GEOCHEMISTRY OF TAILINGS AT MALANJKHAND COPPER MINE, MADHYA PRADESH

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

**BACHELOR OF TECHNOLOGY
IN
MINING ENGINEERING**

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CERTIFICATE

This is to certify that the thesis entitled "**Geochemistry of mine tailings at Malanjkhand Copper Mine, Madhya Pradesh**" submitted by Sri Subhashis Sahu (Roll No. 110MN0535) and Sri Sumit Kumar Basantray (Roll No. 110MN0387) in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Mining Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in this thesis has not formed the basis for the award of any Degree or Diploma or similar title of any University or Institution.

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CONTENTS

ABSTRACT

This study aimed at mineralogically characterizing and finding the metal content of the tailings coming out from the mining of copper at Malanjkhand copper mine, located in north east of Balaghat, Madhya Pradesh which is the largest copper deposit in India producing nearly 2.2 million tonnes of copper tailings annually. The tailings were characterized geochemically by taking samples from the tailing pond. The mineralogy of the samples were studied and the concentrations of copper, lead, zinc, cadmium, manganese and nickel were measured. The tailings mostly consisted of quartz, kaolinite, muscovite, plagioclase, pyrite, chalcopyrite, orthoclase, goethite, chloride and jarosite. Copper, cadmium and lead were above their respective crustal abundance and the concentration of copper was found to be the maximum.

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CHAPTER 1

INTRODUCTION

1.1.   INTRODUCTION

Metals or minerals are required for several purposes such as for industries, developing products etc. and the ore which is mined out from the earth has to be processed in various beneficiation plants. The materials which are left over after the process of separating the valuable or required part of an ore are referred to as tailings. They are a mixture of water and finely ground rock that is left over after the mineral concentrate is removed (USGS, 2014). Since it is not possible to completely extract the required part, generating tailings or waste is obvious. These are generated from every mine and are considered under the category of solid wastes (USEPA, 1994). Tailings have an adverse effect to the environment. The arrangement for storing tailings is done away from the ecologically unstable/sensitive areas. The chemicals or elements should be below the threshold levels so that the impact on the environment should be minimum.

The total world production of copper is 18 million metric tons per year (USGS, 2014). The demand of copper is increasing every year by 575,000 tons and it is accelerating (Leonard, 2006). Figure 1.1 shows the region wise production of copper across the world. During the year 2012 the production of copper in India was 689,312 tonnes and the demand is expected to almost double itself in the year 2020 (MPPCB, 2011). Therefore, intense mining activities for Cu and its beneficiation is expected.
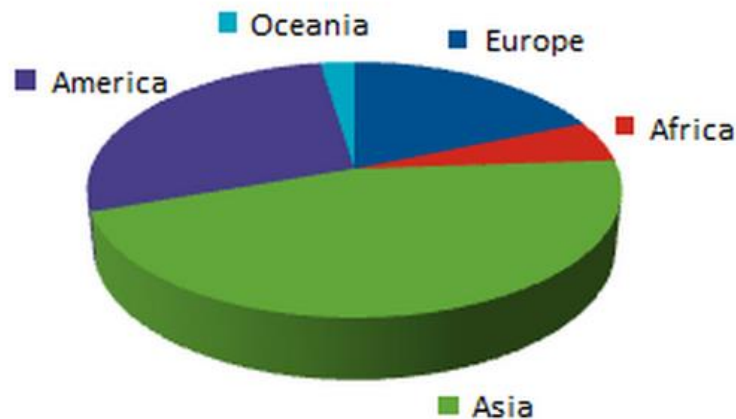

Fig.1.1: World copper production (Source: www.world-bureau.com)

Copper mine tailings have high levels of heavy metal concentration which proves to be toxic to vegetation. The pH of the water around the tailings is lowered to about 2-4 in some cases which makes it unsuitable for drinking and other purposes (Jambor et al., 2003; Alvarez et al., 2006). The heavy metals present in the tailings are released into water bodies due to their mobility (Jang et al., 2005). They may also cause serious diseases to humans via crops and water as it easily gets accumulated in the body organs (Lee et al., 2007). Heavy metals decrease water and nutrient uptake by plants, decrease root respiration, inhibit cell mitosis and reduce enzymatic activity in soil (Gemmell, 1977). Copper mining and its beneficiation release large amounts of dusts which comprises of trace elements, oxides of sulphur and particulate matter that affect the air quality adversely. Transportation of these gases and sulphur dioxide released from smelters causes acid deposition, lessening of visibility, layers of coating of houses, damage to flora and frequent health problems (Hester et al., 1995).

Malanjkhand copper deposit is the largest single copper deposit in Asia. The Malanjkhand copper deposit has its own beneficiation plant of 2 million tonnes capacity for processing copper. It has more than 70 percent of the known copper reserves in the country. The Malanjkhand copper project produces about 3 million tonnes of ore at 1.05 percent copper (MPPCB, 2011). About 2.2 million tonnes of tailings are being deposited every year (Pandey et al., 2007).

1.2.   OBJECTIVES

With the above background in mind, this project work has been attempted to study the following aspects at the Malanjkhand copper mine:

- ➢ To study the of mineralogy of the tailings
- ➢ To determine the concentration and distribution of metals in the tailings

CHAPTER 2

LITERATURE REVIEW

The elements and compounds discovered and liberated during mining and beneficiation can affect the environment in very diverse ways, although it depends upon the concentration or extent of the elements or compounds liberated. Most of the mining wastes contain minerals formed under environmental conditions such as high temperature, high pressure etc. When exposed to different environmental conditions or even after processing of the ore, the minerals may breakdown which results in elements coming out of their mineral forms which have the potential to cause serious environmental damage. This behavior of the elements can be described by the fact that they have come out of their mineral forms and are exposed to a new ecosystem (Franks et al., 2011).

Various cases of severe environmental damage have been witnessed in the past due to tailings. The gold mining operations in Johannesburg, South Africa has resulted in the production of large amounts of tailings which were being deposited in the tailing impoundments. The bad management of dams led to seepage that adversely affected the soil and water quality. Seepage also posed a threat to the underground dolomitic aquifers. Elements such as Co, Ni, and Zn were found to be present in the tailings and having an adverse effect on the soil quality (Rosner et al., 1999). Large amount of acid water and mud containing toxic metals such as Bi, Co, Th, Cd, Cu, and Sb were released in the surroundings of Do˜nana Park as a result of the spillage accident of the mine tailings in Aznalcollar, South West of Spain. These heavy metals contaminated the water bodies (Grimalt et al., 1999). In El Salvador copper mine, Chile the tailings affected the coastal shores of North Chile. The tailings mainly consisted of Cd, Cu, Fe, Mn, Ni, Pb and Zn and they undesirably affected the biodiversity of the area (Ramirez et al., 2005).

2.1 CASE EXAMPLES OF COPPER MINE TAILINGS COMPOSITION

2.1.1 MINE TAILINGS AT THE COPPER BELT, ZAMBIA

The total copper reserves (identified & inferred) were 146 million tonnes at 2.3 percent. There are two sulfidic mine tailings within the Zambian copper belt namely Chambishi (age-40 years) and Mindolo (age-less than 10 years). Pore water in the Chambishi area had 568 mg/l of Ca and 1820 mg/l of sulphate. The Fe and Mn concentrations are below 0.1 mg/l and concentrations of Cu and Co are below 0.05 mg/l. The secondary minerals detected through X-Ray diffraction

were gypsum, poorly crystalline Fe (III) phases marked by red colour and haematite (Sracek et al., 2009).

2.1.2 COPPER MINE TAILINGS, DUCKTOWN, TENNESSEE

The closure of mining operations led to the generation of 800-900 acres of barren copper mine tailings. The heavy metal concentrations were found to be 2-100 mg/kg Cu, 5-500 mg/kg Ni, 20-300 mg/kg Mn, 10-300 mg/kg Zn, 0.6-1.1 mg/kg Cd and about 54 mg/kg Cr. Such levels of metals were toxic to the vegetation. There were acceptable calcium and magnesium but the levels of copper levels but the levels of copper were high due to the nature of the deposit. Cd and Cr concentrations were also slightly higher than normal (Branson et al., 2004)..

2.1.3 COPPER MINE, ONTARIO, CANADA

The copper and nickel ores appearing in this area are sulfidic in nature and were discovered in 1883. The area covered by the tailings dams is about 2226 ha. The mineralogy of the tailings sample showed about 50% feldspar, 20% amphiboles (chlorite), 10% of Quartz, and other minerals such as biotite, pyrrhotite etc. The tailings samples also contained about 81 ppm of Cu, 87 ppm of Ni and 59-441 ppm of Fe (Peters, 1984).

2.1.4 MOSABONI COPPER MINE

Mosaboni copper mine, in the Singhbhum Shear zone in east India is a large producer of copper. The tailing materials show the presence of different forms of heavy metals like Zn, Fe, Mn, Cu, Co, Ni and Pb. The samples contained minerals abundant in pyrite, chalcopyrite, molybdenite, pyrrhotite and other sulfidic minerals. The order of metal mobility was in the order of Cu>Ni>Mn>Zn>Co>Pb (Maiti et al., 2005).

2.2 ENVIRONMENTAL EFFECTS OF COPPER MINING

Copper mining affects the environment in many diverse ways. It has various effect on environmental parameters such as water quality, soil quality etc. Each and every phase of production of copper i.e. milling, smelting, refining and electrowinning have possible effects on surface and groundwater quality. Land disposal practices that fail to contain the wastes, run-on and run-off controls that are inadequate to prevent surface water from flowing through impoundments, or groundwater infiltrating surface impoundments are the reasons why the water

quality is getting adversely affected. Open pit mining is often associated with land disturbances on a large scale which hampers the natural flow of surface and ground water and also lower the water table in the mine area. This lowering of water table leads to the scarcity of water, land subsidence, and fracturing; the latter speeds up the transfer of contaminants into and through an aquifer (USEPA, 1994).

As the copper mine tailings are associated with a number of heavy metals, they too have an impact on the environment. The precipitation of copper occurs on reaction with carbonates, sulfides and hydroxides (Kabata-Pendias and Pendias, 1992). Hence, it easily gets deposited on surface adversely affecting the soil quality as it decreases the water and nutrient uptake by plants and the root respiration (Gemmell, 1977). When the concentration of calcium and phosphorus is high in soils, the zinc content gets immobilized. This effect is the highest in acidic conditions. In the presence of a basic environment the lead content can be precipitated as a hydroxide carbonate or. Nickel gets oxidized by Fe and Mn oxides. It is highly stable in aqueous conditions and can be transported over long distances. Cadmium is coupled with zinc and has a higher mobility in acidic environments and has a higher affinity towards sulphur phosphate (Kabata-Pendias and Pendias, 1992).

2.4 MALANJKHAND COPPER DEPOSIT

Malanjkhand copper deposit is an open cast copper mine located in Malanjkhand having coordinates 22º0'54''N and 80º43'20''E. It is the biggest base metal copper open pit mine in India. It is situated at a distance of 90 Km North East of Balaghat in Madhya Pradesh, at an altitude of 576mRL (meters Reduced Level). It is located in the tehsil of Bihar, which is 22 Km away from the project, on the way to the district town, Balaghat, Madhya Pradesh.

Malanjkhand copper project was established in the year 1982. Hindustan Copper Limited set up the initial project for the exploitation of the copper ore through open pit mine. Geological Survey of India took systematic geological exploration at this deposit in the year 1969. It is the largest open cast copper mine in Asia. The copper deposit in Malanjkhand is presently in the exploitation phase and the exploitation is carried out M/s Hindustan Copper Limited. The zone of mineralization could be found in the approximately 2.6 Km long arcuate Malanjkhand hill (elevation about 600 m above m.s.l.) (GSI, 1994).

The basement rocks have an overlying Precambrian metasediments of Chilpi Ghat Series with an erosional unconformity. The granitic rocks range in composition from a biotite granite to quartz diorite and they are highly kaolinised, sericicised and saussuritised in the mineralised zone. Conglomerates, grits, phyllites and shales are the composition of the metasediments. The quartz reefs, associated with the granites have a localized copper mineralization (Pandey et al., 2007).

The sulphide minerals are seen mainly along the shear and fracture planes in the quartz reefs. The ore minerals in decreasing order of abundance are chalcopyrite, pyrite, magnetite, sphalerite, chalcocite, bornite, molybdenite and cobaltite. Chalcopyrite and pyrite make up to 95% of the sulphide minerals (GSI, 1994).

The ore zone has a strike length of about 1.9 km with an average width of about 65 m. and dips at an angle of about 60° towards east. About 68,000 m. of drilling has been done along 27 cross section lines spaced 80 mt to 120 mt apart.

The drilling investigations were carried out by GSI, MECL and the mine development was carried out by Hindustan copper limited. The reserves available upto 600m below the surface was 236.4 million tonnes at 1.28 percent copper out of which 145.7 million tonnes were proven, 50.4 million tonnes were categorized as probable and 40.3 million tonnes as possible reserves (GMRI, 2009).

Copper ore having around 1.05% copper content is subjected to ore processing which involves various processes like grinding, crushing, floatation, thickening, and filtration and it produces a copper concentrate which has around 25% copper. In the beneficiation process 5-7% of ore are transformed into concentrate and the rest are discarded as tailings which counts up to 90-95% of the extracted ore. The copper ore tailings which are the left out materials after extracting copper are stored in the tailing dams constructed at the Malanjkhand Copper Project. And as time progresses the quantity of copper ore tailings keep on increasing (Pandey et al., 2007).

CHAPTER 3

METHODOLOGY

3.1 SAMPLE COLLECTION

Tailing samples were collected from the tailing pond through grab sampling process. The tailing samples were dried, crushed and sieved through 230 mesh size.

3.2 MINERALOGICAL STUDY

The collected tailing samples were air dried for 2 days for removal of external moisture. The samples were then crushed to -200 mesh size. The powdered sample was then put into the mould for putting it in the Multipurpose X-Ray Diffraction System (Rigaku Japan/Ultima-IV). This machine used a copper target of wavelength 1.54 Å. The graph obtained was then analysed with the help of available XRD data for minerals.

Figure 3.1: X-Ray Diffraction Analyser

3.3.1 ELEMENTAL STUDY

Total concentration of Cu, Pb, Zn, Mn, Ni and Cd was measured using AAS after the microwave digestion using an acid mixture of nitric acid, hydrofluoric acid and distilled water (Sandroni et al., 2003).

The fractionation study of metals in tailing was done by sequential extraction process using the BCR method (Rauret et al., 1999). It follows the process of selective extraction and the release of metals into the solution takes place. The concentrations are then measured by atomic absorption spectroscopy.

It is accomplished in four steps summarized as follows:

1. Extraction of all exchangeable acid and water soluble metals by using acetic acid (CH_3COOH).
2. Extraction of all reducible metals by using hydroxylamine hydrochloride ($NH_2OH.HCl$).
3. Extraction of all oxidisable metals using hydrogen peroxide (H_2O_2) and ammonium acetate (CH_3COONH_4).
4. Extraction of the residual non silica bound metals using aqua regia (HCl: HNO_3:: 3:1).

3.3.2 EXPERIMENTAL PROCEDURE:

Part I: For extracting all exchangeable acid and water soluble metals

1. Firstly 100 ml of 0.11 M acetic acid was prepared.
2. About 1 gm of the powdered sample (-200 mesh size) was taken and dried to remove moisture.
3. Each sample was taken in a 50 ml centrifuge tube and 25 ml of the 0.11 M acetic acid solution was added to it.
4. A stopper was attached and the centrifuge tubes were shaken at 100 rpm for 16 hours (overnight) at 25ºC in a mechanical shaker. There should be no time lag between addition of the solution to the sample and shaking.
5. After completion of shaking the extract from the solid residue was separated by centrifuging the tubes at 6000 rpm for seven minutes.
6. The supernant liquid was decanted and put into a plastic container and the residue was taken for the next step.

7. The supernant liquid separated was then acidified below a pH < 2 using nitric acid and taken for analysis.

Part II: For extracting all reducible metals

1. 100 ml of 0.5 M hydroxylamine hydrochloride was prepared.
2. 25 ml of the prepared solution was added to the residue obtained from Part I in a 50 ml centrifuge tube.
3. A stopper was attached to each tube and the centrifuge tubes were shaken at 100 rpm for 16 hours (overnight) at 25ºC in a mechanical shaker. There should be no time lag between addition of the solution to the sample and shaking.
4. The centrifugation and decantation process was same as in Part I (step 5 and step 6).
5. The supernant liquid separated was then acidified below a pH < 2 using nitric acid and taken for analysis.

Part III: For extracting all oxidisable metals

1. 50 ml of 8.8 M hydrogen peroxide and 150 ml of 1 M ammonium acetate were prepared.
2. To the residue obtained in Part II, 5 ml of 8.8 M hydrogen peroxide was added in small aliquots to avoid a possibly violent reaction.
3. The centrifuge tube was loosely covered and it was digested at room temperature for 60 minutes with occasional manual shaking.
4. The digestion was continued for another hour at 85±2ºC in a paraffin bath.
5. The volume was then reduced to less than 3 ml by further heating of the uncovered tube.
6. 5 ml of 8.8 M hydrogen peroxide was again added and the covered test tubes were heated again at 85±2ºC and digested for another hour.
7. The cover was removed and the volume was decreased to about 1ml.
8. 30 ml of the 1 M ammonium acetate solution prepared earlier was added to it.
9. The centrifuge tubes were then shaken at 100 rpm for 16 hours (overnight) at 25ºC in a mechanical shaker. There should be no time lag between addition of the solution (ammonium acetate) to the sample and shaking.
10. The centrifugation and decantation process was same as in Part I (step 5 and step 6).
11. The supernant liquid separated was then acidified below a pH < 2 using nitric acid and taken for analysis.

Part IV: For extracting all residual metals.

1. 120 ml of aqua regia was prepared by adding 30 ml of conc. Nitric acid to 90 ml of conc. Hydrochloric acid.
2. 25 ml of the aqua regia solution prepared was added to each of the residues obtained in Part III.
3. A stopper was added and the centrifuge tubes were shaken at 100 rpm for 16 hours (overnight) at 25ºC in a mechanical shaker. There should be no time lag between addition of the solution (aqua regia) to the sample and shaking.
4. The centrifugation and decantation process was same as in Part I (step 5 and step 6).
5. The supernant liquid separated was then acidified below a pH < 2 using nitric acid and taken for analysis.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 MINERALOGY

The X-Ray Diffraction pattern of the tailing samples are shown in Figure 4.1 and 4.2. It was observed that the samples mainly dominated by quartz, orthoclase followed by chlorite, kaolinite, muscovite, plagioclase. Trace amount of pyrite and chalcopyrite were also identified. At some places tailing materials consist of goethite, jarosite along with quartz and kaolinite.
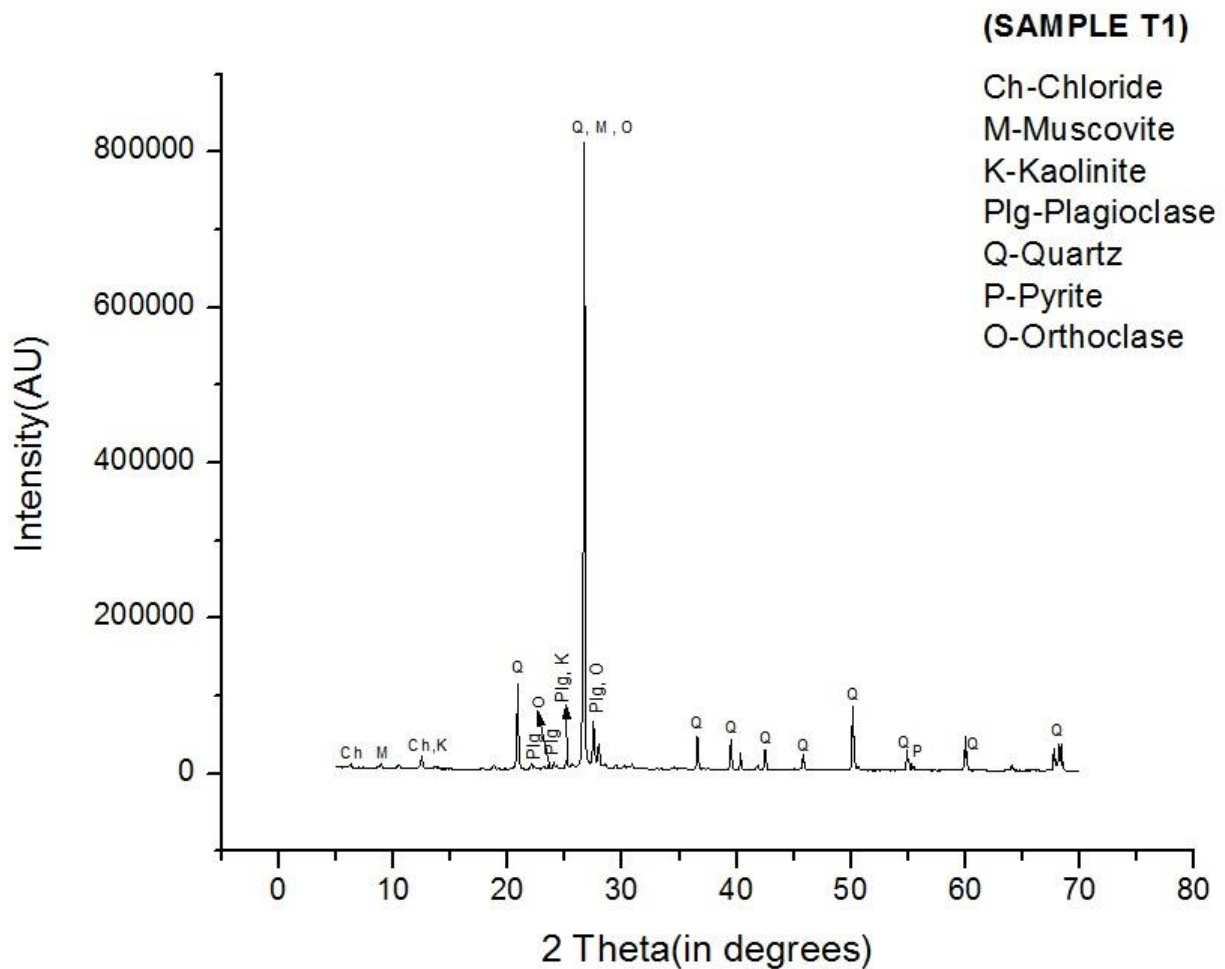
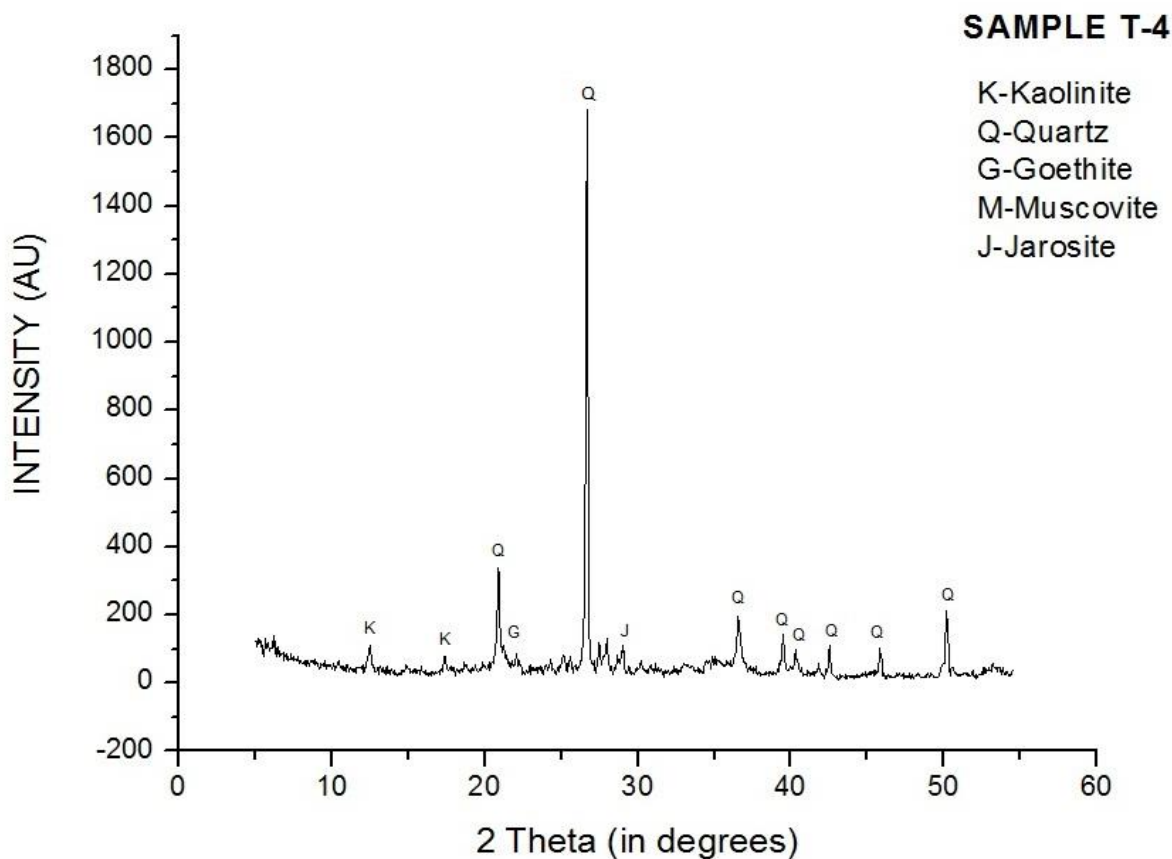**Figure 4.1:** X-Ray diffraction pattern of tailing sample

Figure 4.2: X-Ray diffraction pattern of tailing sample

4.2 TRACE ELEMENTS

The metal concentration in the tailing is given in Table 4.1. It was observed that the concentration of Cu varied from 80 to 810 ppm, the concentration of Zn varied from 20 to 95 ppm, the concentration of Mn varied from 40 to 200 ppm, the concentration of Cd varied from 0.2-0.6 ppm, the concentration of Pb varied from 4 to 30 ppm and the concentration of Ni varied from 5 to 25 ppm. Except Mn and Ni, all other metals are above their respective crustal abundances in most of the samples. The percentage distribution of the average concentrations is as shown in Table 4.2.

The sequential extraction for the samples was carried out by the BCR method (Rauret et al.,1998). Different chemicals were used for different stages. 0.11 M Acetic acid for the exchangeable metal concentration, 0.5 M of Hydroxylamine hydrochloride for the reducible content, a combination of 8.8 M Hydrogen peroxide and 1 M Ammonium acetate for the oxidisable content and Aqua regia for the residual content.

The exchangeable (water soluble), reducible, oxidisable and residual metal concentrations were obtained. Considering the elemental distribution of the samples, from Table 4.2, it can be observed that about 75 percent of copper was distributed among the exchangeable and the residual content. However, the quantity of copper in each stage is significantly higher than other metals. It was also observed that about 65 percent of cadmium was in the acid extractable stage. It means that about 0.45 ppm, which is still higher than the crustal abundance of cadmium, is soluble in water or weak acids. Considering Pb, it was observed that more than 75 percent was extracted in the Aqua Regia step which indicates the presence of crystalline phases of Pb which are less susceptible to dissolution. Zn, Mn and Ni also followed the same trend as Cu, with the majority of the metal distributed among the exchangeable and residual proportions of the metals. In each case more than 85 percent of the metals were extracted in the acid extractable stage and the Aqua Regia stage. This trend was followed in the individual samples as well. But in the case of T-2 it was observed that more than 85 percent of every element was extracted in the Aqua Regia step. This indicates that the metals present in the sample T-2 are in crystalline phases and are less prone to dissolution.

Table 4.1: Total concentrations of the elements in tailings

ELEMENT	TOTAL CONCENTRATION(in ppm)	CRUSTAL ABUNDANT (in ppm)
Copper	490.14	25
Zinc	49.75	65
Manganese	108.32	527
Cadmium	0.848	0.01
Lead	18.98	14.8
Nickel	13.272	56

Table 4.2: Elemental distribution for the Samples

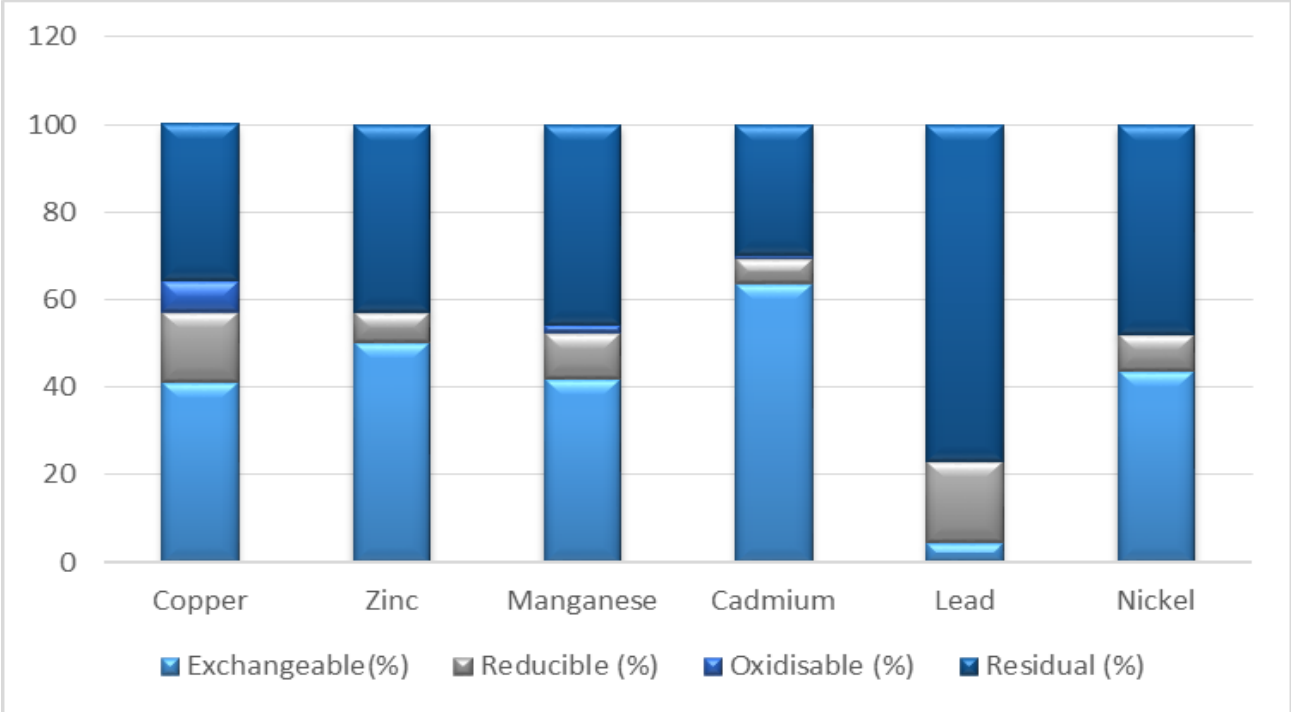| Element	Exchangeable(%)	Reducible (%)	Oxidisable (%)	Residual (%)
Copper	40.97	16.27	7.05	35.76
Zinc	50.17	7.02	0	42.81
Manganese	41.83	10.54	1.87	45.76
Cadmium	63.65	5.66	0.99	29.7
Lead	4.36	18.81	0	76.83
Nickel	43.58	8.59	0	47.83

Figure 4.3: Distribution of elements in the samples

CHAPTER 5

CONCLUSION

The mining and processing of copper ore produces large quantities of wastes in the form of tailings. In the Malanjkhand copper project nearly 75% of the ore is dumped as tailings which amounts to about 2.2 million tonnes of tailings per year. The mine wastes are associated with sulphidic minerals such as Pyrite, Chalcopyrite and other minerals such as Quartz, Muscovite, Pagioclase, Orthoclase, Kaolinite, Goethite and Jarosite. The metal mobility was also found to be in the order of Cd> Zn > Ni > Mn > Cu > Pb. Regarding the distribution of metals, about 40% of the total Copper, 63% of the total Cadmium and about 42% of Nickel and Manganese present was found to be soluble in water. The reducible and oxidisable contents were significantly lower, whereas the residual metal content was again higher. The metals found in excess of the crustal abundant were Copper, Cadmium and Lead. Thus, these metals are likely to have a significant impact on the environment around Malanjkhand Copper Mine.

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