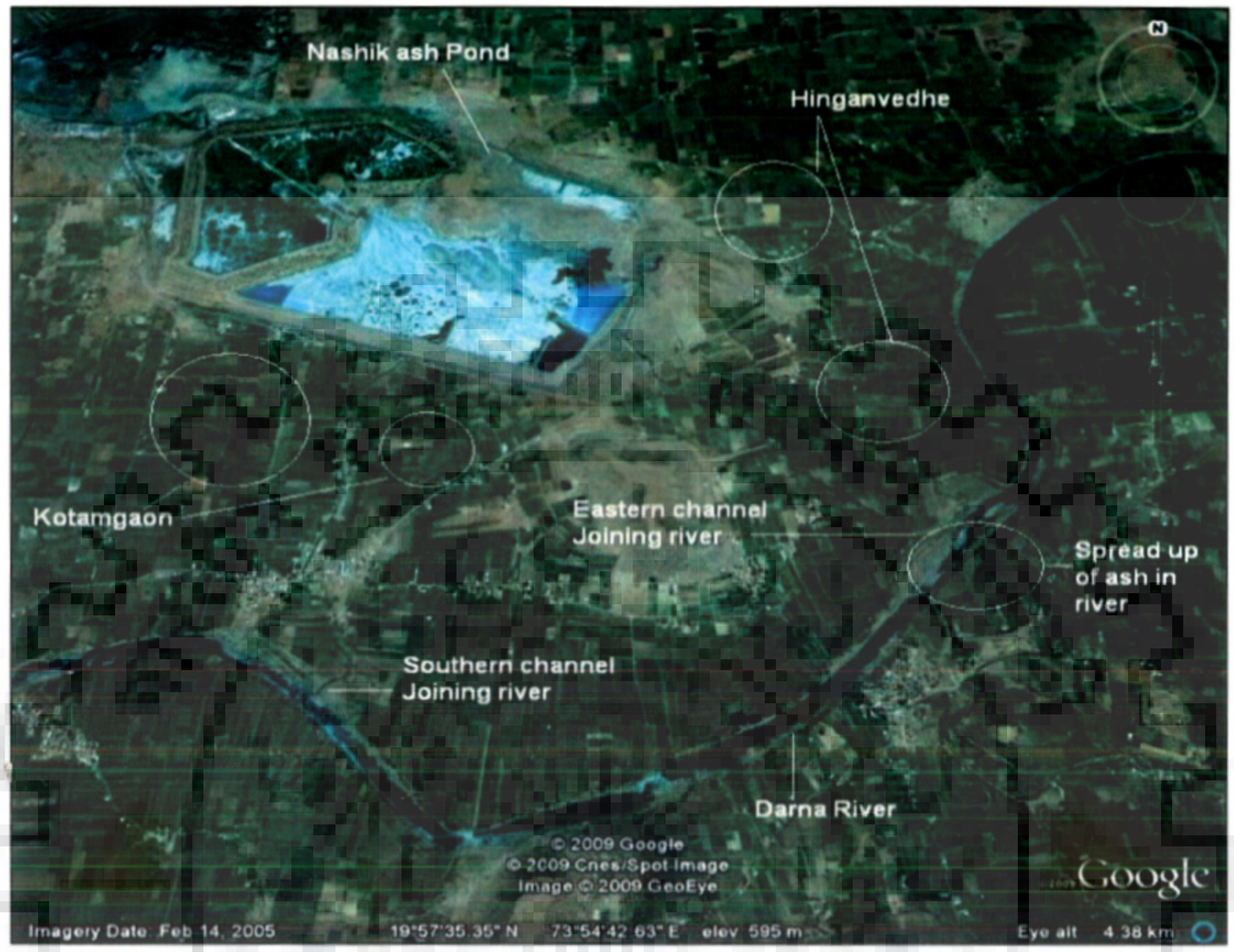

Figure 8.5 Arial view of Nashik ash pond and locations of sample collection

8.5.1 Analysis of Immediately Disposed Fly Ash Slurry Water

The pH measured for immediately disposed fly ash slurry water was between 8.39- 8.66, which is alkaline. Same is also confirmed by measuring the pH of hopper ash which is 8.7. Total dissolved solids (TDS) and EC are also exceeding the limit of drinking water limit as shown in Table 8.1. Not a single metal is exceeding the limit for drinking water limit. This may be due to alkaline nature of fly ash. In alkaline fly ash leaching of trace metals is less compared to acidic fly ash.

Table 8.1 Metal analysis of immediately disposed fly ash slurry water

Sr No	pH	EC µs/cm	TDS mg/l	Fe mg/l	Mn mg/l	Zn mg/l	Ni mg/l	Cd mg/l	Cu mg/l
1	8.51	1163	573	0.1421	0.0134	0.0433	0.0258	0.0052	0.003
2	8.39	1186	585	0.1081	0.0141	0.0487	0.0433	0.0066	0.007
3	8.66	1157	570	0.1137	0.0076	0.0486	0.0184	0.0053	0.0045
4	8.63	1172	578	0.1303	0.0215	0.056	0.057	0.0064	0.009
CPCB	6.5-8.5	250	NA	0.3	0.1	5	NA	0.01	0.05
WHO	NA	250	NA	0.3	0.5	NA	0.02	0.003	2
USEPA	6.5-8.5	NA	500	0.3	NA	5	NA	NA	1

NA: Not Available

8.5.2 Analysis of Ash Pond Decant Water from the whole Ash Pond

When fly ash disposed in the slurry form leaching of metals takes place, leachate will travel through unsaturated zone and would join ground water table. Some portion of ash pond decant water is diverted to water recycling plant and some part of decant water may overflow and joins the adjoining water body or in case of Nashik ash pond it is used for irrigation purpose. This is observed through actual site visit. The pH of the ash pond decant water was consistently in the range of 8- 8.52 as shown in Table 8.2. TDS and EC both are exceeding the drinking water standard limit. In utilizing ash pond decant water with high TDS and alkalinity, there is need to investigate the effect of such water on slurry transportation pipe system to control scaling or corrosion of pipes. It is also necessary to treat this water before disposing them into natural streams or rivers.

Table 8.2 Metal Analysis of ash pond decant water from the total area of ash pond

Sample No	pH	EC µs/cm	TDS mg/l	Fe mg/l	Mn mg/l	Zn mg/l	Ni mg/l	Cd mg/l	Cu mg/l
1	8.43	1041	512	0.083	0.0116	0.0307	0.0332	0.046	0.0017
2	8.26	*1040*	*511*	*0.1382*	*0.006*	*0.0415*	*0.0098*	0.032	*0.0043*
3	8.05	1031	507	0.0708	0.0069	0.045	0.0145	0.045	0.0037
4	8.52	943	462	0.0803	0.015	0.035	0.0235	0.033	0.0017
5	8.08	1448	719	0.1429	0.0196	0.0566	0.0367	0.047	0.0039
6	8.49	898	440	0.1082	0.0066	0.0457	0.0158	0.026	0.0024
7	8.42	1049	516	0.0889	0.006	0.0498	0.03	0.025	0.0031
8	8.38	1023	502	0.0789	0.0096	0.0582	0.018	0.026	0.0038
9	8.3	1049	515	0.1026	0.008	0.0552	0.0323	0.033	0.0029
10	8.41	1016	499	0.0922	0.0103	0.0227	0.0413	0.029	0.004
11	8.31	1003	492	0.152	0.0055	0.0271	0.0193	0.035	0.0054
12	8.24	1161	572	0.193	0.0082	0.0337	0.0144	0.029	0.0025
13	8.26	1167	575	0.1611	0.006	0.0437	0.0082	0.032	0.0022
14	8.2	1193	589	0.2122	0.188	0.0486	0.04	0.03	0.0301
15	8.21	1139	561	0.1313	0.0097	0.0405	0.0239	0.031	0.0091
CPCB	6.5-8.5	250	NA	0.3	0.1	5	NA	0.01	0.05
WHO	NA	250	NA	0.3	0.5	NA	0.02	0.003	2
USEPA	6.5-8.5	NA	500	0.3	NA	5	NA	NA	1

NA: Not Available

8.5.3 Analysis of Effluent from Eastern and Southern Ash Pond Effluent Channel

In most of the power plant effluent is discharged in to natural stream. It is reported in literature that ash pond overflows due to inadequate design of ash pond (Prasad, B., 2004) or overflow is diverted to the river (Mehra, A., et al., 1998) near to the power plant. Samples colleted along the Eastern channel are analyzed and the results are given in Table 8.3. The pH values of the effluents are in the range of 6.1-8.12. The concentrations of the metals in the ash pond decant water are exceeding the limit particularly for Fe, Mn, Ni and Cd. Ash pond decant water is overflowing from the bund and later joins the Dama river and corresponding results are given in Table 8.3 (sample no 2-13) and when it get mixed with river water except Fe all the metals are below permissible limit. TDS and EC is also exceeded the permissible limit as shown in the Table 8.3. Even after mixing with river water EC and TDS are above permissible limit and may impart alkalinity to the river water.

Table 8.3 Metal analysis of ash pond effluent from Eastern channel joining Darna River

Sample no	pH	EC µs/cm	TDS mg/l	Fe mg/l	Mn mg/l	Zn mg/l	Ni mg/l	Cd mg/l	Cu mg/l
1	7.25	2100	1055	**0.961**	**0.275**	0.147	**0.03**	**0.021**	0.106
2	8.06	1312	649	0.192	0.016	0.107	0.0107	0.002	0.021
3	8.12	1319	653	0.015	0.022	0.079	0.0079	0.001	0.032
4	6.83	1308	647	0.123	0.03	0.101	0.0101	0.003	0.034
5	7.99	1313	649	0.096	0.012	0.108	0.0108	0.0015	0.066
6	6.68	1497	744	0.189	0.031	0.122	0.0122	0.005	0.039
7	7.19	1469	729	0.279	0.025	0.132	0.0132	0.002	0.128
8	6.36	1515	753	0.135	0.012	0.149	0.0149	0.0025	0.053
9	6.31	1474	732	0.194	0.026	0.078	0.0078	0.002	0.051
10	6.19	1397	692	0.266	0.033	0.074	0.0074	0.0021	0.056
11	6.1	1329	658	**0.403**	0.05	0.068	0.05	0.002	0.058
12	6.43	1459	724	0.205	0.023	0.071	0.0071	0.0025	0.056
13	7.64	1457	723	**0.466**	0.062	0.078	0.0078	0.001	0.047
14 R/W	7.23	1390	689	**0.425**	0.021	0.091	0.0091	0.0015	0.062
CPCB	6.5-8.5	250	NA	0.3	0.1	5	NA	0.01	0.05
WHO	NA	250	NA	0.3	0.5	NA	0.02	0.003	2
USEPA	6.5-8.5	NA	500	0.3	NA	5	NA	NA	1

NA: Not Available

Ash pond effluent samples colleted along the Southern channel are analyzed and the results are given in Table 8.4. As the pH values of the effluent can be seen from Table 8.4, are in the range of 7.6– 8.14. The concentrations of the metals in the ash pond decant water are not exceeding the limit particularly for metals. TDS and EC both have exceeded the permissible limit as shown in the Table 8.4. Ash pond decant water is collected at water reuse and recycling plant and overflow is diverted to river through Southern channel which joins the Darna river. The corresponding results are given in *sample no 1–11 (Table 8.4) and when it get mixed with river water all the metal* concentrations are below permissible limit via dilution. Therefore, disposal of ash pond effluent via Southern channel is not likely to pollute river water for selected metal pools. Even TDS and EC are also decreased via dilution in river water.

Table 8.4 Metal analysis of ash pond effluent from Southern channel joining Darna River

Sample no	pH	EC µs/cm	TDS mg/l	Fe mg/l	Mn mg/l	Zn mg/l	Ni mg/l	Cd mg/l	Cu mg/l
1	8.14	1021	530	0.1313	0.0097	0.0405	0.0289	0.0021	0.0091
2	8.1	1067	502	0.2122	0.188	0.0486	0.0341	0.002	0.0301
3	8	989	499	0.193	0.0082	0.0337	0.0194	0.0019	0.0025
4	8.06	1003	515	0.1611	0.006	0.0437	0.0132	0.0022	0.0022
5	8.01	1082	532	0.1815	0.0236	0.0397	0.0187	0.0029	0.0016
6	7.97	1081	532	0.2048	0.0438	0.0449	0.013	0.003	0.0023
7	7.77	1134	558	**0.3095**	0.0318	0.0481	0.0211	0.0021	0.0014
8	7.81	1156	570	0.102	0.01	0.0373	0.0155	0.0028	0.0019
9	8.13	1105	544	0.2456	0.0013	0.0431	0.0207	0.0041	0.0011
10	8.06	1159	571	0.2363	0.0154	0.0422	0.0241	0.0046	0.0019
11	7.84	1232	608	0.244	0.0111	0.052	**0.0438**	0.0072	0.0002
D/S RW	7.62	883	418	0.1965	0.0084	0.042	0.0084	0.0022	0.0014
D/S RW	7.7	349	167.9	0.1052	0.0177	0.311	**0.0438**	0.0025	0.006
U/S RW	7.77	107.9	51.2	0.1199	0.0098	0.0503	0.0213	0.0002	0.0002
U/S RW	7.69	88.7	42	0.0525	0.0073	0.0277	0.0117	0.0005	0.0015
CPCB	6.5-8.5	250	NA	0.3	0.1	5	NA	0.01	0.05
WHO	NA	250	NA	0.3	0.5	NA	0.02	0.003	2
USEPA	6.5-8.5	NA	500	0.3	NA	5	NA	NA	1

NA: Not Available

8.5.4 Analysis of Groundwater of Open Dug wells from Hinganvedhe and Kotamgaon villages

Groundwater samples from open dugwells were collected from Hinganvedhe and Kotam gaon villages and various parameters were determined. The results of metal analysis for Hinganvedhe village are given in Table 8.5. The pH values of the groundwater of dug wells form Hinganvedhe village are in the range of 6.4-7.41. TDS and EC are exceeding the permissible limit. Concentration of Fe, Mn, Ni and Cd are above permissible limit, which may cause potential health hazard. The wells located near the ash pond show elevated concentrations of metals such as Fe, Mn, Ni and Cd. Away from the ash pond the concentrations of metals are within permissible limit except for Fe. This may be due to attenuation of metals during seepage via adsorption and precipitation.

Table 8.5 Metal analysis of Groundwater at the Hinganvedhe village

Well no	pH	EC µs/cm	TDS mg/l	Fe mg/l	Mn mg/l	Zn mg/l	Ni mg/l	Cd mg/l	Cu mg/l
1	7.2	1519	755	**1.8**	**0.287**	0.0463	0.0157	**0.0061**	0.0033
2	6.97	339	163.4	**1.82**	**0.2107**	*0.0342*	*0.0097*	*0.0018*	*0.0004*
3	6.68	1095	539	**0.3256**	0.0087	0.0456	**0.0289**	**0.0055**	0.0089
4	6.73	927	454	**0.3927**	0.0107	0.0352	**0.0551**	**0.0035**	0.0036
5	6.78	1115	549	**0.3461**	0.0087	0.0395	**0.0232**	**0.0038**	0.0034
6	7.06	321	154.6	0.1128	0.011	0.0431	0.0058	0.0013	0.007
7	7.26	997	489	0.1322	0.0087	0.0472	0.017	0.003	0.0052
8	7.05	898	440	0.192	0.0118	0.0915	0.0178	0.0037	0.0042
9	6.4	1294	640	0.2799	0.0434	0.0649	0.0129	0.0042	0.003
10	7.03	1294	617	**0.3636**	0.0585	0.0667	0.0285	0.0018	0.0052
11	7.33	1045	514	0.165	0.0085	0.0639	0.0125	0.0047	0.0054
12	7.35	1401	695	**0.4451**	0.0114	0.0679	0.0134	0.0044	0.0035
13	7.14	1387	688	**1.0811**	0.0089	0.0887	0.0276	0.0055	0.0043
14	7.23	1523	757	0.1423	0.0095	0.0682	0.058	0.0059	0.0026
15	7.01	1071	527	0.0727	0.0801	0.0736	0.013	0.0055	0.0012
16	6.85	1149	566	0.0152	0.0064	0.0628	0.0124	0.0025	0.0049
17	6.77	1061	521	0.0805	0.0076	0.061	0.0195	0.003	0.0025
18	7.15	1427	708	0.0925	0.0065	0.059	0.0113	0.0025	0.0043
19	7.41	1421	705	0.1215	0.012	0.0036	0.027	0.0048	0.006
CPCB	6.5-8.5	250	NA	0.3	0.1	5	NA	0.01	0.05
WHO	NA	250	NA	0.3	0.5	NA	0.02	0.003	2
USEPA	6.5-8.5	NA	500	0.3	NA	5	NA	NA	1

NA: *Not Available*

Similarly the results of samples collected from Kotamgaon village are given in Table 8.6. The pH values of the groundwater of dug wells form Kotamgaon village are in the range of 7.26-8.24 as can be seen in Table 8.6. TDS and EC are exceeding the permissible limit. Concentration of Fe, Mn Ni and Cd are above permissible limit, particularly for the dugwells which are located near to the ash pond. For the rest of the wells it is within permissible limit. Thus this point may be the zone of attenuation and therefore well nos 4 to 14 do not show any elevated concentrations of metals.

Table 8.6 Metal analysis of groundwater from dug wells at the Kotamgaon village

Well *no*	*pH*	EC *µs/cm*	TDS *mg/l*	Fe *mg/l*	Mn *mg/l*	Zn *mg/l*	Ni *mg/l*	Cd *mg/l*	Cu *mg/l*
1	7.26	1242	613	**0.318**	**0.2187**	0.041	**0.0299**	**0.0062**	0.0096
2	7.6	1272	629	**0.3662**	**0.215**	0.0372	**0.024**	**0.0034**	0.0014
3	7.77	1210	597	**0.3503**	0.0155	0.039	**0.0252**	**0.0041**	0.0009
4	7.92	1196	590	0.0367	0.014	0.0334	0.0137	0.0028	0.0002
5	7.91	1028	505	0.0405	0.0117	0.0292	0.011	0.0027	0.0002
6	7.83	1325	656	0.0335	0.015	0.039	0.0255	0.0017	0.0007
7	8.24	1040	511	0.0321	0.014	4.8	0.013	0.0016	0.0008
8	7.92	1039	510	0.0256	0.0146	0.041	0.0224	0.0013	0.0006
9	8.2	1037	509	0.0254	0.0102	0.0666	0.0181	0.0025	0.0012
10	8.07	1014	498	0.2077	0.0132	0.0452	0.0293	0.0015	0.0003
11	8.05	1149	566	0.0119	0.0243	0.0108	0.018	0.0016	0.003
12	8.09	1013	497	0.1856	0.025	0.0415	0.0279	0.0025	0.0001
13	7.74	1338	662	0.2067	0.0089	0.0597	0.0111	0.008	0.0031
14	7.95	1023	502	0.1806	0.034	0.056	0.0323	0.0052	0.0004
CPCB	6.5-8.5	250	NA	0.3	0.1	5	NA	0.01	0.05
WHO	NA	250	NA	0.3	0.5	NA	0.02	0.003	2
USEPA	6.5-8.5	NA	500	0.3	NA	5	NA	NA	1

NA: Not Available

Farmers from Kotamgaon and Hinganvedhe villages are using Darna river water (which is already ash mixed or elevated concentrations of leached metals) directly for irrigation purpose. The two channels (Eastern and Southern) are flowing through the field of farmers and later joins the Darna river. The concentrations of metals in the groundwater may be due to wind blown ash particles, especially when Cd and Ni present. Concentrations of Fe and Mn in groundwater may be from seepage near to ash pond area. Currently the concentrations of Zn and Cu in the groundwater are under permissible limit. However continous and cumulative addition of these elements by ash pond leachate has the potential to make the groundwater more polluted in future.

8.6 HEALTH HAZARDS OF Fe, Mn, Ni, Zn, Cu and Cd

The most common and harmful heavy metals are; lead, copper, nickel, chromium cadmium and zinc. They are stable elements which cannot be metabolized by the body and cannot be released through food chain of human beings. The primary concern about the presence of iron in drinking water is its objectionable taste. Iron greater than 0.3 mg/l and manganese greater than 0.5 mg/lit are objectionable because of their tendency to discolor plumbing fixtures, beverages, laundry, glasses and dishware. Iron causes reddish-brown stains whereas manganese acts in a similar way but causes brownish-black stains. Iron and manganese can affect the flavor and color of food and water. They may react with tannins in coffee, tea and some alcoholic beverages to produce a black sludge, which affects both, taste and appearance. Besides, they cause constipation and hair loss. Presence of iron in the water also results in an astringent taste. There are many problems that result from iron toxicity. These include anorexia, oligura, diarrhoea, hypothermia, diphasic shock, metabolic acidosis and even death. In addition to these, the patient may experience vascular congestion of the gastrointestinal tract, liver, kidneys, heart, brain, spleen, adrenals and thymus. With acute iron poisoning, much of the damage to the gastrointestinal tract and liver may result from the high localized iron concentration and free radical production leading to heptatoxicity via lipid peroxidation and destruction of the hepatic mitochondria.

Nickel can cause a variety of pathologic effects like skin allergy, lung fibrosis and cancer. The most important health problems due to exposure to nickel and nickel compounds are allergic dermatitis (nickel itch) and increased incidence of cancers. Nickel is genotoxic and mutagenic as well. The symptoms of acute poisoning of cadmium in man are vomiting, abdominal cramps and headaches. After inhalation shortness of breath, general weakness and respiratory insufficiency occurs. Chronic exposure to cadimium results in respiratory disorders, kidney damage, liver dysfunction, anaemia and hypertension (Arora, R., et al., 1984). Copper, zinc and arsenic adversely affect the growth and reproduction of fish. Precipitation of mucus on gills of fish exposed to upper head. Fish accumulates theses metals in kidney, liver, bones and gills. These metals have noxious effect on the nervous system (Arora, R., et al., 1984). The presence of iron 0.1 mg/lit will damage the gills of the fish (Dalzell, D. J. B., et al., 1999). People who drink, over a period of years, an average amount of water contaminated with coal combustion waste have higher risk of cancer (Keating., M., 2001).

8.7 PHYSICAL OBSERVATIONS THROUGH SITE VISITS

During field visits at the Nashik ash pond, some physical observations are noted. Due to ash pond effluent discharge from East side, fly ash is traveled along with effluent and due to excess fill up of channel it is spilled in the field as shown in Figure 8.6. Due to this agricultural potential of soil is reduced. During monsoon period, it initiates leaching of metals and contaminates surrounding soil and surface water. Due to over flow of fly ash from Eastern effluent channel almost 0.8-1 km stretch of river bed is occupied by fly ash which is shown in Figure 8.7.

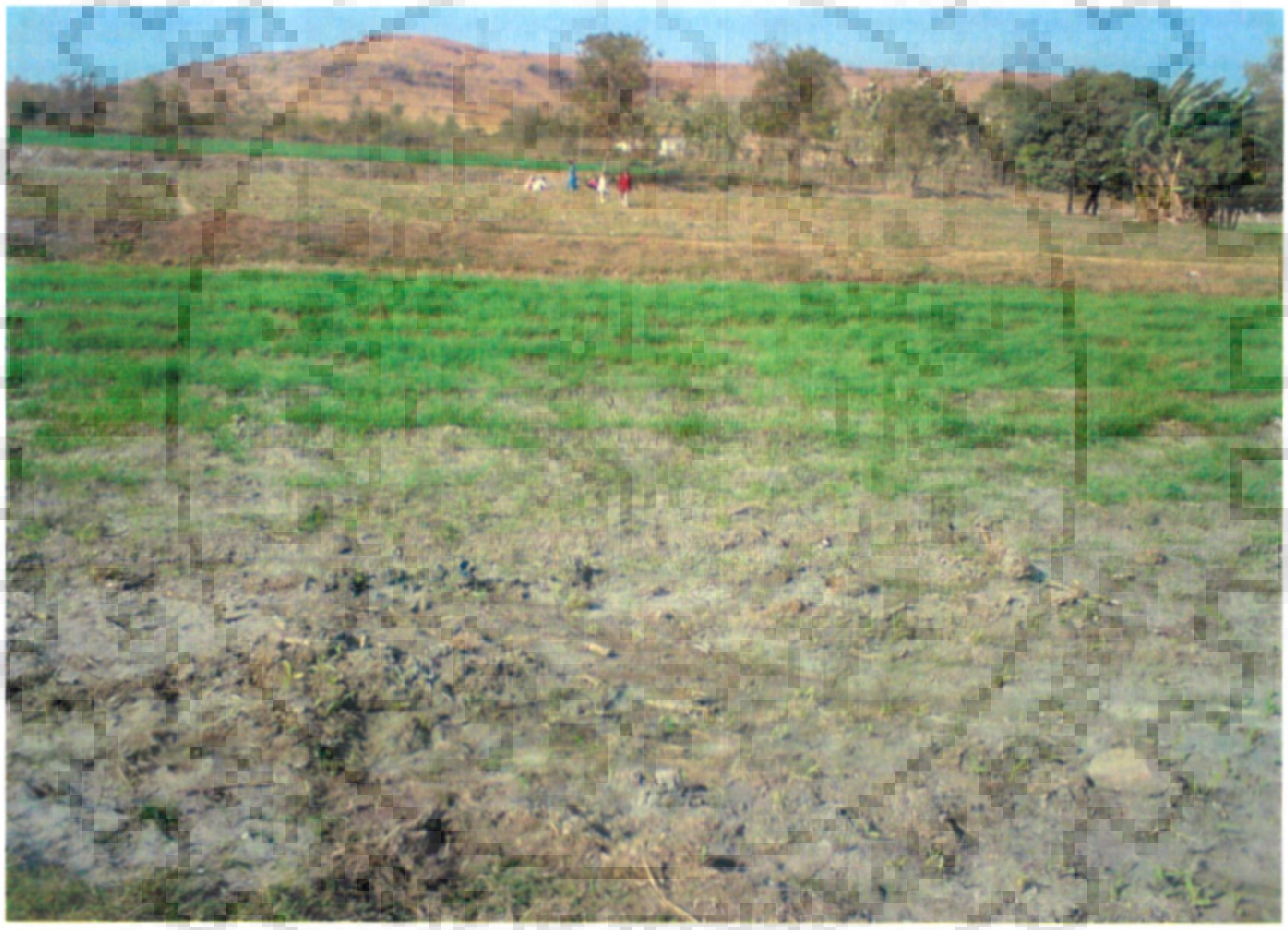

Figure 8.6 Fly ash spills in agricultural field

Figure 8.7.Spread up of fly ash in Darna river

Some farmers are using ash pond decant water for irrigation directly as illustrated in Figure 8.8 and for future provision they also store water in the open dug well as shown in Figure 8.9. Though fly ash contains some nutrients, its cumulative build up in longer run affects the agricultural productivity of land.

Figure 8.8 Ash pond effluent are directly used for irrigation

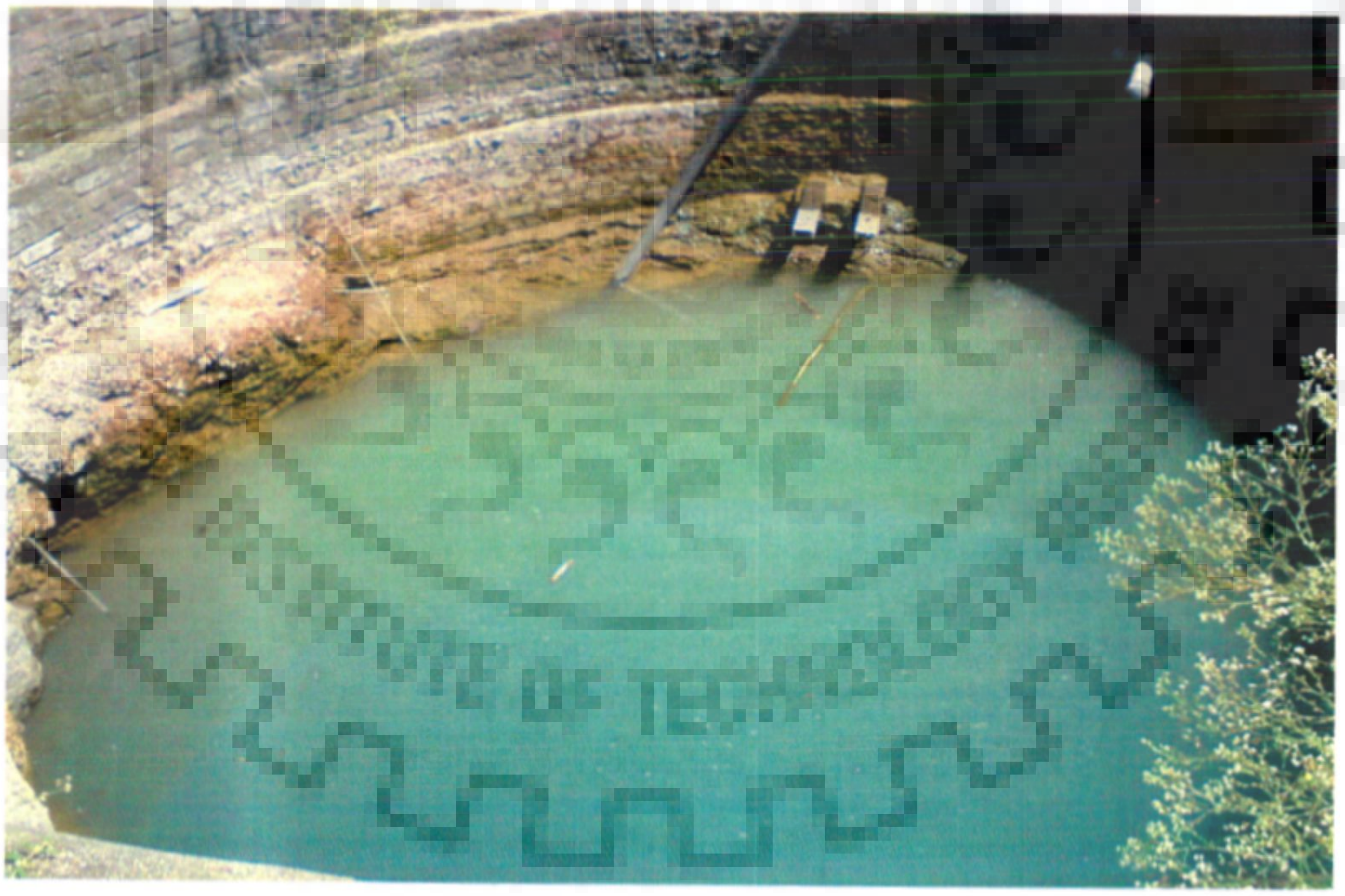

Figure 8.9 Lift irrigation water is directly poured in the open dug well

8.8 CONTROL STRATEGIES

Considering these health hazard to human beings and aquatic environment, it is essential to treat those leachate while discharging them into natural stream or disposing them on ground. It is also necessary to control the seepage of leachate through ash pond, so that groundwater can be protected. World Bank (1998) has given guideline to monitor and treat leachates and overflows from settling ponds in addition to disposing them in lined places to avoid contamination of water bodies.

Use of sedimentation ponds for removal of heavy metals (Lagnese, K. M., et al.,1993), and by applying adsorption- coprecipitation (Benjamin, M. M., et al., 1982) of various contaminats on hydrous iron oxide surface metals can be removed. The addition of appropriate chemicals directly to ash sluice waters can effectively control metal release by forming insoluble compounds which precipitate in ash pond. Lime, CaO is the chemical of choice and is effective in promoting the formation of insoluble hydroxide. Since ash pond water is generally low in dissolved carbonate, the addition of soda ash, Na_2Co_3, may prove more effective by forming metal carbonates which are generally more insoluble than respective hydroxide.

Lechate can be collected and taken to the sump well and then pumped for further treatment. The pollutant from leachate can be removed by chemical treatment followed by activated carbon treatment before its disposal. Since this treatment is quite costly the alternate approach of storage of the leachate in lined solar evaporation pond in which duckweed or water hyacinth is grown to remove the chemical pollutants (Hajarnavis, et al., 2003). Use dry ash handling system or installed lining materials in the ash pond to reduce seepage or infiltration of leachate. Chemical liners are expensive and sometimes subject to degradation. Natural lining materials, such as clays are cheaper. Clay liners may need replacement at regular intervals.

Revegetation of abandoned ash disposal sites is also desirable since it stabilizes the surface against wind and water erosion and also provides a more aesthetically pleasing landscape around thermal power plant Haynes (2009). Phytoremediation offers an effective way to prevent cycling of toxic metals from fly ash and growing of multipurpose tree species on the problem soils is an environmentally safe strategy for gainful utilization of fly ash (Jala, S., 2006). Fly ash disposal site of Khaperkheda thermal power station, Khaperkheda in Maharashtra state, India was amended with farmyard manure. After the amendment of farmyard manure and biofertilizer inoculation, the concentration of different metals such as cadimium, copper, zinc, nickel, chromium, iron, manganese and lead are reduced by 25%, 46%, 25%, 48%, 31%, 65%, 23% and 47% respectively, because organic amendments such as mature compost and manure, which contain a high proportion of organic matter helps in decreasing the bioavailability of heavy metals in soil, thus permitting the reestablishment of vegetation on contaminated site (Juwarkar 2007). Mycorrhizae also play a crucial role in protecting plant roots from heavy metals (Galli et al.1994). Mycorrhizae through their mycelia network accumulate heavy metals from the fly ash and retain them within their cell, thereby reducing the toxicity of the metals to the plant.

Groundwater is the only source of drinking water for the people in Kotamgaon and Hinganvedehe and its protection is primary concern. Though fly ash from Nashik power plant is alkaline in nature, it is likely to pose problem in longer run through seepage, and irrigation with ash pond decant water. It was also observed after the analysis of the groundwater samples, that wells near the ash ponds are moderately contaminated and it is likely to aggravate further. It is reported in the literature, that in Indian context the increased level of trace metals in groundwater near the ash pond (Sen, P. K., et al., 1996; Suresh, I. V., et al., 1998; Praharaj, T., et al., 2002; Mandal, A., et al., 2005; Twardowska, I., et al., 2003) are found. Leachates from poorly planned and designed waste disposal ponds and landfills present potential threat of groundwater contamination. This could occur due to inadequately lined ponds, providing a greater opportunity for groundwater contamination, since the soil below the impoundment is usually saturated and under considerable hydraulic head it reaches the groundwater. Therefore it is essential to provide liners to the ash pond to control seepage and protect groundwater from heavy metal contamination. Low permeability clay liners are best suited due to their surface characteristics as well as economics involved.

8.9 CONCLUDING REMARKS

Top layer of soil surrounding of the ash pond is occupied by fly ash and it is from wind blown particles of fly ash. The leachates produced from the fly ash are alkaline in nature. For the initial operating period of the ash pond, leaching of fly ash may not likely to pose any problem to groundwater but cumulative build up of ash may create problem to groundwater.

Analysis of groundwater from open dugwells of Kotamgaon and Hinganvedhe villages revealed that the groundwater quality is deteriorated due to the presence of fly ash ions such as Fe, Mn Cd and Ni. Contamination is likely to increase with the passage of time. Apart from input from ash pond, use of ash pond effluent for irrigation, seepage from Eastern and Southern effluent channel and leaching of top soil (contaminated due to fly ash dispersal) contributes to groundwater. There is significant potential exists for environmental impacts from uncontrolled seepage of rainwater and slurry water through ash deposits in the absence of liner, once the operating life of ash pond is over. Provision of low cost liner is necessary to protect the groundwater contamination from ash pond. It would be appropriate to adopt suitable rainwater harvesting and artificial recharge techniques to compensate for the possible pollution likely to occur due to toxic leachate travel via unsaturated zone to groundwater. With recharge structures it is possible that the toxicity of leachates, may be diluted.

CHAPTER 9

INFILTRATION OF LEACHATE FROM AN ASH POND THROUGH A LINER

9.1 GENERAL

Environmental assessment for a new thermal power plant of 50 MW units or larger in respect of ambient air, water, and land is a prerequisite in order to establish emission requirements and other measures on a site-specific basis. Guidelines in respect of liquid effluent levels to be achieved daily without dilution have been given in Thermal–Power-Guidelines for New Plants (Pollution Prevention and Abatement Handbook Part-III. 1998). Fly ash handling systems may be generally categorised as dry or wet, even though the dry handling system involves wetting the ash to 10-20% moisture content to improve handling and to mitigate the dust generated during disposal. In wet systems, the ash is mixed with water to produce a liquid slurry with 5-20% solids by weight. This is discharged to settling ponds often with bottom ash and Flue Gas Desulfurization (FGD) sludges as well. These ponds may be used as final disposal site, or the settled solids may be dredged and removed for final disposal in a landfill. Where ever feasible, decanted water from ash disposal ponds should be recycled to formulate ash slurry. Where there are heavy metals present in ash residues or in FGD sludges, care must be taken to monitor and treat the leachate and to its disposal to avoid contamination of water bodies.

A composite liner and a leachate collection system are placed in the ash pond in order to prevent the leachate from joining the water table. As the saturated hydraulic conductivity of a liner is less than that of the underlying soil, the leachate would percolate from the liner in isolated jets and all the soil pores would not get filled. In this chapter, the unsaturated flow of leachate through the soil layer underlying a geo-synthetic liner is analyzed using Green and Ampt infiltration theory. The head boundary condition at the bottom of the compacted liner is of Dirichelt type. This head boundary condition varies with time and is unknown a priori. Also the degree of saturation behind the moving front in the soil layer is unknown. According to Horton's infiltration theory, the rate of infiltration decreases with time under a constant ponding depth. This phenomenon holds true if the degree of saturation behind the moving front in the unsaturated soil layer is such that the corresponding unsaturated hydraulic conductivity of the under lying soil layer is equal to the saturated hydraulic conductivity of the liner. Using this postulation, the relation between cumulative infiltrated quantity and time of infiltration has been derived in this chapter. Rate of infiltration of leachate from an ash pond having 0.3 m thick brick lining has been quantified at the time the wetting front joins the water table which lies at a depth of 10 m below the ash pond.

9.2 INFILTRATION FROM ASH POND

In general, as fly ash slurry contains about 80% water, infiltration would occur once the slurry is discharged into an ash-pond. For environmental protection a composite liner and a leachate collection system are placed in the ash pond as shown in Figure 9.1 Keramida (2000,).

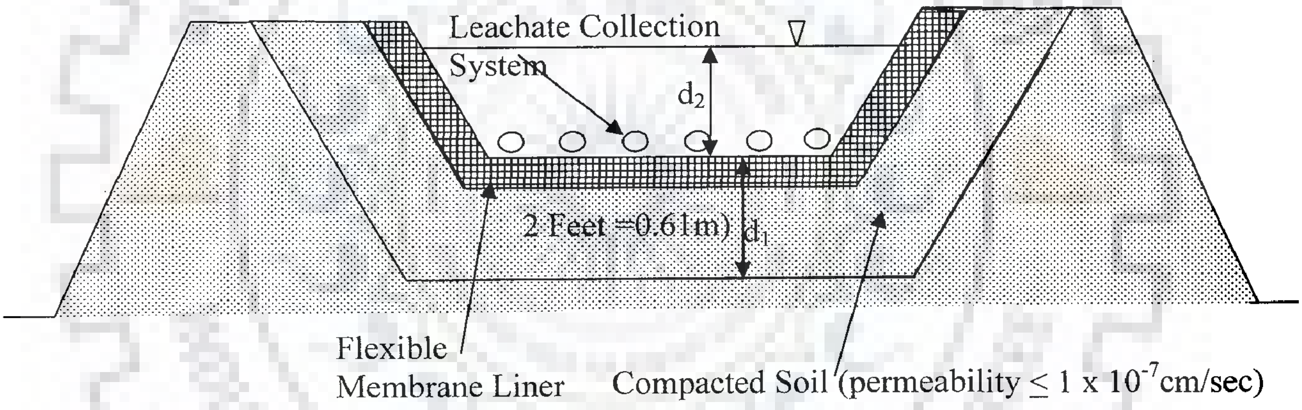

Figure 9.1 Composite Liner and Leachate Collection System (not to scale)

Prior to the disposal of slurry into the ash-pond, the zone beneath the ash-pond up to the under lying water table would be in an unsaturated state. If the difference between the values of seepage coefficients (hydraulic conductivities) of the liner and underlying soil is significant, then the leachate would percolate from the saturated liner to the underlying soil in isolated jets (Polubarinova-Kochina, 1962) and would not fill all the soil pores. The bottom boundary of the liner behaves like a constant pressure head boundary. The flow through the unsaturated zone is analyzed using principle of Green and Ampt infiltration theory. The flow of leachate from the ash pond is assumed to be one-dimensional and in vertical direction. The depth of slurry water is assumed to be equal to d_2. A section of flow domain is shown in Figure 2.

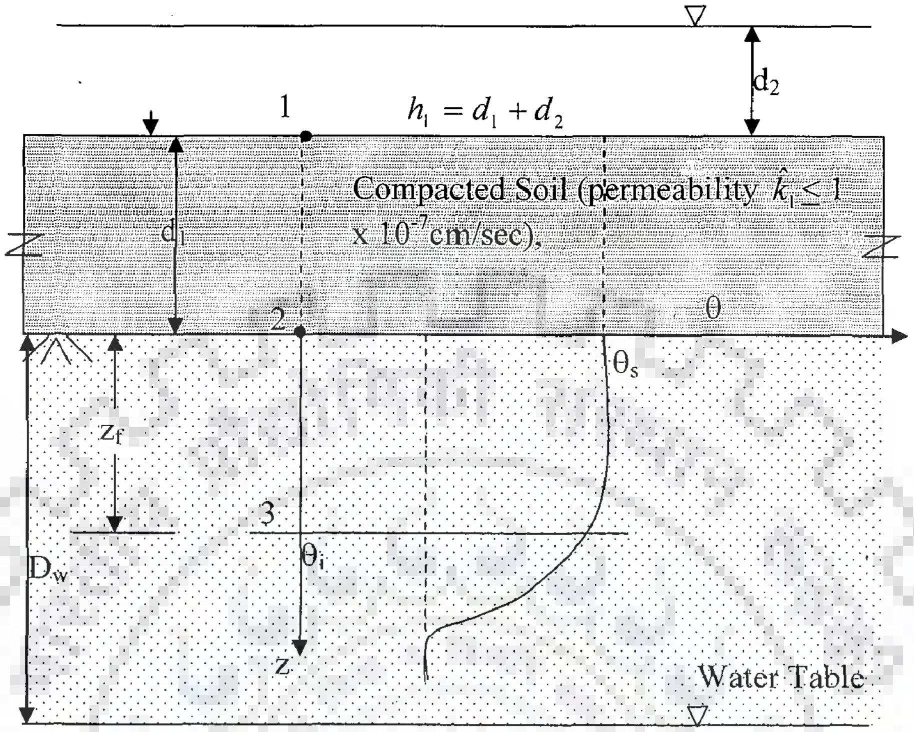

Figure 9.2 Unsaturated flow through a liner

Referring to Figure 9.2, the *z* axis being positive down wards, the hydraulic head, *h*, is defined as:

$$h = \frac{p_w}{\gamma_w} - z \qquad (9.1)$$

Accordingly, the hydraulic heads at points 1, 2, and 3 are: $h_1 = d_1 + d_2$; $h_2 = -h_{c2}(t)$; $h_3 = -H_f - z_f$ in which d_1 = thickness of the liner; d_2 = the maximum depth of leachate maintained in the ash pond, H_f = average suction head acting at the moving front; z_f = position of the moving front at time *t*; $h_{c2}(t)$ = unknown suction head at the bottom of the liner in the ash-pond bed. The discharge from ash-pond bed through the liner at any time is the infiltration rate. Applying Green –Ampt theory:

$$-\tilde{k}_1 \frac{\left[-h_{c2}(t) - d_1 - d_2\right]}{d_1} = -k_2(\hat{\theta}) \frac{(-H_f - z_f) + h_{c2}(t)}{z_f} \qquad (9.2)$$

$\tilde{k}_1$= hydraulic conductivity of the liner; $k_2(\hat{\theta})$= hydraulic conductivity of the unsaturated soil beneath ash-pond. $\hat{\theta}$ = moisture content of the unsaturated soil behind the moving front, which is to be ascertained. Based on Horton's infiltration theory, that rate of infiltration decreases with time under a constant ponding depth, it has been postulated that in case of infiltration through a two layered soil system under a constant depth of ponding, where the upper layer has less hydraulic conductivity than that of the lower layer, the soil behind the moving front in the lower layer remains in an unsaturated state. The degree of saturation of the lower layer is such that the unsaturated hydraulic conductivity $k_2(\hat{\theta})$ of the lower layer is equal to the saturated hydraulic conductivity $\tilde{k}_1$ of the upper layer. With this postulation Horton's theory is not violated. Applying this condition in (9.2)

$$\frac{[d_1 + d_2 + h_{c2}(t)]}{d_1} = \frac{-h_{c2}(t) + H_f + z_f}{z_f} \tag{9.3}$$

Solving for the unknown $h_{c2}(t)$ from (9.3)

$$h_{c2}(t) = \frac{H_f - z_f d_2 / d_1}{1 + z_f / d_1} \tag{9.4}$$

Let the time be measured since the slurry water is discharged to the ash pond. Let w_0 be the depth of water required to fill the void space in the liner. Let t_0 be the time required to fill the void space. As w_0 is a very small quantity t_0 is presumed to be very small. Defining

$$w = w_0 + z_f(\hat{\theta} - \theta_i) \tag{9.5}$$

The infiltration rate I at time $t > t_0$ is given by:

$$I = \frac{dw}{dt} = \tilde{k}_1 \frac{d_1 + d_2 + \dfrac{H_f - z_f d_2 / d_1}{1 + z_f / d_1}}{d_1} = (\hat{\theta} - \theta_i)\frac{dz_f}{dt} \tag{9.6}$$

Simplifying, (9.6) reduces to

$$\tilde{k}_1 \frac{d_1 + d_2 + z_f + H_f}{d_1 + z_f} = (\hat{\theta} - \theta_i)\frac{dz_f}{dt} \tag{9.7}$$

or

$$\tilde{k}_1 \frac{(\hat{\theta} - \theta_i)(d_1 + d_2 + H_f) + z_f(\hat{\theta} - \theta_i)}{(\hat{\theta} - \theta_i)d_1 + z_f(\hat{\theta} - \theta_i)} = (\hat{\theta} - \theta_i)\frac{dz_f}{dt} \tag{9.8}$$

Incorporating $z_f(\hat{\theta} - \theta_i) = w - w_0$ and $(\hat{\theta} - \theta_i)\dfrac{dz_f}{dt} = \dfrac{dw}{dt}$ in (9.8)

$$\tilde{k}_1 \frac{\left(\hat{\theta}-\theta_i\right)\left(d_1+d_2+H_f\right)+w-w_0}{\left(\hat{\theta}-\theta_i\right)d_1+w-w_0} = \frac{dw}{dt} \tag{9.9}$$

Rearranging

$$\tilde{k}_1 dt = \frac{\left(\hat{\theta}-\theta_i\right)d_1+w-w_0+\left(\hat{\theta}-\theta_i\right)d_2-\left(\hat{\theta}-\theta_i\right)d_2+H_f\left(\hat{\theta}-\theta_i\right)-H_f\left(\hat{\theta}-\theta_i\right)}{\left(\hat{\theta}-\theta_i\right)\left(d_1+d_2+H_f\right)+w-w_0} dw \tag{9.10}$$

Integrating

$$\tilde{k}_1 t = w-(H_f+d_2)\left(\hat{\theta}-\theta_i\right)\ln\left\{\left(\hat{\theta}-\theta_i\right)\left(d_1+d_2+H_f\right)+w-w_0\right\}+\mathrm{A} \tag{9.11}$$

At $t=t_0$ $w=w_0$. Applying this condition in (9.11),

$$A=\tilde{k}_1 t_0-w_0+(H_f+d_2)\left(\hat{\theta}-\theta_i\right)\ln\left\{\left(\hat{\theta}-\theta_i\right)\left(d_1+d_2+H_f\right)\right\} \tag{9.12}$$

Incorporating A in (9.11)

$$\begin{aligned}\tilde{k}_1\left(t-t_0\right)=w-w_0-(H_f+d_2)\left(\hat{\theta}-\theta_i\right)\ln\left\{\left(\hat{\theta}-\theta_i\right)\left(d_1+d_2+H_f\right)+w-w_0\right\}\\ +(H_f+d_2)\left(\hat{\theta}-\theta_i\right)\ln\left\{\left(\hat{\theta}-\theta_i\right)\left(d_1+d_2+H_f\right)\right\}\end{aligned} \tag{9.13}$$

Simplifying

$$\tilde{k}_1\left(t-t_0\right)=w-w_0-\left(H_f+d_2\right)\left(\hat{\theta}-\theta_i\right)\ln\left\{1+\frac{w-w_0}{\left(\hat{\theta}-\theta_i\right)\left(d_1+d_2+H_f\right)}\right\} \tag{9.14}$$

Since t_0 and w_0 are likely to be very small quantities, the relation between cumulative infiltrated quantity and time is approximated as:

$$t=\frac{w}{\tilde{k}_1}-\frac{\left(\hat{\theta}-\theta_i\right)\left(H_f+d_2\right)}{\tilde{k}_1}\ln\left\{1+\frac{w}{\left(\hat{\theta}-\theta_i\right)\left(d_1+d_2+H_f\right)}\right\} \tag{9.15}$$

θ_i = initial moisture content of the soil in the unsaturated zone. $\hat{\theta}$ = moisture content behind the moving front in the soil layer which can be determined from the following relationship of $k_2(\theta)$ versus θ:

According to Van Genuchtan (1980), the relationship between soil moisture content, θ and hydraulic conductivity, $k_2(\theta)$ is given by:

$$k_2(\theta)=\tilde{k}_2\left(\frac{\theta-\theta_i}{\theta_s-\theta_i}\right)^l\left\{1-\left[1-\left(\frac{\theta-\theta_i}{\theta_s-\theta_i}\right)^{\frac{1}{m}}\right]^m\right\}^2 \qquad (9.16)$$

where θ = volumetric soil moisture content, θ_s= volumetric saturated soil moisture content, θ_i= volumetric residual soil moisture content, α = empirical parameter cm^{-1} depends on soil type, $n\, and\, m$ are the empirical parameters depend on soil type, $m=1-1/n$, l= pore connectivity parameter $\cong 0.5$, $\tilde{k}_2$ = saturated hydraulic conductivity of the soil underlying the liner. As per the postulation at $\theta=\hat{\theta}$, the hydraulic conductivity of the unsaturated soil behind the moving front is equal to the hydraulic conductivity of the liner. Hence,

$$k_2(\hat{\theta})=\tilde{k}_2\left(\frac{\hat{\theta}-\theta_i}{\theta_s-\theta_i}\right)^l\left\{1-\left[1-\left(\frac{\hat{\theta}-\theta_i}{\theta_s-\theta_i}\right)^{\frac{1}{m}}\right]^m\right\}^2=\tilde{k}_1 \qquad (9.17)$$

As $\hat{k}_1$ and $\hat{k}_2$ are known, $\hat{\theta}$ is obtained from Equation 9.17, following an iteration procedure.

At the time the moving front reaches the water table, the cumulative infiltrated quantity is given by: $w=(\hat{\theta}-\theta_i)D_w$, where D_w = depth to water table below the liner. Thus arrival time of the leachate at the water-table position is obtained from (9.15) as:

$$t_a=\frac{(\hat{\theta}-\theta_i)D_w}{\tilde{k}_1}-\frac{(\hat{\theta}-\theta_i)(H_f+d_2)}{\tilde{k}_1}\ln\left\{1+\frac{D_w}{d_1+d_2+H_f}\right\} \qquad (9.18)$$

If there is no lining material $d_1=0$ and, $\hat{\theta}=\theta_s$ and the relation between cumulative infiltrated quantity and time reduces to

$$t=\frac{w}{\tilde{k}_2}-\frac{(\theta_s-\theta_i)(H_f+d_2)}{\tilde{k}_2}\ln\left\{1+\frac{w}{(\theta_s-\theta_i)(H_f+d_2)}\right\} \qquad (9.19)$$

The time at which the saturation front touches the water table is given by

$$t_a=\frac{(\theta_s-\theta_i)D_w}{\tilde{k}_2}-\frac{(\theta_s-\theta_i)(H_f+d_2)}{\tilde{k}_2}\ln\left\{1+\frac{D_w}{H_f+d_2}\right\} \qquad (9.20)$$

Prior to the moving front reaching the water table, the wetting front soil suction head prevails and it ceases to act as soon as the moving front reaches the water table. Infiltration rate from the pond without lining just prior to the saturation moving front joining the water table is given by:

$$I(t_a) = \tilde{k}_2 \frac{H_f + d_2 + D_w}{D_w} \tag{9.21}$$

With lining the infiltration rate just prior to the unsaturated moving front joining the water table is:

$$I(t_a) = \tilde{k}_1 \frac{H_f + d_1 + d_2 + D_w}{d_1 + D_w} \tag{9.22}$$

Assuming that rise in water level height is nominal, the dimensionless recharge rate from unit area of the ash pond without lining is:

$$s / \tilde{k}_2 = \frac{d_2 + D_w}{D_w} \tag{9.23}$$

With lining the dimensionless recharge rate is

$$s / \tilde{k}_1 = \frac{d_1 + d_2 + D_w}{d_1 + D_w} \tag{9.24}$$

9.3 RESULTS AND DISCUSSION

The time of arrival of leachate wetting front at ground water table, that lies at a finite depth below an ash pond since ponding of the leachate in a lined ash pond has been calculated for five soil classes namely: Sand, Sandy loam, Clay loam, Silty-clay and Clay. The porosity, effective porosity, the residual soil moisture content after gravity flow ceases, saturated hydraulic conductivity, and wetting front soil suction head for each soil class are taken from Chow et al (1988). The parameters l, m appearing in the relation between $k_2(\theta)$ and θ for each soil class have been taken from van Genuchten et al (1992). The values of the parameter n for Sand, Sandy loam, Clay loam, Silty clay and Clay are taken as 2.68, 1.89, 1.31, 1.09, and 1.09 respectively. The parameter l has been taken as 0.5. The thickness of the liner is assumed to be 0.3 m. Results have been given for depth of ponding equal to *0.5 m*. Water table is assumed to be lying either at a depth of 5 m or 10 m below the ash pond bed. The infiltration rate when the wetting front reaches very near to the water table has been quantified. After the front reaches the water table the suction head ceases to act. Assuming that the rise in water table height is nominal consequent to recharge from the ash pond, the steady seepage rate of leachate has been quantified applying Darcy's law. The leachate volume joining ground water can be quantified multiplying the seepage rate per unit area with ash pond leachate spread area.

The moisture content $\hat{\theta}$ behind the moving front, the arrival time t_a of the leachate at the water table, the infiltration rate $I(t_a)$ and the steady seepage rate s are presented in Table1 for the case in which water table lies at a depth of 5m below the ash pond. Results have been given for hydraulic conductivity of lining, $\widetilde{k}_1$ ranging from 3.6×10^{-4} to 3.6×10^{-2} cm/ hour besides for brick lining whose hydraulic conductivity is 2.9×10^{-2} cm/hour (INCID, 2000). In Table2, results are presented for the case in which water table lies at a depth of 10m below the ash pond.

As seen from the tables, for hydraulic conductivity of lining, $\widetilde{k}_1 \geq 2.9 \times 10^{-2}$ cm/hour, leachate movement from an ash pond in Clay and Silty clay soils occurs through the soil in almost saturated state as behind the wetting front $\hat{\theta} \cong \theta_s$. In such case the arrival time t_a can be computed directly from equation (9.18) replacing $\hat{\theta}$ by θ_s.In Sandyloam soil, in the absence of a liner, the leachate would reach the water table that lies at a depth of 10m below the ash pond 13 days after ponding. With brick lining, $\left(\widetilde{k}_1 = 2.9 \times 10^{-2}\ cm/hour\right)$ the leachate would reach 308.7 days after ponding. With very impervious lining having hydraulic conductivity $\widetilde{k}_1 = 3.6 \times 10^{-4}$ cm/ hour, the leachate would reach the water table 10206 days after ponding. The seepage rate from unit leachate spread area being directly proportional to hydraulic conductivity of the liner, the seepage rate would be reduced by 100 times if an impervious liner is provided instead of a brick liner. Thus an impervious liner is preferable to brick lining if the ash pond happens to be located in a Sandy loam soil.

As per the postulation, the saturated hydraulic conductivity of the lining material and the unsaturated hydraulic conductivity of soil medium behind the moving wetting front are equal. Therefore, the seepage rate as well as the infiltration rate by the time the wetting front is very close to the water table is directly proportional to the hydraulic conductivity of the liner. The constant of proportionality as seen from equation (9.22) is $\frac{H_f + d_1 + d_2 + D_w}{d_1 + D_w}$ for infiltration case or is equal to $\frac{d_1 + d_2 + D_w}{d_1 + D_w}$ during steady state seepage. As seen from the Tables 9.1 and 9.2the constant of proportionality is marginally greater than 1.

9.3.1 An Example

An ash pond is underlain by sandy loam soil. The ponded leachate depth $d_2 = 0.5\ m$. The water table lies at a depth $D_w = 5\ m$. The ash pond is lined with brick and the thickness of lining $d_1 = 0.3m$ The hydraulic conductivity of brick lining is $0.0288\ cm/hour$. The leachate would join the water table 162.9 days after ponding. If the ash pond area is $159 hectares$, $12027\ m^3/day$ of leachate will join the water table. With a less permeable liner having hydraulic conductivity equal to $3.6 \times 10^{-4}\ cm/hour$, the leachate volume is $150\ m^3/day$.

9.4 CONCLUDING REMARKS

Based on Green and Ampt theory and a postulation for satisfying Horton's infiltration theory, simple analytical expressions are derived for computing the arrival time of leachate wetting front at water table below an ash pond, and the seepage rate. For Sandy loam soil, lining having hydraulic conductivity of the order of $3.6 \times 10^{-4}\ cm/hour$ is preferable to brick lining as the arrival time at water table which lies at a depth of 10m is 10206 days after ponding. The seepage from a lined ash pond is directly proportional to hydraulic conductivity of the liner.

Table 9.1-Leachate arrival time at ground water table after the first filling of the ash pond and dimensionless infiltration rate prior to the front joining the water table for different soil groups, and dimension less recharge rate for different soil groups corresponding to $d_2 = 0.5m, D_w = 5.0m$

Soil calss	θ_s	θ_r	H_f (cm)	$\tilde{k}_2$ (cm/hr)	n	$\tilde{k}_1$ (cm/hr)	$\hat{\theta}$	d_1 (m)	t_a (day)	$I(t_a)/\tilde{k}_1$	$s/\tilde{k}_1$	$I(t_a)/\tilde{k}_2$	$s/\tilde{k}_2$
Sand	0.435	0.02	4.95	11.78	2.68	-	-	0.0	0.55	-	-	1.109	1.1
						3.6E-04	0.052	0.3	1462	1.014	1.09	-	-
						3.6E-03	0.0796	0.3	272	1.014	1.09	-	-
						3.6E-02	1.3043	0.3	50.36	1.014	1.09	-	-
						2.9E-02	0.124	0.3	59.32	1.014	1.09	-	-
Sandy loam	0.453	0.041	11.01	1.09	1.89	-	-	0.0	5.74	-	-	1.122	1.1
						3.6E-04	0.145	0.3	4641.5	1.115	1.094	-	-
						3.6E-03	0.251	0.3	745.5	1.115	1.094	-	-
						3.6E-02	0.343	0.3	117.1	1.115	1.094	-	-
						2.9E-02	0.333	0.3	140.4	1.115	1.09	-	-
Clay loam	0.464	0.155	20.8	0.1	1.31	-	-	0.0	45.3	-	-	1.142	1.1
						3.6E-04	0.377	0.3	9602	1.134	1.09	-	-
						3.6E-03	0.429	0.3	1184	1.134	1.09	-	-
						3.6E-02	0.462	0.3	133	1.134	1.09	-	-
						2.9E-02	0.461	0.3	165	1.134	1.09	-	-
Silty clay	0.479	0.056	29.22	0.05	1.09	-	-	0.0	121	-	-	1.158	1.1
						3.6E-04	0.4648	0.3	17215	1.149	1.09	-	-
						3.6E-03	0.4782	0.3	1778	1.149	1.09	-	-
						3.6E-02	$\cong 0.479$	0.3	178	1.149	1.09	-	-
						2.9E-02	$\cong 0.479$	0.3	223	1.149	1.09	-	-
Clay	0.475	0.09	31.63	0.03	1.09	-	-	0.0	181.6	-	-	1.163	1.1
						3.6E-04	0.466	0.3	15726	1.154	1.09	-	-
						3.6E-03	0.4748	0.3	1608.5	1.154	1.09	-	-
						3.6E-02	$\cong 0.475$	0.3	160.9	1.154	1.09	-	-
						2.9E-02	$\cong 0.475$	0.3	201	1.154	1.09	-	-

Table 9.2-Leachate arrival time at ground water table after the first filling of the ash pond and dimensionless infiltration rate prior to the front joining the water table for different soil groups, and dimension less recharge rate for different soil groups corresponding to $d_2 = 0.5m, D_w = 10.0m$

Soil calss	θ_s	θ_r	H_f (cm)	$\tilde{k}_2$ (cm/hr)	n	$\tilde{k}_1$ (cm/hr)	$\hat{\theta}$	d_1 (m)	t_a (day)	$I(t_a)/\tilde{k}_1$	$s/\tilde{k}_1$	$I(t_a)/\tilde{k}_2$	$s/\tilde{k}_2$
Sand	0.437	0.02	4.95	11.78	2.68	-	-	0.0	1.235	-	-	1.055	1.05
						3.6E-04	0.052	0.3	3191	1.053	1.048	-	-
						3.6E-03	0.0796	0.3	593.8	1.053	1.048	-	-
						3.6E-02	1.3043	0.3	109.9	1.053	1.048	-	-
						2.9E-02	0.124	0.3	129.5	1.053	1.048	-	-
Sandy loam	0.453	0.041	11.01	1.09	1.89	-	-	0.0	13	-	-	1.061	1.05
						3.6E-04	0.145	0.3	10205.8	1.059	1.0485	-	-
						3.6E-03	0.251	0.3	1639.2	1.059	1.0485	-	-
						3.6E-02	0.343	0.3	257.5	1.059	1.0485	-	-
						2.9E-02	0.333	0.3	308.7	1.059	1.0485	-	-
Clay loam	0.464	0.155	20.8	0.1	1.31	-	-	0.0	104	-	-	1.071	1.05
						3.6E-04	0.377	0.3	21352	1.068	1.048		
						3.6E-03	0.429	0.3	2633.6	1.068	1.048		
						3.6E-02	0.462	0.3	295.6	1.068	1.048		
						2.9E-02	0.461	0.3	367.9	1.068	1.048		
Silty clay	0.479	0.056	29.22	0.05	1.09	-	-	0.0	279.6	-	-	1.079	1.05
						3.6E-04	0.4648	0.3	38627	1.0769	1.048	-	-
						3.6E-03	0.4782	0.3	3989	1.0769	1.0485	-	-
						3.6E-02	$\cong 0.479$	0.3	399.7	1.0769	1.0485	-	-
						2.9E-02	$\cong 0.479$	0.3	499.6	1.0769	1.0485	-	-
Clay	0.475	0.09	31.63	0.03	1.09	-	-	0.0	422	-	-	1.082	1.05
						3.6E-04	0.466	0.3	35376	1.079	1.048	-	-
						3.6E-03	0.4748	0.3	3618	1.079	1.048	-	-
						3.6E-02	$\cong 0.475$	0.3	362	1.079	1.048	-	-
						2.9E-02	$\cong 0.475$	0.3	452.5	1.079	1.048	-	-

CHAPTER 10

CONCLUSIONS

10.1 PRELUDE

A survey on utilization of fly ash from four thermal power plants in India reveals that the utilization of the fly ash is on the lower side as compared to global utilization level, which is an indication that wet disposal of fly ash prevails at the sources of the fly ash. To encourage the utilization of fly ash, information about chemical and physical properties as well as mineralogy and morphology of fly ash are required. To predict the consequences of wet disposal of fly ash on environment, laboratory measurement of the different constituents of fly ash, mobility of the metals present in the fly ash slurry through soil medium, metal concentrations in ash pond effluent, concentrations of the metal element in surface water and groundwater around ash pond are absolutely necessary. Detailed experiments on fly ash from four thermal power plants where coals of different types are used have been conducted both in neutral and acidic environment.

A mathematical expression has been derived which assumes the variations of distribution coefficients is constant for different elements present in the fly ash. Using the observed concentration the distribution coefficient has been determined solving the inverse problem making use of solution of the direct problem. The study has focused primarily on the leaching of metals from fly ash, their transport through soil and contamination of surface water and groundwater likely to occur due to wet disposal of fly ash. In this study, using Green and Ampt infiltration theory, the arrival time of the leachate from a lined ash pond at water table has been derived. The performance of low permeable liner in restricting the infiltration of leachate from the ash pond has been studied. The conclusions of this study and recommendations for the future research work are presented in this chapter.

10.2 CONCLUSIONS

Based on the experimental studies, field investigations and mathematical verifications of the test results, the following conclusions are drawn:

1. The chemical composition of fly ash plays important role in fly ash utilization, disposal and environmental impact assessment studies. In the present study classification of fly ash has been done and it is found that sum of SiO_2, Al_2O_3 and Fe_2O_3 is greater than 70%, as per ASTM (C618) specification, the ash used in the investigation is class F fly ash (low calcium ash). This is confirmed by source of coal used for generation of power. In all the power plants coal used is bituminous coal and ash produced from bituminous coal is always class F fly ash. Low calcium ash produce either neutral or mildly acidic leachate pH, which is a matter of environmental concern. Presence of low Ca makes it susceptible to land disposal and reduces its chances of utilization in construction or cement production.

2. All the fly ash samples were comprised mainly of amorphous alumino-silicates spheres and a smaller amount of iron rich spheres. The major elemental concentrations, as determined by EDAX, were consistent with X-ray diffraction data. XRD analysis identified the minerals where it is found that Quartz (SiO_2), Mullite ($3Al_2O_3$, $2SiO_2$) in most predominant phase and Hematite (Fe_2O_3) and Magnetite (Fe_3O_4) in minor phase. Sillimanite (Al_2O_3, $2SiO_2$) was additionally observed in Dadri fly ash and Albite ($Na\,Al\,Si_3\,O_8$) was also observed in Nashik fly ash.

3. Scanning electron micrographic (SEM) study confirms the presence of spherical particles, cenosphers, plerosphers, potato shape, irregular, holey (clinker like) particles, platy particles, and broken sphere. Atomic force microscopy gives surface roughness and particle size in nano scale, and also number of grains are displayed directly.

4. Through 'Laser Particle Size Analyzer' it is found that more than 90% particles are in the range of 0.1 μm-40 μm, 0.1μm-30μm, 0.1μm-65μm and 0.1μm-10μm for Bhatinda fly ash (BFA), Dadri fly ash (DFA), Nashik fly ash (NFA) and Surathgarh fly ash (NFA) respectively and it is also confirmed with scanning electron micrographic observations. Predominantly silt size particles have potential to become airborne in certain conditions and care should be taken to keep the ash pond surface free from fugitive dust pollution. With the particle size analysis, it can be concluded that it is suitable as filling material.

5. The cascade leaching test carried out in the present study closely simulates natural leaching of ash in the ash pond. The leaching trend showed initial high concentration and then decreasing to lower level. The pH of leachate is the vital parameter which controls the mobility of metals or the leaching of metals. Among metals studied in the present study, Cd is most easily water extractable element and this may pose problem in aquatic environment. Cu and Ni show lowest mobility in neutral environment. Data obtained through cascade leaching test is matching with ash slurry water concentrations for Nashik fly ash. Scanning Electron Micrograph of post leached samples clearly indicates that the surface of fly ash is leached.

6. The mobilization of metal ions from the oxides surface is primarily desorption phenomenon. To account the desorption phenomena a mathematical model is formulated, which gives metal concentrations in aqueous phase. Fly ash is heterogeneous material and therefore composite exponential decay models were fitted using MATLAB curve fitting tools however for some metals in neutral as well as acidic environment single exponential decay models were fitted to give better regression coefficient than composite exponential decay models. Using these graphs or the corresponding equations, the leachate concentration at future time can be extrapolated.

7. From the laboratory study it is found that leachate concentration varies exponentially with the stage of leaching. Leaching of fly ash with successive lumped and constant volume of leachant is based on the assumption that the distribution coefficient does not change during successive stages of leaching. Making use of the observed concentration, the model which is based on constant distribution coefficient, it is found that the distribution coefficient does not remain constant and it varies with the concentration of the leachate. Since the concentration changes, in successive stages of leaching, therefore, the distribution coefficient, which is found to be linearly dependent on leachate concentration will change during leaching process. The model developed is also applicable when the leachate influx volume changes from stage to stage of leaching.

8. Open percolation column test with soil and fly ash slurry reveals that most of the metals get attenuated during transport due to adsorption and precipitation. During slurry disposal, lower layer receives upper layer, which reduces hydraulic conductivity. Though the studies carried out in this work discover that it is not likely to pollute the groundwater due to heavy metals, it is likely to pollute unsaturated zone beneath the ash pond, therefore it would be appropriate to provide liner to ash pond.

9. Among two channels studied for ash pond effluent disposal, effluent from Eastern channel joining, Darna river concentration of iron is exceeding the effluent standard limit and for Southern channel only one sample is exceeding Fe concentration limit.

10. Concentration of Fe, Mn, Ni and Cd near to ash pond wells are more compare to wells located away from ash pond at Kotamgaon and Hinganvedhe villages. The concentration of metals Fe, Ni and Cd exceeds drinking water permissible limit of CPCB India, WHO and USEPA. Water is not fit for drinking purpose. These elevated concentrations in the groundwater may be through seepage from ash pond, use of ash pond effluent or lifted water of Darna river (which is already polluted due to ash pond effluent or settled ash in river bed) for irrigation.

11. In this study, using Green and Ampt infiltration theory, the arrival time of the infiltrating leachate from a lined ash pond at water table has been derived. The performance of the low permeable liner in controling infiltration rate and arrival time at a water table beneath the ash pond has been investigated. The need of provision of a liner is investigated for different soil groups.

11.3 RECOMMENDATIONS FOR FUTURE RESEARCH

1. To investigate the leachability of metals, field lysimeter would give more correct concentrations of leached metals, which can better represent field situation. Therefore leaching studies with field lysimeters are advocated. Regular monitoring of groundwater throughout the season and pre-post disposal of fly ash slurry would give the extent of contamination during those disposal scenarios. Field lysimeter data coupled with laboratory data would be handy for remediation method to be used.

2. Fly ash is heterogeneous material and though most of the fly ash generated in India is alkaline nature, many coal ashes are enriched in arsenic, boron, selenium and chromium and it is likely that large quantities will be released to the aqueous phase upon extended contact with water depending on prevailing pH conditions. Boron is known to leach from coal ash in substantial quantities and to be extremely mobile in the soil system. Further work is needed to study the leaching behavior of these metals and also to accurately predict its sorption as well as transport from the ash pond , particularly in the case of As(III) for Nashik fly ash and Boron for Bhatinda fly ash.

3. Experimental investigations are necessary for infiltration of fly ash slurries in different soil profile, which can be useful for quantification of leachate produced and leachate joining to groundwater table. To connect the infiltrated volume to surrogate time requires separate study.

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PUBLICATIONS

Following Publications are made from the Thesis

Sr. No	Title of Research paper	Journal/Seminar	Status/Details
Published			
1	Leaching studies and metal analysis of fly ash from Thermal Power Plant of India	Journal of Solid waste Technology & Management, USA	Vol-35, No.2, May 2009, pp 115-123
2	FE-SEM EDAX Studies on fly ash particles	JERAD , An International Research Journal of Natural Sciences, Technology and Social Sciences for Environment	Vol-04, No.01, July-Sept, 2009, pp 55-61
3	Issues and challenges associated with fly ash disposal in India	Journal Enironmental Pollution Control. India.	Vol-11, No.6, Sep-Oct 2008, pp 69-72
4	Fly ash Disposal in India	National Conference	16-17 June, 2008 pp. 518-523.
5	Determination of chemical composition of Bottom and pond ash with the help of FESEM-EDAX	National Conference	23-24, January, 2009, pp 210-212
Submitted			
6	Open percolation column leaching studies on fly ash from India and changes in morphology, mineralogy and particle size due to leaching	Elsevier science Journal FUEL Manuscript No. JFUE-D-09-00830	Under review
7	Mineralogy, Morphology and Leaching of fly ash slurry at different L/S ratio	International Journal Inderscience Publishers	Under review
8	Infiltration of leachate from an ash pond Through a liner	International Conference at I I T Chennai Sep. 2010	Accepted.

ANNEXURE-I

A sample calculations

Element : Fe

Total mass of a fly ash containing all elements considered in the leaching test: 100 gm.

Mass of Fe in 1 kg of fly ash obtained from acid digestion test (Table 4.3): 10407 mg

Therefore, mass of a Fe present in 100 gm of fly ash: 1.0407 gm

Sum of mass of all elements present in the fly ash as measured from acid digestion test (Table 4.5) : 12166 mg/kg =12.166 gm/kg= 1.2166gm/100 gm

Unleached part which remains constant during cascade leaching test in 100 gm of fly ash = 100-1.2166= 98.7834 gm. ; therefore, ρ = 98.7834 gm.

Total mass of Fe before leaching = $\rho M_i(0)$=1.0407 gm

Therefore, $M_i(0) = \frac{1.0407}{\rho} = \frac{1.0407}{98.7834} = 0.010535$

Performing mass balance

Initial mass present in the fly ash -Leached quantity during first stage = Fe present after leaching

$$\rho M_i(0) - VC_i(1) = \rho M_i(1) = \rho \frac{C_i(1)}{k}$$

$$k = \frac{\rho C_i(1)}{M_i(0)\rho - VC_i(1)}$$

$$k = \frac{98.7384(gm) \times 0.8(mg/lit)}{1.047(gm) - 0.2(lit) * 0.8(mg/lit)}$$

$$k = \frac{0.0008(gm/lit) \times 98.7384(gm)}{1.047(gm) - \{0.2(lit) \times 0.0008(gm/lit)\}}$$

$$k = 7.5455E - 05(kg/lit)$$