EFFECT OF USING TANNERY SLUDGE IN CONCRETE

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A thesis submitted by

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CERTIFICATE OF APPROVAL

We hereby recommended that the thesis titled **"EFFECT OF USING TANNERY SLUDGE IN CONCRETE"**, submitted by **SONIA HASSAN**, Student Number-0409042132(P) be accepted as fulfilling this part of requirements for the degree of Masters of Engineering in Civil and Environmental on 25th October, 2014.

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Abstract

Leather is one of the prospective industries of Bangladesh. Bangladesh annually exports millions of dollars worth of leather goods to some 70 countries, including Australia, U.S. and Japan. At the same time, this is one of the industries in Bangladesh, which causes alarming environmental pollution. In this study, an attempt has been taken to analyze the use of tannery sludge in a suitable sludge stabilization process to reduce the heavy metal concentration in it. For this purpose, solidification, a stabilization process that involves mixing the waste with a binder to reduce the contamination leachability by physical and chemical means, was used to assess the stabilization of heavy metals present in the sludge. The main objective of this study is to assess the likelihood of stabilization of the heavy metals in tannery sludge with the concrete mix and to assess the usability of the sludge mixed concrete in construction work.

To conduct the study, raw sludge sample was collected from Apex Tannery and the preselected properties of the raw sludge were determined. The heavy metal contents of the sludge sample were determined in terms of total Cadmium (Cd), Lead (Pb), Chromium (Cr) and Copper (Cu). Subsequently, the sludge was mixed with cement, aggregates to prepare concrete specimen, and left to solidify for 28 days. The compressive strengths as well as other physical properties and chemical constituents of the mixes were determined to analyze their performance.

During the study, 0%, 1%, 5%, 10%, 15%, and 20% of sludge were used by weight of cement replacing equal weight of the sand to prepare the mix. The sludge sample was oven dried, powdered and sieved to achieve a uniform gradation. 0.50 water/ cement ratio was used for all the mixes. Concrete Strength decreased with the increasing addition of sludge on the mixes. The result showed that the sludge/ cement ratio up to 5% met the requirement for both physical and chemical properties. The repeatability test also confirmed initial test results found for 5% of sludge/ cement addition in concrete. In both cases 15% compromise of strength was founded compared to the sludge free concrete.

The TCLP test results of the crushed concrete showed that the high concentration of chromium and the lead contents of the raw sludge were stabilized to desired range. A remarkable amount of stabilization was taken place for all ranges of sludge addition in concrete.

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ABBREVIATIONS

ACI	American Concrete Institute
ASTM	American Society for Testing and Materials
ECA’95	Environmental Conservation Act 1995
ECR’97	Environmental Conservation Rules 1997
LDR	Land Disposal Restriction
NIST	National Institute of Standard and Technology
OPC	Ordinary Portland Cement
SPLP	Synthetic Precipitation Leaching Procedure
TC	Toxicity Characteristics
TCLP	Toxicity Characteristics Leaching Procedure

CHAPTER ONE
INTRODUCTION

1.1 General

Tannery is one of the major industries in Bangladesh. Bangladesh earns significant amount of foreign currency by exporting leather goods from its tanning industries. A recent report has revealed that leather and leather products are one of the major external trade sectors, which contribute up to 1.39% share on the total export earnings. However, tanning industries pose a serious environmental hazard for Dhaka, the hugely populated capital city of Bangladesh. Hazaribagh (Dhaka) is one of the most concerned tanning industry concentrated zones in Bangladesh. Hazaribagh is situated on the south-west part of the Dhaka and the largest tanning industrial area of the country, has around 400 tanning units. The River Buriganga is flowing on the western side of the area. The total households of the upazila are 25,914 units and the total population is almost 1, 27,370. From the tanning units of Hazaribagh area, roughly 15000 m^3 of untreated wastes containing various chemicals go to the low-lying areas and to the nearest water bodies including river Buriganga.

The leather industry sector of Bangladesh has been almost entirely supported by the local raw material resources i.e. buffalo and cowhides, goat and ship skins. The tannery industries of Bangladesh process 211 square feet of raw hide and skin. A large amount of solid waste (about 69.1 T/day in lean period) is generated by leather manufacturing process in Hazaribagh area. The physical look and smell of the Hazaribagh area is alarming and intolerable. Trimmed leather, fleshes from cow and buffalo hides, hair, liquid and solid wastes generated at different stages of production are spread and piled all over Hazaribagh in large quantity. The tanning process requires a huge amount of chromium and a significant fraction of this chromium is discharged along with the effluent from the industry. The sludge of the tannery has a high level of contamination especially heavy metals. The notable heavy metals of concern in Bangladesh are Lead, Chromium, Cadmium, Copper, Mercury, Aluminum etc.

The large quantity of wastes-solid and liquid- accumulated in the low land on the west side of Hazaribagh, is terrible. Liquid waste is pumped out round the clock on the other side of the Dhaka protection embankment in that area. This liquid waste ultimately goes into water of the Buriganga River and causes immense harm to the fishes and other species in the water. Eventually, the tannery waste is poisoning the soil, water and air. Tannery wastes also cause harm to health, houses and utensils of those situated around the area.

The national environmental legislation known as Environmental Conservation Act, 1995, is currently the main legislative document relating to Environmental Protection in Bangladesh, which repealed the earlier Environmental Pollution Control Ordinance of 1997 and has been promulgated in 1995. One of the main objectives of ECA 1995 is to regulate of the industries and other development activities discharge permit. Also the Department of Environment (DOE) has promulgated the Environment Conservation Rules 1997 under the ECA 1995 to evaluate, review the Environmental Impact Assessment (EIA) of various projects and activities, and procedures be established for approval. In ECR, 1997, the tannery industry falls in red category and the waste needed to be treated before disposal. However, the industries are virtually on their own in setting up course of action regarding the sludge disposal. Bangladesh Government has been trying to relocate Hazaribagh Tannery State to Savar. But the shifting is now getting delayed over the last decade due to the delay in setting up of the common effluent treatment plant (ETP) of the proposed industrial zone.

In recent years, however, the intensities of pollution have increased because of the problems brought about by the high rate of industrialization and the applicability of the methods of removal. Presently reuse of the hazourdous industrial waste is advocated worldwide. Solidification has been considered as an option of the disposal of sludge from tannery containing heavy metals. Solidification is a process, in which wastes are mixed with various binding materials to obtain a new product, with improved physical properties of wastes, in which the concentration of the heavy metal is subsequently reduced. Concrete based stabilization of the industrial sludge has been practiced in some of the countries as an effective solution in reducing leachability of heavy metal containing waste by solidification. This approach may also serve as economically viable and environmental friendly option for Bangladesh. However, detailed study seems necessary for determining the proper mix design and methodology concerning the stabilization of the sludge with concrete without significantly sacrificing the strength. Thus, the present study plans to focus on the above mentioned issues.

1.2 Objectives

The overall objective of the study is to assess the use of tannery sludge in concrete and to assess the performance of the sludge mixed concrete. The specific objectives of the study are:

- To assess the characteristics of the sludge collected from the tannery.
- To assess the compressive strength of the concrete mixed with different ratios of tannery sludge
- To conduct repeatability test to recommend the addition of a suitable sludge/ cement ratio, partially replacing the fine aggregate in the mix
- To assess the heavy metal (Cr, Pb, Cd and Cu) leaching from the solidified concrete.
- To assess the effect of sludge addition on the workability and setting time of the concrete.

1.3 Scope of the Study

The main elements of the mixture used in this study were tannery sludge and cement. An assessment of the effectiveness of a solidification process can be made only by testing the quality of the material used and produced. In this study the collected tannery sludge sample was mixed with the binding material (i.e. cement) and aggregates to obtain the new product (i.e. concrete). The properties evaluated for the solidified concrete were compressive strength, workability, setting time and the amount of the toxic material that can be leached from it. The quality of the mixtures differs according to the proportions of the additives. For better understanding, a large number of samples need to be analyzed from different tannery. In this study sludge sample from Apex tannery has been used. In case of the assessment with sludge from other industry, the process may need to be modified.

The sludge sample was collected in untreated and partially degraded condition, which was later dried and sieved before mixing into the concrete. The heavy metals of concern for this study were Lead (Pb), Chromium (Cr), Copper (Cu) and Cadmium (Cd). The primary purpose of the study is to stabilize the leachate by the solidification process and reduce the risk of the leaching of heavy metals by the means of stabilization. In addition, the variation of the compressive strength and other physical properties of the sludge mixed concrete were evaluated to validate the stability of the concrete.

In this study, an attempt has been taken to use the hazardous tannery sludge in the concrete mix. Hence, the concrete mix to be proposed is not aimed at large scale production for commercial purpose, but for the small-scale development and facilities that do not requires higher strength. The use of this type of concrete mix is proposed considering the compressive strength found and the leaching of the heavy metals concern of this study.

1.4 Organization of the Study

The present study consists of five chapters. Chapter one titled “Introduction” gives an introduction of the study along with the background and objective of the study.

Chapter two titled “Literature Review” contains a brief review of the relevant literature. Tanning process, characteristics of the tannery sludge, health and environmental impact of heavy metals and the background of the concrete based stabilization of the sludge are presented in this chapter.

Chapter three titled “Methodology” presents the methodology adopted for carrying out the present study. It includes collection of samples, experimental set up, and procedures. The preparation and method of analysis of leachate from concrete has been described in this chapter.

Chapter four titled “Result and Discussion” examines the constituents of sludge sample, heavy metals, performance of the concrete casted in terms of workability, setting time and compressive strength, analysis of the leachate stabilization.

Finally, chapter five “Conclusion and Recommendation” attempts to bring the major findings of the study together with recommendations for further study in this field.

Chapter Two

LITERATURE REVIEW

2.1 Introduction

Tannery industries generate sludge containing various types of organic particles and toxic chemicals, which are discharged in open drains and ultimately find its way on to land surface and in natural waters near the tannery. The magnitude of pollution from tannery sludge has already taken considerable dimension to threaten public health and the environment. This chapter contains a review of the relevant literature.

2.2 Characteristics of Tannery Waste and Effluent

2.2.1 Unhairing and Fleshing Effluent

The effluent from unhairing operation is more or less continuous and contains mostly hairs and sulphides. Fleshing operation gives rise to an effluent which is also more or less continuous and contains fatty and fleshy matters in suspension.

2.2.2 Vegetable Tanning Effluent

The spent vegetable tan liquor is probably the strongest fraction in a composite tannery effluent. Although its discharge is batch wise or intermittent and constitutes about 10% of total volume of effluent, it is acidic in nature and has a persistent color, which is difficult to remove by known chemical or biological method, and characteristic offensive odor.

2.2.3 Chrome Tanning Effluent

The spent chrome tan liquor is greenish in color and highly acidic. The waste contains a high concentration of trivalent chromium ranges from 100 to 200 mg/ l. Hexavalent chromium is not generally present in the waste chrome liquor because of the reducing agent used and one bath process is utilized.

2.2.4 Dyeing and Fat Liquoring Wastes

The effluent from the dyeing and fat liquoring process is generally small in volume and discharged intermittently. The principle components are the residual of various dyes used in tannery and oily emulsion.

2.3 Leather Manufacturing Process

The production process in tannery can be splitted into four main categories:

a. Pre- tanning (Beam house) operation , b. Tanning operation, c. Post tanning operation and d. Finishing operation

2.3.1 Pre- tanning (Beam house) Operation

At this stage the hide is prepared for tanning by cleaning and conditioning and by ensuring the correct moisture content. Collagen and elastic fibers, which are the basis of the leather, are treated to improve their reactivity towards tanning agents. This stage produces the biggest part of the of the effluent load. The different stages of pre- tanning operations are soaking, unhairing, liming, de-liming, bating and pickling.

2.3.2 Tanning Operation

This is the process to stabilize the collagen structure of the height by blocking the reactive function using natural o synthetic chemicals is called tanning. Also tanning imparts a a particular 'feel' to the resulting leather. For tanning a numbers of chemicals are available, but chrome being the most commonly used. During the tanning process at least about 300 kg chemicals (lime, salt, etc) are added per ton of hides.

A number of tanning process are available that can be used alone, or in combination with each other. In the tanning process no direct solid are generated but since only a part of chemicals are taken up by the hide, acidic effluent containing unused chemicals will be generated. Treatment of the effluent in this operation will generate sludge that creates pollution.

2.3.3 Post Tanning Operation

The hide after the tanning operation called the wet blue leather, which has a blue color due to the chrome salt. The wet blue hides are classified according to the thickness, surface texture, appearance, presence of scars etc.

2.3.4 Drying and Finishing

The operation for definitive commercial look to the leather is called the drying tanned finishing. The operation include drying, buffing, finishing.

2.4 Solid Waste or Sludge Management Practices

The process of tanning produces both liquid and solid wastes. The solid wastes are predominantly from the initial and final stages of processing while the effluents are produced mostly during tanning and dying. The 149 operating tanneries daily produce 14910 m^3 of waste water during the peak time and about 9100 m^3 waste water during the off-peak period. The effluents contain dissolved lime, hydrogen sulfide, acids, chromium dyes, oils, organic matter and suspended solids. The waste water is discharged into open drains and ultimately finds its way onto land surfaces and into natural waters in the vicinity. About 150 Mt of solid waste is produced per day, of which 59% comes from the hides and skins processed. Part of the solid waste is collected by the Dhaka City Corporation and taken to land-fill sites but most of it accumulates in the swamp-sludge.

2.5 Impact of Heavy Metals on Environment

Tannery waste can cause severe damage not only to the human being but also to the environment and ecology, if discharge without proper treatment. In Dhaka, at Hazaribagh, the tannery industries discharge their total emission to the surrounding environment including the river Buriganga, nearby land and in the surrounding air without any treatment or taking any preventive measure to reduce the adverse effect.

2.5.1 Surface Water and Ground Water

The wet land and the surface water bodies on the south-west, west and west- north of the tannery industrial area at Hajaribagh are already polluted and have been turned into tannery waste lagoon and is unacceptable for any kind of use. The waste water from the lagoon was collected during a survey by the DOE and analyzed in the DOE laboratory. High level of pollution load detected in the waste water sample from the lagoon. The most important surface water body outside the embankment is the river Buriganga. The regular monitoring result of the DOE proved that the river is highly polluted. And the Chromium concentration at the drinking water intake point is also alarming. An investigation was conducted to assess the effect of tannery waste on the dissolve oxygen (DO) of the river. The DO was found 0.5-3.0 mg/l (DOE 1992), is far below the Bangladesh Quality Standard which is 4.5 to 8.0 mg/l (ECR, 1997).

A survey conducted by DOE, found the concentration of chromium in ground water is 0.02- 0.04 mg/l (DOE, 1993-94) whereas according to Bangladesh EQS, the standard of chromium in ground water is 0.05 mg/l. pollution of ground water is very close to the limit, which is very alarming.

2.5.2 Land

Heavy metals such as Zn, Cu, Pb , Ni and Cr are present in all soils but are actually found at low concentration of the heavy metals is usually from .1-200 mg/ kg (Chilton and Kinniburg, 2003). Higher concentration usually occurs in soil below or near landfills and in agricultural land that have been irrigated with contaminated water and which has use of metal rich pesticides. The major activity of the soil system occurs in the upper 300 mm (12 inch) of the soil mantle. Heavy metals are removed on the absorption of on soil particles. Absorption of phosphates and heavy metals may occur at the deeper levels as the capacity of the upper layer is exhausted. While no clear limit of to the capacity is evident, the absorptive capacity is thought to exceed the tolerance limit in plants. Hence the first effect would be on the crop and not to the ground water (McGhee, 1991).

In tannery industrial area at Hazaribagh, the soil on both sides of the flood protection embankment is highly contaminated with tannery waste. The soil has significantly increased concentration of different organic and inorganic pollutant and heavy metals (DOE, 1992). Chloride concentration is very high. There is also increased concentration of Nitrogen, NH_4-N, Nh_3-N, phosphorous and sulphur on the surface of the soil (DOE, 1992). Even at a depth of 1.2 meter accumulation of Nitrogen was found that the tannery industries are not discharging. Chromium as heavy metal, which is inherent to the tanning process, but significant amount of zinc, copper, manganese and lead as well.

The concentration of chromium found in the Hazaribagh soil is 2942 ppm (DOE, 1992). Uniform chromium distribution within the soil profile down to 1.2 meter was found and it can be concluded that the tannery waste has severely contaminated of soils with chromium. Other heavy metals such as zinc, copper and lead have been found at high concentration. Phenol, hydrocarbons, available N (NH_4^+, NO_3), chloride, SO_4, TOC (Total Organic Carbon) and Electric Conductivity (EC) have also been found exceeding critical limits in soil for agriculture production and general use.

2.5.3 Vegetation

The relationship between soil contamination and crop contamination is complicated and depends on many soil and plant factors. Chilton and Kinnniburgh (2003) suggested some critical factors such as ability of the soil to absorb the heavy metal and thereby maintain a low concentration in the soil solution and the interactions between various heavy metals, e.g. Cd uptake can be affected by competition from other metal such as Zn and Cu. Soil pH strongly affects the amount of absorption. Absorption of most trace metals is much lower under acidic conditions potentially resulting in greater plant uptake and great toxicity. Most heavy metals are reported to be very strongly bound by the natural organic matter and so tend to be at high concentration where organic contents are high. Ashfaque (1999) while working with sediment of Dhanmondi Lake observed the same phenomenon.

Most of the tanneries in Bangladesh are located in the city of Dhaka. Dhaka has three interconnected river systems, the Turag to the north-west, the Buriganga to the south-west and the Sitalakhya to the southeast, with the Turag flowing into the Buriganga. The Hazaribagh tanneries are located on the southwest periphery of Dhaka alongside the river Buriganga. On each side of Dhaka, a flood protection embankment has been constructed to make Dhaka flash-flood free.

As stated earlier, the tanneries discharge the effluents and wastes into the river system. Consequently, there is a large area of acid sludge alongside the flood protection embankment, and the liquid wastes are dumped in the river through a flood-control regulator-cum sluice near Hazaribagh. During monsoon months, the flood protection embankments protect Dhaka from heavy flooding while making it difficult to flush-out the waste water, thereby creating a great environmental hazard in the neighborhoods of the tanneries. On the other hand, during the dry season the waste water is flushed out into the river, causing pollution of the river water and ultimately affecting the aquatic flora and fauna. Likewise the dumping of the solid wastes is seriously affecting the soil and plants, besides vitiating the air, groundwater and human health.

Mathur et al (1998) studied the heavy metal uptake in some selected crops grown in land contaminated by the leachate from fly ash dykes near a disposal site in Madhya Prodesh of India. The heavy metals covered in this study include Pb, Cd, Cr etc. The study suggested that different plants species may have some resistance against toxic metals through metal uptake rate is a common phenomenon in useful crops and vegetations.

Somashekhar et al. (1997) studied the concentration of heavy metals in top soils and crops when the land is irrigated with metal rich waste waters. The suggested concentration of heavy metals has a positive correlation with the amount of the metal in the soil while the rate of accumulation is dependent on the availability of the metals in soil to the plants. The concentration of heavy metal in soil was found to be dependent on the effluent characteristics, i.e. weather acidic or alkali, and it was concluded that moderately acidic soil favors greater accumulations of metal ions.

2.5.4 Aquatic Plant

Various types of aquatic plants, particularly macrophytes, are present in the Buriganga River. Macrophytes absorb macro- and micronutrients from the ambient water for their growth and nutrition. The macrophytes also absorb pollutants from the river water and store them in their cells. When biota further absorb up the food-chain, such as humans, animals and fish, eat the macrophytes the biota is also affected by some of these undesirable substances. In this way, various pollutants enter the food chain, and are likely to cause degradation of the natural system.

Macrophyte in Buriganga river gets polluted from the source points Hazaribagh tannery. Water samples were analyzed. The concentrations of ions determined in the wet and the dry seasons in the macrophytes and the water of the Buriganga River at the source points. The concentrations of P, Fe, Cu, Zn and Pb tend to be higher in the macrophytes at source of the Hazaribagh location during the dry season than during the wet season. However, different macrophyte species absorb different amounts of pollutants.

Of the heavy metals, tanneries have been found to discharge not only Cr, which is an inherent product of the tanning process, but also significant amounts of Zn, M n, Cu and Pb. High levels of Cr with Zn, Cu and Pb have been observed at the main waste disposal point, exceeding the toxic level range in soils. The extractable fractions of heavy metals give some indication of their phyto availability and mobility in soil of that area. Many of these heavy metals are being carried down to the groundwater and are causing severe environmental concern. Cr appears to be concentrated more in the surface 0-15 cm.

Analysis of the standing field crops and aquatic plants showed that the concentrations of N, P, K, S, Fe, Cu, Mn, Zn, Cl, Cd, Pb were concealed with total contents of these elements in the soil. Grass accumulated more Cr than paddy and water hyacinth, and exceeded toxic limits. Transfer coefficients for Zn, Cu and Mn into rice, water hyacinth and grass were higher in rice plants than in grasses and water hyacinth. Rice and wheat were grown in a pot experiment in soils from the tannery area with high contents of Cr. The adverse effect was more pronounced in light soils than in heavy soils (Nazmul Islam 1994).

2.5.5 Fish

Fish species subject o heavy metal contaminated waters are likely to accumulate metals in different parts of the body. Hafiz (1998) found evidence of bio accumulation of heavy metal in fish of Dhanmondi Lake by observing presence of copper in excessive amount of various parts of fish. Maximum Copper concentration of 7.44 mg/ kg was found in stomach. Lead, Cadmium, etc contamination of fish is common (Friberg et al. 1974). The bottom feeding species are more likely to be affected by contamination due to presence of heavy metal in bottom sediment of polluted water bodies in very high concentration.

In order to assess the impact of the metal, long-term detailed investigation are generally required for obtaining reliable data on the density, productivity, and diversity of fish populations. However such criteria are not part of most monitoring and impact studies and are restricted to the assessment of the effect of most industrial project on aquatic environment.

Reduced growth and fecundity are often taken as a measure of the response of fish to metal. Even though such data are relatively easy to obtain, it may be difficult to distinguish the influence of reduced food supply from the toxic effect of heavy metal in impacted waters. Hagen and Langeland (1973) investigate the impact of polluted snow in the water quality and organism in Norwegian Lakes. Elevated concentration of zink and lead levels in lake waters were found and it was concluded that the metals were probably chronically toxic to fish and their food. However the study failed to distinguish the toxic effect of low pH and oxygen levels from those of metal.

2.5.6 Water

A study on the water quality of the river Buriganga near the discharge point and at a point in mid-river during April- September (wet season) and October- March (dry season) revealed that tannery effluents heavily pollute the river water, much so that the dissolved oxygen in the river water was found to be nil during the dry season and no fish or other aquatic animals were found living, up to 500 m downstream of the sluice gate (Chowdhury et al. 1996). Concentrations of Fe, Mn, Cu and Pb were tested and only trace quantities were found, indicating that they remain precipitated on the river bed because of the pH of the water.

2.6 Health Aspects of Heavy Metal

Health impact from the tannery disposal wastes is either death or increased probabilities of death and sufferings by illness including skin diseases, fevers, headaches etc. In Hazaribagh and surrounding areas, many vegetables farms are irrigated with waste water from polluted Buriganga river. Studies by FAO/WHO (1993) have found that metal concentrations are high and increased consumption of these vegetables, health problems for consumers in future are inevitable. Severe effects include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death.

Hazaribagh area has a high incidence of a number of health problems. In this area the peoples are frequently suffering from abdominal skin ulcer, scabies, discomfort/gastritis, peptic ulcer, lung diseases, respiratory diseases, dermatitis, nasal ulcer/loss of smelling capacity, red eye/other eye illness, running nose, erosion and discoloration of teeth, asthma, puffiness of face and oedema, diarrhoeal disease, high fever, conjunctivitis, urinary tract infection, jaundice, hypertension etc. A high number of mentally retarded children have been found, most of them were born in this area (IULTCS, 2004).

According to the report of the Bangladesh Society for Environment and Human Development, about half a million residents of Hazaribagh, Bangladesh, are at risks of serious illness due to chemical pollution from tanneries near their homes. The report says, large numbers of the 8000-12000 tannery workers aged 30-35 years suffer from gastrointestinal disease (58%), dermatological disease (31%), hypertension (10%), and jaundice (10%) that could be related to the pollution. Ninety percent of these workers die before the age of 50 *Vs* less than 60% for the country as a whole. About a quarter of these workers are less than 11 years of age (Maurice, 2001).

2.6.1 Chromium

Chromium (III) is thought to be an essential element in mammals, its toxicity being very low. On the contrary, chromium (VI) is highly toxic to man, even if its effects are generally local, involving the respiratory tract and the skin. Once absorbed, chromium (VI) is quickly reduced to the trivalent form which accounts for this entire element present in the blood stream or taken up by tissues. As a result, any differences in systemic toxicity can only be attributed to differential solubility and absorption rates. The kidney should be regarded as the critical organ, although tubular damage following occupational exposure is mostly due to acute absorption and transient in nature. Two main features of kidney damage were, however, apparent. The first one is the lack of dose-effect/response relationships, i.e. the lack of any progression toward more severe impairments when the exposure intensity increases. The second one is that the recent absorption rates more than the cumulated dose is responsible for the observed nephrotoxic effects (Franchini and Mutti, 1988).

Cr (VI) can enter the body when people breathe air, eat food, or drink water containing it. Cr (VI) is also found in house dust and soil, which can be ingested or inhaled. Of the various forms of chromium, Cr (VI) is the most toxic. Certain Cr (VI) compounds have been found to be carcinogenic in humans, but the evidence to date indicates that the carcinogenicity is site-specific—limited to the lung and sinonasal cavity—and dependent on high exposures, such as might be encountered in an industrial setting. Cr (VI) can cause a wide range of other health effects. Inhaling relatively high concentrations of some forms of Cr (VI) can cause a runny nose, sneezing, itching, nosebleeds, ulcers, and holes in the nasal septum. Short-term high-level inhalational exposure can cause adverse effects at the contact site, including ulcers, irritation of the nasal mucosa, and holes in the nasal septum.

Ingestion of very high doses of Cr (VI) can cause kidney and liver damage, nausea, irritation of the gastrointestinal tract, stomach ulcers, convulsions, and death. Dermal exposures may cause skin ulcers or allergic reactions (Cr [VI] is one of the most highly allergenic metals, second only to nickel). According to the International Agency for Research on Cancer (IARC), ingested Cr (VI) is largely converted to Cr (III) in the stomach, a fact that many chromium experts believe prevents ingestional exposures from posing significant health dangers, since Cr (III) is not readily absorbed into the body. The saliva, gastric juice, intestinal bacteria, blood, liver, epithelial lining fluid, pulmonary alveolar macrophages, peripheral lung parynchema, and bronchial tree have all been associated with eliminating Cr (VI) from the body.

Chromium is one of the most harmful chemicals found in the tannery waste of Hazaribagh because of its carcinogenic potential. It may cause cancer. Chromium wounds skin, liquor chrome enters the body through hair pores and comes into direct contact with the skin (O'Flaherty et al., 1956-65). Acidic effluents can cause severe respiratory problems. Gaseous emissions from the tanneries contain sulphur dioxide that is converted into sulfuric acid on contact with moisture and can damage lungs (SEHD, 1998).

2.6.2 Cadmium

The major sources of cadmium exposure in the general population are cereals, vegetables, and shellfish. There is increasing evidence that toxic effects may occur at much lower exposure levels (Alfven et al. 2000; Buchet et al. 1990; Järup et al. 2000; Noonan et al. 2002) than those observed in occupational settings or in severely polluted environments. Still, the attempts to estimate the level of critical exposure for kidney effects have so far displayed large variations. Furthermore, possible effects in populations residing in areas with no particular industrial cadmium emission are undetermined.

Cadmium is taken up from the lung and gastrointestinal tract and transported via the blood to liver and kidney. On long-term exposure to cadmium, renal tubular dysfunction may develop both in humans and experimental animals (Friberg et al., 1974). Data from animal experiments demonstrate that initially after exposure cadmium in blood is bound to albumin and proteins with a molecular weight higher than albumin (Nordberg, M. Studies on metallothionein and cadmium (Environ,1978). Such cadmium is mainly taken up by the liver. Cadmium induces the synthesis of metallothionein in liver and other tissues. Metallothionein is a low molecular weight protein involved in cadmium, zinc and copper metabolism (Nordberg, 1984.)

Cadmium accumulates in the renal cortex and induces tubular toxicity (Barbier et al. 2005), which is first detected as increased urinary excretion of low-molecular-weight proteins and tubular enzymes. Glomerular dysfunction may also emerge, as demonstrated in heavily exposed subjects (Järup et al. 1995; Kido et al. 1990; Roels et al. 1989). It is not known, however, whether the glomerulus is affected by long-term low-level environmental exposure. Diabetes, an increasing health problem in many areas (King et al. 1998) and one of the leading causes of incident end-stage renal disease (Hostetter, 2001), has been suggested to augment the risk of cadmium-induced kidney damage (Buchet et al. 1990). Also, hypertension and intake of nephrotoxic non-steroid anti-inflammatory drugs (NSAIDs) (Fored et al. 2001) might interact with cadmium. However, these possible interactions need to be confirmed.

2.6.3 Lead

Many environmentally important Lead compounds such as halides, sulfates, phosphates and hydroxides are insoluble and thus are of relatively low toxicity in aquatic system. By contrast soluble lead compounds are intermediate between hard and soft acids in the interaction towards oxygen and sulfur- containing ligands. The major source of lead in humans is through the respiratory tract. This reflects the strong association of lead with urban airborne particulates. In human lead resembles calcium in deposition and transport, accounting for the high concentration of lead in the skeletal compartment. The three systems in the body most sensitive to lead are the blood- forming system, the nervous system, and the renal system. Acute lead poisoning is reported to cause damage the nervous system causing insomnia, irritability and convulsions (Peavy et al., 1985; McGhee, 1991).

Cooper (1976) reported that the incidence of renal tumors and other carcinomas in lead smelter and battery plant workers was not higher than control levels. Furthermore, lead acetate is not magnetic using the Ames (Salmonella) test. By contrast inorganic lead compounds induce renal carcinoma in rats and mice.

2.6.4 Copper

Copper (Cu), a redox active metal, is an essential nutrient for all species studied to date. During the past decade, there has been increasing interest in the concept that marginal deficits of this element can contribute to the development and progression of a number of disease states including cardiovascular disease and diabetes. Deficits of this nutrient during pregnancy can result in gross structural malformations in the concepts, and persistent neurological and immunological abnormalities in the offspring.

Excessive amounts of Cu in the body can also pose a risk. Acute Cu toxicity can result in a number of pathologies, and in severe cases, death. Chronic Cu toxicity can result in liver disease and severe neurological defects. The concept that elevated ceruloplasmin is a risk factor for certain diseases is discussed. The role of reactive oxygen species, with the subsequent oxidative deterioration of biological macromolecules in the toxicities associated with transition metal ions, is reviewed. Recent studies have shown that metals, including iron, copper, chromium, and vanadium undergo redox cycling, while cadmium, mercury, and nickel, as well as lead, deplete glutathione and protein-bound sulf-hydryl groups, resulting in the production of reactive oxygen species as superoxide ion, hydrogen peroxide, and hydroxyl radical.

As a consequence, enhanced lipid per-oxidation, DNA damage, and altered calcium and sulfhydryl homeostasis occur. Fenton-like reactions may be commonly associated with most membranous fractions including mitochondria, microcosms, and paroxysms. This review summarizes current studies that have been conducted with transition metal ions as well as lead, regarding the production of reactive oxygen species and oxidative tissue damage (Bagchi et al., 1995).

2.7 Leaching from Tannery Sludge

Leaching is the process of release of contaminants from within the waste the waste to the percolating water in soluble or suspended form (Peavy et al., 1985). Poon et al. (1995) defined leaching as the process by which a component of waste is removed mechanically or chemically into solution from the solidified matrix by passage of solvent such as water. The fluid to which the contaminants are leached is called the leachant and the leachant after contamination (i.e. after percolation through solid waste and having extracted dissolved or suspended materials from it) is termed the leachate. The overall ability of a stabilized material to leach contaminates is termed as leachability.

In most landfills the liquid portion of the leachate is composed of the liquid produced from decomposition of the wastes and the liquid that entered the landfill from external sources drainage, rainfall, and ground water and from springs (Peavy et al., 1985). The leachability of particular waste type depends on the physical and chemical properties of both the waste and the leachant as well as on the condition of the ambient environment it is subjected to. The leachability of inorganic or organic constituent from waste differs for different disposal scenario (e.g. co-disposal in municipal landfill, mono disposal of mining waste, etc) and type of leachant. The factor affecting the leaching of contaminants from waste may be contaminant specific and magnitude and scale of their influence may differ widely (Batchelor, 1999, Rivey 1999, Kimmel, 1999).

Different factors affect the leaching potential of organic constituents. They are- Partitioning or Solubility - since organic compounds are rarely available in the landfill as crystalline solids, partitioning is the predominant consideration, Presence of organic carbon - this factor will impact the concentration of the organic constituents in the aqueous phase, Liquid-to-solid ratio, Non-aqueous phase extraction. Batchelor (1999) suggested some additional other factors that can play a role, including the presence or absence of surfaces in the waste (e.g., particle size considerations), the presence or absence of ligands (e.g., citrate) within the waste and the leaching fluid.

It was also reported that the pH of the leachant is determined by the acid neutralizing capacity and the base neutralizing capacity of the waste itself (an important consideration for waste stabilized with alkaline materials such as lime). The pH of the leaching fluid plays a major role in establishing the pH of the leachant, as does the liquid-to-solid ratio. The overall final pH of the leachate is much more important than the pH of the actual leaching fluid itself in determining the actual metal concentration in the leachate. Thus, the important matter is to know the pH of the final leachate, and attempts to predict leachate concentrations should rely on the pH of the leachate, not the original leaching fluid.

2.8 Cement Based Stabilization Process of Tannery Sludge

The process of tanning produces both liquid and solid wastes. The solid wastes are

Pre-dominantly from the initial and final stages of processing while the effluents are produced mostly during tanning and dying. In tannery industries, treatment methods that must be used to combat pollution include segregation of process waste water, sedimentation, neutralization and biological treatment. Unfortunately, except for two modern tanneries, BATA and Dhaka Leather Complex, none of the tanneries has a treatment plant. Few leather industries reuse any of the liquid wastes. Most of the wastes and effluents are subjected to natural decomposition in the environment, causing serials of pollution problems affecting oil, water, air and human life. Currently, about 90% of the finished trimming wastes are used by local shoemakers.

About half the tanneries apply some kind of solid waste reuse. The government of Bangladesh made an attempt to relocate the tanneries from the present area to a proposed site outside Dhaka and offered a compensation of US $1.4million for this purpose. An Asian Development Bank study concluded that US $18.4 million would be needed to develop an area with waste treatment facilities; but because of lack of funds, the relocation scheme has been abandoned. Instead, the Government has decided to establish a common effluent treatment plant with the assistance of the United Nations Industrial Development Organization (UNIDO).

Solidification/stabilization *(S/S)* is an economical process for the disposal of many types of hazardous wastes. The method involves mixing liquid or semisolid wastes with binders to produce a solid which is structurally sound and relatively impermeable. Binders often consist of Type **I** Portland cement (Ordinary Portland Cement, OPC) or OPC plus fly ash, kiln dust, other pozzolanic and industrial byproducts. Sometimes polymers, by themselves or in various combinations, are used**.** The mechanisms of *S/S* are very incompletely understood. The process usually involves addition of a heavy metal waste to a cementitious binder, with or without pretreatment with lime. The hydroxides are subsequently immobilized in the dense matrix of binder, where ionic transport is decreased as the porosity and permeability are reduced. Very few detailed micro structural and micro chemical studies of OPC with complex wastes exist, and the waste itself has been investigated even less. (Environ. Sci. Technol., Vol. 26, No. 7, 1992).

Solidification is one of the most effective methods of dealing with heavy metal contaminated sites. By this method mobility of hazardous substances and contaminates is significantly reduced in the environment through both physical and chemical means (Kitamura *et al.*, 2002). In general, solidification is typically a process that involves mixing the waste with a binder to reduce the contamination leachability by physical and chemical means, which convert the waste into an environmentally acceptable waste form for safe disposal or construction (Spence and Shi, 2004; USEPA 1999, 2001, and 2004). Therefore, the main objective of solidification / stabilization is to achieve and maintain the desired physical properties and to chemically stabilize or permanently bind contaminants (Conner, 1990). Moreover, the stabilized wastes may attain adequate stress-strain properties to enable their utilization in construction applications, such as engineering fill, road or pavement sub-grade backfill, and base material (Dermata and Meng, 2003).

For the purpose of solidification, many organic and inorganic binders have been used, most of which have stabilizing characteristics. Ordinary Portland Cement (OPC) is the most widely used binder due to its cost effectiveness, availability and compatibility with a variety of wastes (Spence and Shi, 2004), (USEPA, 1999, 2001, and 2004). Cement-based solidification has been widely used in the world for about 50 years (Alunno and Medici, 1995; Conner and Hoeffiner, 1998; Malviya and Chaudhary, 2006). The high strength, low permeability and relatively high durability of hydraulic cement make it a good binder for this waste management technique (Conner, 1990). The overall process of cement hydration includes a combination of solution process, interfacial phenomena and soil-state reaction. It is extremely complex, especially in the presence of heavy metals (Chen et al., 2009).

The influence of cement chemistry on the properties of solidified wastes forms was studied (Hills et al., 1996). In this study Portland cements with alite bore composition ranging from 25 to 65%, and ferrite and aluminates fixed at 10% were used. The waste used was a commercially blended and neutralized hazardous waste, which was solidified at three loading rates. The cement composition mainly the amount of calcium silicate hydrate (CSH) was seen to influence the strength development and the differences in phase development were more apparent at the highest waste additions. The morphology of the inner gel products appeared to be different based on the Ca/Si ratio. The metallic waste species had the optimum lowest leaching level (Al-Tabbaa and Perera, 2006).

2.9 An Overview of Existing Leaching Test

Leaching tests are designed to determine the leachability of a waste type subject to a particular idealized disposal scenario. Leaching test have been developed and still developing in different countries.

Within the US, standardized leaching protocols have been published by a number of concerned authorities like American Society for Testing and Materials, the International Atomic Energy Agency, The Us Army, ANSI/ANS and the ISO. These methods address different waste management scenarios, leaching properties and waste types and thus often vary widely in the underlying concept and assumptions.

Test have been developed to account for the variability in the ratio of volume of leachant to solid waste, chemical composition of leaching fluid, testing of monolithic and granular waste, as well as stabilized and solidified wastes. (Hartwell, 1999 and Batchelor, 1999).

2.10 The Concept of TCLP

Toxicity Characteristics Leaching Procedure (TCLP) developed by the United States of Environmental Protection Agency (USEPA) is widely used to classify hazardous solid wastes and evaluate the worst leaching conditions in a landfill environment (USEPA, 1986). Toxicity Characteristics Leaching Procedure or TCLP is standard leaching test procedure of USEPA, EPA SW-846 method 1311 (USEPA, 1992a). This is mandatory test in the US for analyzing the leaching potential of industrial waste prior to disposal.

The Toxicity Characteristic Leaching Procedure (TCLP) is a "second generation" extraction procedure developed by the USEPA. It is proposed as a replacement for the EP (Extraction Procedure) test as a waste characterization tool. At 1980, the USEPA recognized that the EP addressed only a small portion of the recognized toxic constituents (Friedman 1985). The USEPA initiated work to develop a leaching procedure that would address additional toxic constituents of hazardous waste, primarily a number of organic compounds. The TCLP has been proposed as a method of addressing the shortcomings of the EP (Friedman 1985). Since the TCLP was first published in the Federal Register (USEPA 1986a), it has undergone several modifications.

The "Resource Conservation and Recovery Act of 1976" (RCRA) directed EPA to establish the criteria to differentiate hazardous-and nonhazardous wastes. The USEPA established three methods for defining hazardous waste. The four characteristics that the USEPA established to define a non-listed waste as a hazardous waste include: ignitability, reactivity, corrosivity, and toxicity. Toxicity characteristic was developed to identify those wastes, which might result in contamination of ground water if improperly managed. (Bricka et al., 1992)

There are many laboratory leaching tests that have been reported in the literature. ASTM has developed standard leaching tests, which use alternate leaching fluids with very little additional difference in the test methodology. EPA has one regulatory test for the classification of solid wastes under RCRA; the TCLP (Method 1311). EPA also has the Synthetic Precipitation Leaching Procedure (SPLP) (Method 1312). The TCLP is expected to simulate leaching of solid wastes placed in a municipal landfill, while the SPLP is designed to simulate a mono-disposal situation. The TCLP and SPLP have been widely used to generate leachate concentrations for all types of solids for both inorganic and organic constituents (Murarka, 1999).

The research program at EPA for formulating TCLP parameters and steps observed that the batch extraction provides leachate results, which are more representative of field condition. The leaching fluid used was to be designed to simulate the result of rainwater infiltration the landfill, reacting with the municipal solid waste, and then leaching through the waste being tested. For purpose an acetate buffer leaching fluid to simulate the effect of decomposing municipal waste was recommended (EPA , 2002).

The numerical limits for the RCRA toxicity characteristics (TC) were derived using the same scenario and were set at levels that would prevent the ground water contamination from reaching levels that poses potential environmental and health effects. A fraction of the table of TC regulatory standard covering major heavy metal is provided in Table 2.1 and Table 2.2.

Table 2.1: Toxicity characteristics regulatory standard covering major heavy metals (Source: 40 CFR, Part 261.31, USEPA 1992b)

Heavy Metal	**Concentration in TCLP leachate (mg/l)**
Lead (Pb)	5.0
Chromium (Cr)	5.0
Cadmium (Cd)	1.0
Copper (Cu)	N/A

Table 2.2: Toxicity characteristics regulatory standard for Land Disposal Restriction (Source: 40 CFR, Part 261.48, USEPA 1992b)

Heavy Metal	**Concentration in TCLP leachate (mg/l)**
Lead (Pb)	0.75
Chromium (Cr)	0.60
Cadmium (Cd)	0.11
Copper (Cu)	N/A

2.11 Some Past and Current Research on Stabilization with Cement

The stabilization of industrial sludge though solidification with concrete has been practiced in some other countries. Poon et al. (1985) studied the mechanisms of metal stabilization by cement based fixation processes. The study aimed at the chemical aspect of the stabilization from the environmental prospective. However the structural integrity of the stabilized waste did not received much attention.

Tay and Show (1991) focused mostly on the engineering properties of the cement made from the sludge. The study suggested that virtually any form of sludge or waste can be used for making cement and aggregate if the cost and energy requirements can be compiled with.

Hills et al. (1992) focused on the applicability of the Ordinary Portland Cement (OPC) as stabilization agent in stabilizing the toxic substances in the industrial sludge. They found cement based stabilization successful on many of sludge samples. Hills et at. (1994) observed reduced leaching from cyanide rich wastes after solidification with cement. The mechanical properties of the resultant content concrete received less attention.

Rahmat (2001) studied the stabilization performance of cement based technique for heavy metals in industrial sludge and analyzed the structural properties of the resultant concrete. The stabilization of the heavy metal was successful. Marked decrease in the strength was observed with increase in the sludge content. However, testing for change in durability of concrete with increase in sludge was not included.

Hossain (2004) studied the performance of the stabilization of heavy metal (Pb, Cd, Cr and Hg) in industrial sludge with concrete mix. This study considered assessment of the effect of sludge addition on the compressive strength, workability and durability of resultant concrete at different scenario. A suitable concrete mix was recommended for construction using sludge partially replacing the fine aggregate in the concrete mix.

CHAPTER THREE

METHODOLOGY

3.1 Introduction

The study may be broadly classified into four categories: 1. Collection of tannery sludge, 2. Preliminary analysis of the sludge sample, 3. Concrete mixing with sludge, 4. Analysis of the properties of the sludge mixed concrete to assess the usability. The concentration of the heavy metal in the sludge sample was determined in the laboratory. The methodologies are elaborately discussed in subsequent sections in this chapter. A flowchart showing the logical sequence of the adopted methodologies is provided in Fig.3.1.

3.2 Collection of Tannery Sludge

Sludge sample from leather industry was considered in this study. The Apex Tannery Ltd (Fig. 3.2) was selected to collect sludge sample. This tannery has functional effluent treatment plant. With assistance of the tannery, authority, the sludge sample was collected directly from the effluent treatment plant with on 15 December 2013. The sludge sample was founded in a partial degraded condition and had some flesh mixed with it. It was collected in poly bags, sealed and kept in cool dry place before analysis.

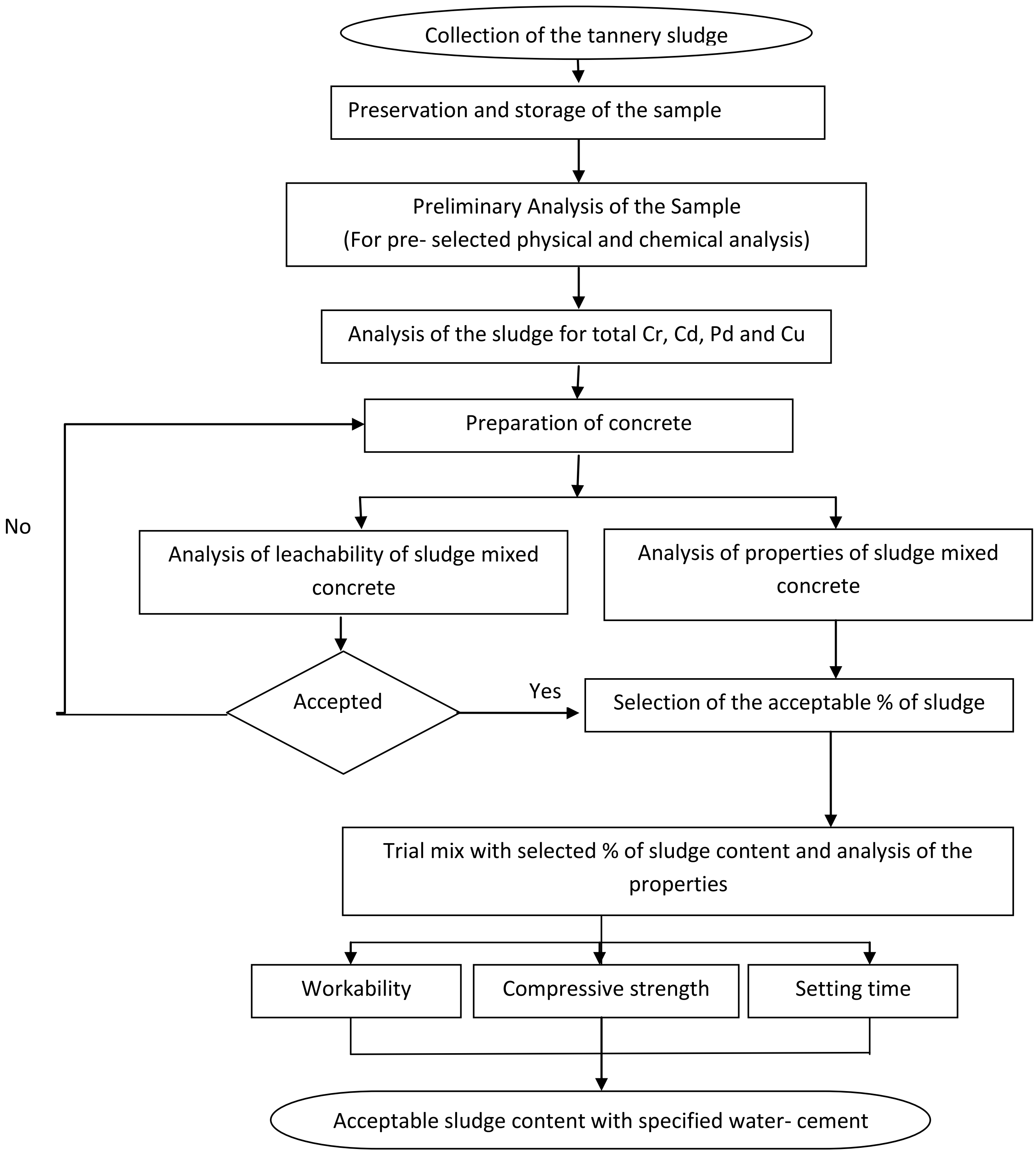

Figure 3.1: The flow diagram of the methodology adopted for the study

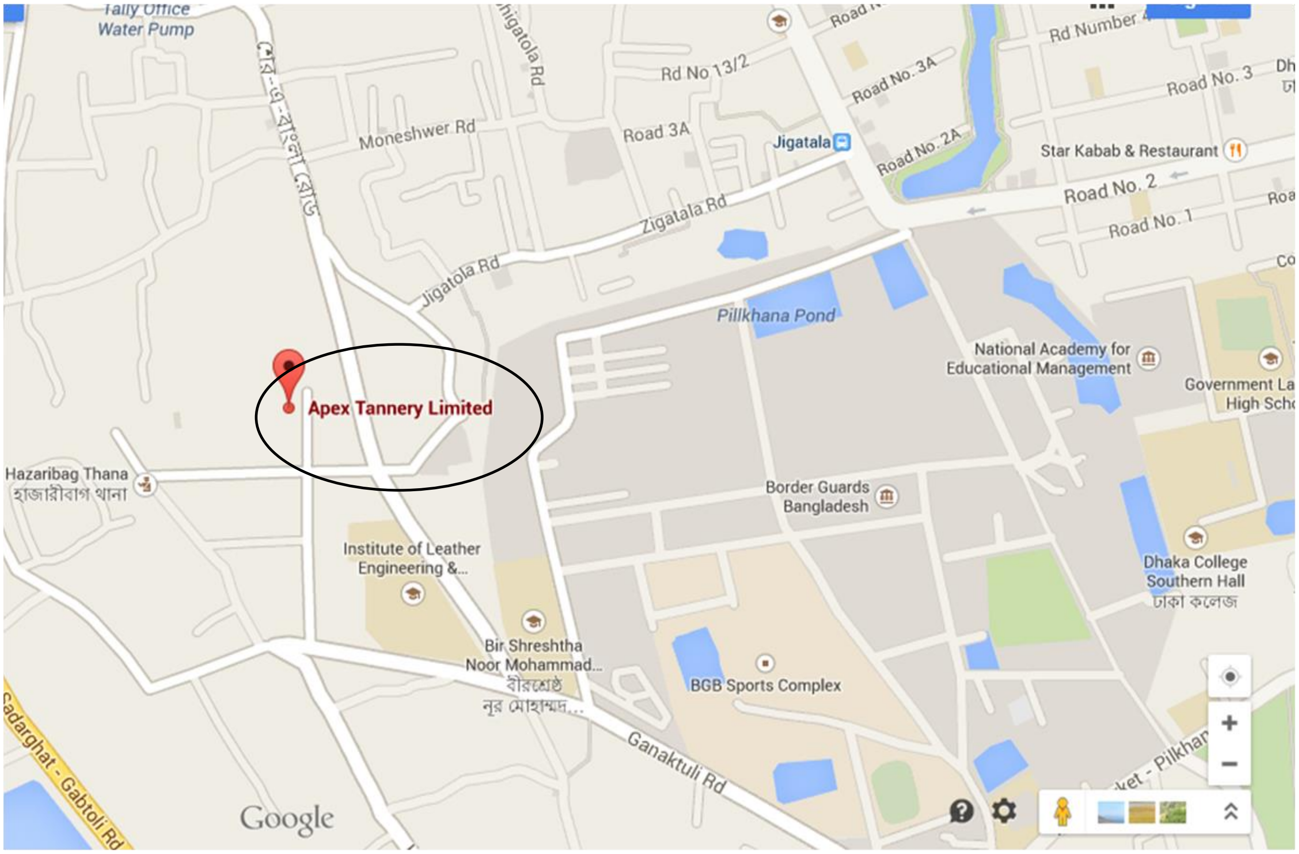

Figure 3.2: Location map of Apex Tannery Ltd in Hazaribag, Dhaka.

3.3 Analysis of Sludge Properties

The characteristics of the sludge sample were analyzed for preselected parameters to record the chemical properties and the leaching potential of the sludge in the open environment. These may influence the workability, strength and setting time of the resultant sludge mixed concrete as indicated in the literature. The properties analyzed include pH, alkalinity, and chloride, sulfide, sulfate, silica, nitrate, etc.

3.3.1 Chemical Analysis of the Sludge Constituents

The methodology applied for analyzing sludge was the standard methodologies applicable for soils and sediments (USEPA, 1992a; Alam et al., 1991). Analysis of the anaoins were done on the standard extract from sludge (Alam et al., 1991). Apart from chloride and pH, all others were performed with HACH DR/2010 Spectrophotometer. The concentrations of the constituents were expressed in mg/ kg of sludge. The methods are described briefly below:

pH: The pH of the sludge sample was analyzed with colorimetric methods using litmas paper. A colorimetric method is a simple and practical procedure. The strip of the litmas paper was taken in and emerged in the raw sample. The color of the paper changed within a second into dark brown. The color of the litmas paper was matched with the colors of the color chart to determine the pH of the sample.

Alkalinity: Sludge and water was mixed 1: 2.5 ratio and stirred vigorously with magnetic stirrer for 30 minutes and allowed to settle for an hour. The supernatant liquid was filtered through filter paper 50 mL of extract was then titrated with (0.02 N) sulfuric acid. The alkalinity of the extract was determined and the result was expressed as mg $CaCO_3$/ kg of sludge.

Organic Content: The organic matter sludge was measured using the Dry combustion Technique adopted for measuring organic carbon in soil (Alam et al., 1991).

Approximately 100 gram of sludge sample was oven dried at 100^oC (Until constant weight) and from there about 25-30 gram of dried sample was taken in a crucible. The initial weight (W_1) was then recorded. The dried sample was then burnt in a muffle furnace (CARBOLITE) at 440^oC- 450 ^oC for six hours (AASHTO 267, equivalent to ASTM 2974) Final weight (W_2) was taken to calculate the percentage of organic matter in the sludge.

% Organic Content= $(W_{1-} W_2)$X 100/ W_1 (3.1)

Chloride: Sludge and water were mixed at 1: 5 (W:V) ratio. The mixture was stirred for 30 minutes. The slurry was then allowed to settle for an hour and the supernatant liquid was filtered through filter paper. The extract was then titrated with standard silver nitrate solution.

Sulfate: Sludge and water were mixed at 1: 5 (W:V) ratio and stirred vigorously for 30 minutes. The slurry was then allowed to settle for an hour and the supernatant liquid was filtered through filter paper. The extract was then analyzed with HCH DR/2010 Spectrophotometer through sulfaVer 4 method (Range 0-70 mg/ L) which is equivalent to USEPA method EPA 375.4 (USEPA, 1992a).

Silica: Sludge and water were mixed at 1: 10 (W:V) ratio and stirred vigorously for 30 minutes. The slurry was then allowed to settle for an hour and the supernatant liquid was filtered through filter paper. The extract was then analyzed with Spectrophotometer through Methylene Blue Method (Range: 0.005-0.80 mg/L) which was equivalent to USEPA method EPA 376.2 (USEPA, 1992a).

Nitrate: Sludge and water were mixed at 1: 10 (W:V) ratio and stirred vigorously for 30 minutes. The slurry was then allowed to settle for an hour and the supernatant liquid was filtered through filter paper. The extract was then analyzed with HCH DR/2010 Spectrophotometer through Cadmium Reduction Method (High range 0-30 mg/ L NO_3-N).

3.3.2 Extraction Method for Chromium, Cadmium, Lead And Copper

The digestion technique adopted for extraction of total metal for chromium, cadmium, lead and copper were the same, which was the aqua regia method. The digested sample was later analyzed with Atomic Absorption Spectrophotometer.

3.4 Preparation of Concrete With Sludge

The sludge sample was oven dried at 110ºc and powdered. The powdered sample was then passed through 4.75 mm sieve to achieve uniformly graded sample of the powdered sludge.

The mix proportion selected for the study was 1:2:4 (cement: sand: coarse aggregate) in weight basis. The sand selected for the mix was Sylhet sand having Fineness Modulus (FM) of 2.70 and having specific gravity of 2.68. The coarse aggregate used for this study was crushed Bholagonj stone of 20 mm downgraded size having specific gravity of 2.7 and Aggregate Crushing Value 22.5% . Ordinary Portland Cement (CEM I) having a specific gravity of 3.15 was used as binder material.

The sludge was to replace the fine aggregate (sand) by equal weight as certain percentage of cement in the concrete mix. Some changes in the volume composition were expected with the introduction of sludge in mix due to the variation of the specific gravity between sludge and sand.

The cylinder specimens of concrete were casted to assess the strength variation and change in workability with increase in sludge content. To achieve a medium slump (35-75 mm) with the coarse aggregate size of 20 mm, water-cement ratio of 0.50 was used to mix the concrete. No admixtures were used for the mixes. A preliminary trial mix was done with water-cement ratio of 0.55 which resulted in very loose concrete with higher slump. Hence the water cement ratio was kept at the recommended maximum of 0 .50 for all the batches. A sludge free batch of concrete was casted with the recommended water-cement ratio for the comparison. The sludge content was varied from 1% to 20% by weight of cement in the mix replacing equal weight of fine aggregate. Workability, slump and setting time of the fresh concrete were recorded. The compressive strength test was conducted to assess the change in strength of the hard concrete. Also the pH of the fresh concrete was recorded with Hanna pH meter (HI 122)during the repeatability test.

Figure 3.3: Concrete trial mix with sludge

3.5 Testing of Concrete

The test of concrete included standard test for workability, setting time and compressive strength test.

3.5.1 Test for Workability of Concrete

Workability is one of the physical parameters of concrete that affects the strength and durability. The cost of labors and appearance of the finished product are also related to this parameter. Concrete is said to be workable when it is easily placed and compacted homogeneously**.** A concrete that can be readily compacted is said to be workable, but to say merely that workability determines the ease of placement and the resistance to segregation, bleeding. Unworkable concrete needs more work or effort to be compacted in place, also honeycombs &/or pockets may also be visible in finished concrete. The workability is an essential property of any concrete mix to be used conveniently during construction.

There have been a wide range of test formulated so far for measurement of the workability of the concrete mix; unfortunately, there is no acceptable test, which will measure directly the workability (Neville, 1996). The slump test (Fig.3.4.) defined in ASTM C143-90a and BS 1881: Part 102: 1983, was chosen as a measure of workability of the mixes. This is the most common practice in Bangladesh. The factors affect the workability of concrete are water content in the concrete mix, amount of cement &

its properties, aggregate grading (Size Distribution), nature of aggregate particles (shape, surface texture, porosity etc.), temperature of the concrete mix, humidity of the environment, mode of compaction, method of placement of concrete, etc. The slump of all the batches were measured and recorded just before casting as per ASTM C143: 90a.

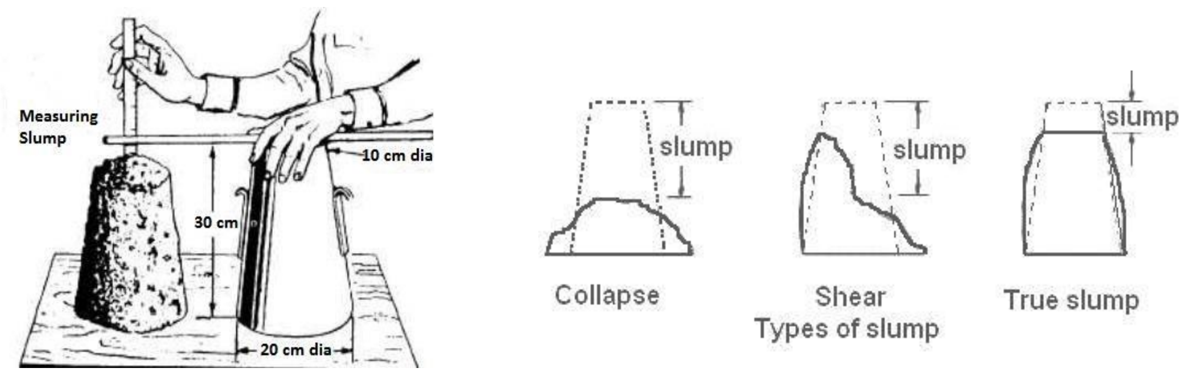

Figure 3.4: Concrete Workability Measuring Procedure

Figure 3.5: Measuring workability of the sludge mixed concrete

3.5.2 Setting Time of Concrete

The hardening of concrete before it gains strength is known as setting of concrete. The practical use of concrete as a construction material depends upon the fact that it is ”plastic” in the freshly mixed state and subsequently becomes hard, with considerable strength. This is the transition process of changing of concrete from plastic state to hardened state. The setting time measuring apparatus is shown in Fig. 3.6.

Figure 3.6: Concrete setting time measuring apparatus

Following are the factors that affect the setting of concrete:

1. Water cement ratio
2. Type and amount of aggregate
3. Cement content
4. Type of cement
5. Suitable temperature
6. Relative humidity
7. Admixtures

3.5.3 Test for Compressive Strength

Concrete is a very strong material when it is placed in compression. It is, however, extremely weak in tension. This is the reason of using reinforcement in concrete structures. The compressive strength of concrete is the major property of concern in design with concrete. This compressive strength test is measured by breaking the cylindrical concrete specimen in a compression-testing machine. The test was performed following the guideline of ASTM C39. It consists of applying a compressive axial load to molded cylinders or cores at a rate that is within a prescribed range until failure occurs. The compressive strength of the specimen was calculated by dividing the maximum load attained during the test by the cross-sectional area of the specimen. The cylinder specimens were prepared as outlined in ASTM C192-90a to measure the 3-day, 7-day and 28-day strength and reported in units of pound force per square inch in US customary units or in Mega-Pascal in SI unit.

In every batch of concrete 9-cylinders were prepared to crush 3 samples for each designated day's test (Fig. 3.7). The machine used for this purpose was ADR 2000, digital compressive strength machine. Concrete compressive strength requirement for concrete can vary from 2500 psi for the residential building structure to 4000 psi and higher in commercial structure (National Ready Mixed Concrete Association, NRMCA).

Figure 3.7: Compressive strength test of the concrete cylinders

3.6 Toxicity Characteristic Leaching Procedure

The toxicity Characteristics Leaching Procedure or TCLP is a standard USEPA test procedure (EPA method 1311). It is applicable for a wide range of wastes. The test is designed to model a theoretical scenario in which waste is placed in an unlined landfill with municipal solid waste and simulates the result of rainwater infiltration the landfill, reacting with the municipal solid waste, and then leaching through the waste being tested (EPA, 2002). Therefore, the result of the test implies long term leaching potential of the waste in the open environment. The test also aims at labeling wastes toxic/ non-toxic following regulatory limits on leaching set forth by EPA (USEPA, 1992b). This is an test is essential test in US to meet the land disposal restrictions.

The procedure is summarized in the following steps:

1. Initial valuation of the sample

   i) Determination of the percent solids in the waste. If the percent solid exceeds 0.5% separation of solid and liquid phase is necessary for separate analysis. The liquid phase is filtered through a 0.6 to 0.8 mm glass fibre filter and considerd the extract. The solid phase undergoes extraction.

   ii) Reduction of particle size to meet the maximum size limit to assess whether the waste is likely to leach significantly or whether the regulatory limit can be exceeded. The USEPA recommended formula (EPA, 2002) for assessing maximum theoretical concentration in the TCLP leachate from waste is illustrated below (Eq 3.2)

$$\frac{(AXB)+(CXD)}{B+\{20(L/kg)XD\}} = E \qquad \text{(Eq 3.2)}$$

Where,

A= Concentration of the analyte in liquid portion of sample (mg/L)

B= Volume of the liquid portion of the sample (L)

C= Concentration of the analyte in solid portion of the sample (mg/kg)

D= Weight of the solid portion of the sample (Kg), and

E= Maximum Theoretical concentration in the leachate (mg/L)

In this study TCLP was performed on the crushed concrete sample and the sample consists of 100% solid as per TCLP. Particle size reduction had to be conducted for the crushed concrete sample.

2. Determination of the appropriate extraction fluid

The next step was for the non volatile solids. There are two types of extraction fluid, namely, extraction fluid I and extraction fluid II respectively. The extraction fluid I (EF-I) is specified to have pH of 4.93+-0.05 and the fluid II (EF-II) is specified to have pH of 2.88+-0.05. the extraction fluid employed is a function of the alkalinity of solid phase of the waste. For this purpose TCLP employs a completely different and lengthy technique for evaluation of pH. The steps are discussed below:

i) 5.0 gram of sample having particle< 1 mm (reduced) is taken and mixed thoroughly with 96.5 ml of de-ionized water and stirred vigorously for 5 minutes with magnetic stirrer and allowed to settle.

ii) If pH<5.0, extraction fluid I (EF-I) selected immediately and step 3 is followed.

iii) If pH>5.0, 3.5 ml of 1 (N) HCL is added, slurry is briefly mixed and covered with a watch glass. Then it is heated to 50ºC and kept at 50ºC for 10 minutes. The sample is then followed to cool and pH is measured again.

iv) If the final pH<5.0, then EF-I is selected, otherwise EF-II is selected.

3. Rotary agitation of the solid phase of sample

i) The solid phase is poured in extraction vessels, specially designed for TCLP,

along with extraction fluid having volume equal to twenty times the weight of solid phase and sealed.

ii) The vessels are then subjected to continuous end over end rotation at 30+- 2 rpm for 18+-2 hours.

for this study the extraction vessel permit 25 gram of sludge with 500 ml of extraction fluid.

4. Filtration of the extract and storage

Following extraction, the liquid extract is separated from the solid phase by positive pressure filtration through a 0.6 to 0.8 Mm glass fiber filter. The pH of the extract is maintained at less than 2.0 for metal analysis.

3.7 Preparation and Storage of Standard Metal Solution

Standard metal solution of different metal (Cr, CD, Pb, Cu) were prepared at the optimum concentration range by appropriate dilution of the stock metal solution (NIST standard) for dilution de-ionized water containing 1.5 ml concentrated HNO3 per liter was used.

3.8 Beer Lambert's Law

Determination of low concentrations by visible ultra violet spectrometer (UV-VIS) is based on Beer- Lambert Law (Ali et al., 1998) which is given by:

$$A = \varepsilon l \qquad \text{(Eq 3.3)}$$

Where,

A= absorbance of radiation at a particular wavelength; =log (I_o/I)

I_o= Intensity of incident radiation

I = intensity of transmitted radiation

ε= Proportionality constant (Molar absorptivity; 1 $mol^{-1}cm^{-1}$)

C= concentration of the absorbing species (mol/L)

l= path length of light beam (cm**)**

The instrument used to measure the absorption of light can range from sophisticated laboratory instruments, which can operate over the whole visible- ultraviolet range to portable colorimeters using natural visible light, which are used as a field instrument. This makes absorption spectrometry one of the most useful and versatile techniques to an environmental analyst.

3.9 Atomic Absorption Spectrometry (AAS)

In this method, a light beam of appropriate wavelength for particular metal is directed through a flame. The flame atomizes the sample, producing atoms in their ground (lowest) electronic energy state. These are capable of absorbing radiation from the lamp.

Although the equipment appears completely different from other forms of absorption spectrometry, the law by which absorption of light is related to concentration is similar to that used for absorption of light related to concentration. The AAS is extremely sensitive technique and for common ions dilution prior to analysis is preferred.

The concentration range over which the law applies for Atomic adsorption Spectrometry (AAS) is usually 0-5 mg/L.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Introduction

The analysis of this study started with the analysis of sludge sample for preselected sludge constituents and their possible influence on the sludge mixed concrete. This study was carried out to analyze the variation in the basic properties of the solidified concrete mixed with sludge. This section highlights the detail analysis of the experimental results and findings. This includes the analysis of the total heavy metal content of the sludge sample, performance evaluation of the concrete batched with different proportion of sludge and leacchability of the sludge mixed concrete. Based on the test results a suitable sludge/ cement ratio was selected and repeatability test was conducted for with the selected sludge/ cement ratio.

4.2 Result of Preliminary Analysis of the Tannery Sludge

The sludge sample was analyzed for determining the characteristics of the sludge in terms of their physical and chemical properties (Table 4.1). The parameters analyzed included pH, alkalinity, percent organic, sulfate, sulfide, nitrate, chloride and silica. These parameters are reported to have bearing on strength of the concrete as well as on the leaching potential of sludge.

The pH of the sludge sample was tested with colorimetric test procedure and the resultant pH was 12.0. As per the Bangladeshi Standard for Tannery Industry Effluent, pH limit is 6-9. The percent organic in the sludge samples were observed to possess

62%. The presence of organic substances in the mix is likely to reduce the strength of the concrete.

Table 4.1: Results of preliminary analysis of the sludge sample

Parameters	Units	Concentration in Sludge
pH	-	12
***Alkalinity (as $CaCO_3$)**	mg/kg	98.23
Organic content	-	61.53
Chloride	mg/kg	105
Sulfate	mg/kg	4200
Sulfide	mg/kg	0.65
Nitrate	mg/kg	281.25
Silica	mg/kg	161.71

* In this method, mixture was prepared by diluting 4 mg sludge per 10 ml of water.

4.3 Heavy Metal Content of the Raw Sludge Sample

The sludge sample was digested with the aqua regia method was selected to determine the concentration of the preselected heavy metals of the sludge. Atomic Absorption Spectrophotometer was used to determine the total heavy metal concentration. The sludge sample was oven dried prior to the test. The average concentration of the result found from the tests are shown in Table 4.2.

Table 4.2: concentration of the heavy metals extracted with aqua regia method

Sl No	Heavy Metal	Concentration (mg/kg)
1	Chromium (Cr)	33.4
2	Cadmium (Cd)	19.6
3	Lead (Pb)	22
4	Copper (Cu)	4.16

The average total metal concentration of Cr, Cd, Pb was high in the sample and the concentration of Cu was moderate. Cr, Pb and Cd had considerable potentiality for leaching. From the total metal concentration results, the theoretical maximum possible concentration of the heavy metals in TCLP leachates were calculated with the USEPA prescribed formula (Eq 3.1).

The results of the theoretical maximum possible concentration of the heavy metals in TCLP leachates indicated that in case of 100% leachate the concentration of Pb, Cr and Cd would exceed the USEPA land disposal regulatory limit (Table 2.2).

4.4 Analysis of the Sludge Mixed Concrete

The mixing proportion of concrete adopted for this study was 1:2:4, which is a conventional weight basis-mixing ratio of cement, sand and aggregate. The water/ cement ratio used for the trial mixes were 0.50.

4.4.1 Physical Properties of the Sludge Mixed Concrete

The physical properties tested for every batches of concrete were workability, setting time and compressive strength. These results were assessed to analyze the variation of the properties of concrete at different sludge content. The sludge of the sludge mixed concrete were varied from 1% to 20% by weight of cement. The results found from the sludge mixed concrete were compared with the sludge free concrete to select proper mixing ratio and to conduct the repeatability test.

4.4.1.1 Workability

The slump value targeted for all the batches of concrete were 60 mm to 70 mm with 0.50 w/c ratio to produce a dense concrete casted with proper compaction. Water/cement ratio less than 0.50 produced too harsh concrete with inconsistent mixing of the materials.

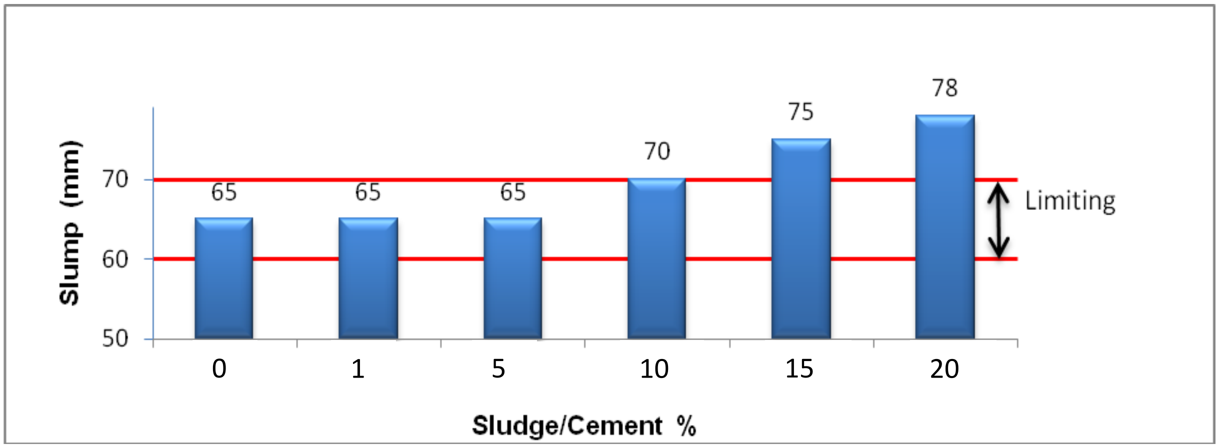

Figure 4.1: Deviation of the Slump of the concrete mixed with sludge/cement ratio of 0-20%

The workability results are shown in the following Fig. 4.1. 1% to 10 % of sludge/ cement mixed concrete had attained the required slump of 60- 70 mm. Sludge/ cement percentage of 1-5% provided slump value of 65 mm, similar to slump of the sludge free concrete. The slump increased gradually for addition of more than 10 % of sludge respectively.

4.4.1.2 Setting Time

The results obtained from the initial setting time and the final setting time tests of the sludge free and sludge mixed concrete were recorded. As per ASTM C403 the average time of initial setting varies between 169 and 252 minutes, and the average time of final setting varies between 240 and 341 minutes in the lab condition, temperature 20- 25° C. The limiting value for the initial setting time targeted for this study were 180- 240 minutes (2-3 hour) and for final setting time was 240-330 minutes (4-6.5 hours).

The results are graphically presented in Fig 4.2. Both the initial and final setting time of the concrete increased gradually with the increased percentage of the sludge addition. The trend line of the graph indicates that up to 7.5% of sludge/cement addition satisfied the limiting value of initial and final setting time. Sludge addition above this range only satisfied the requirement for initial setting time. Above 10% of sludge/cement addition provided an unacceptable value of setting time. The increase in setting time of concrete indicates a delay in the rate of gaining compressive strength in the concrete.

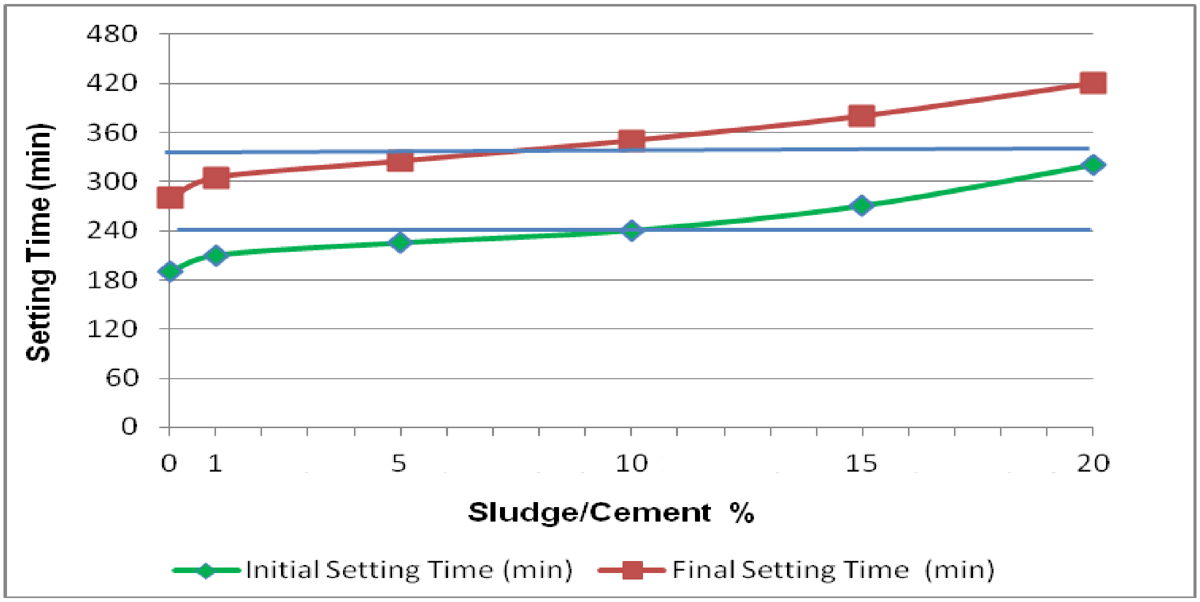

Figure 4.2: The initial and final setting time of the concrete mixed with sludge/cement ratio of 0-20%

4.4.1.3 Compressive Strength

The most important property of the concrete is the compressive strength. The compressive strength test results of the cylinders casted for each batch of concrete was recorded. As recommended by the American Concrete Institute (ACI) for structural concrete, a minimum compressive strength of 2500 psi was targeted for the field condition. For the lab condition, the 28-day strength targeted was 3000 psi to satisfy the strength requirement in the field condition. A graphical presentation of 3 days, 7 days and 28 days compressive strength are presented in Fig. 4.3, Fig. 4.4 and Fig. 4.5 respectively.

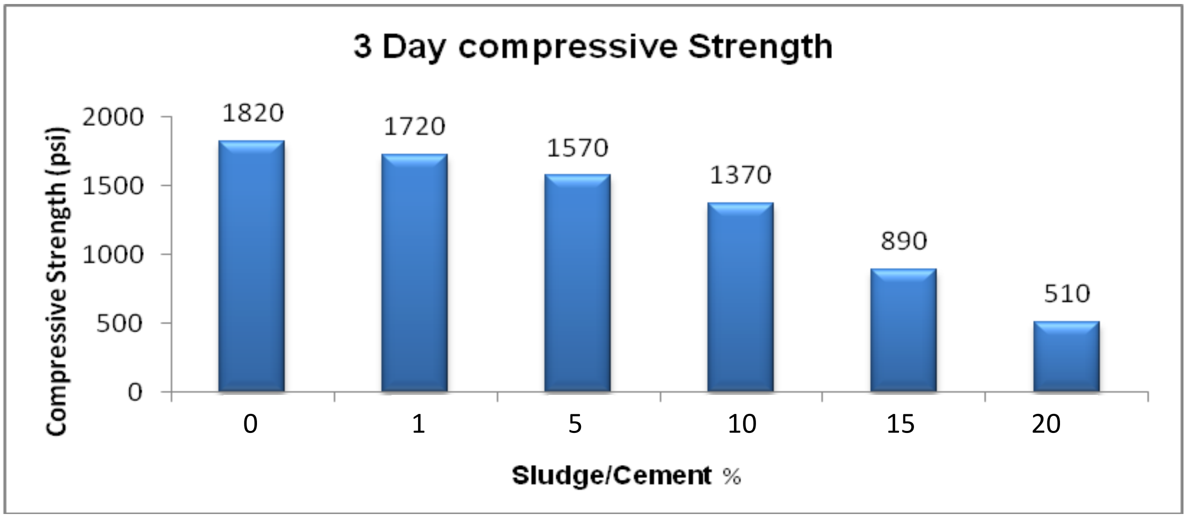

Figure 4.3: 3 days compressive strength of concrete with different sludge/ cement %

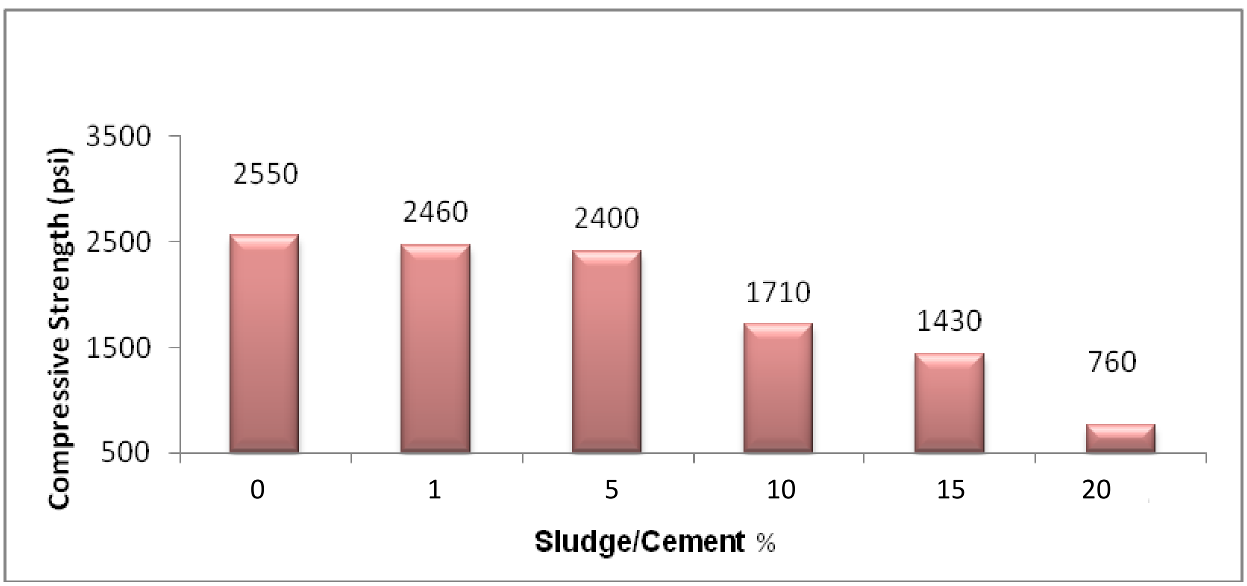

Figure 4.4: 7 days compressive strength of concrete with different sludge/ cement %

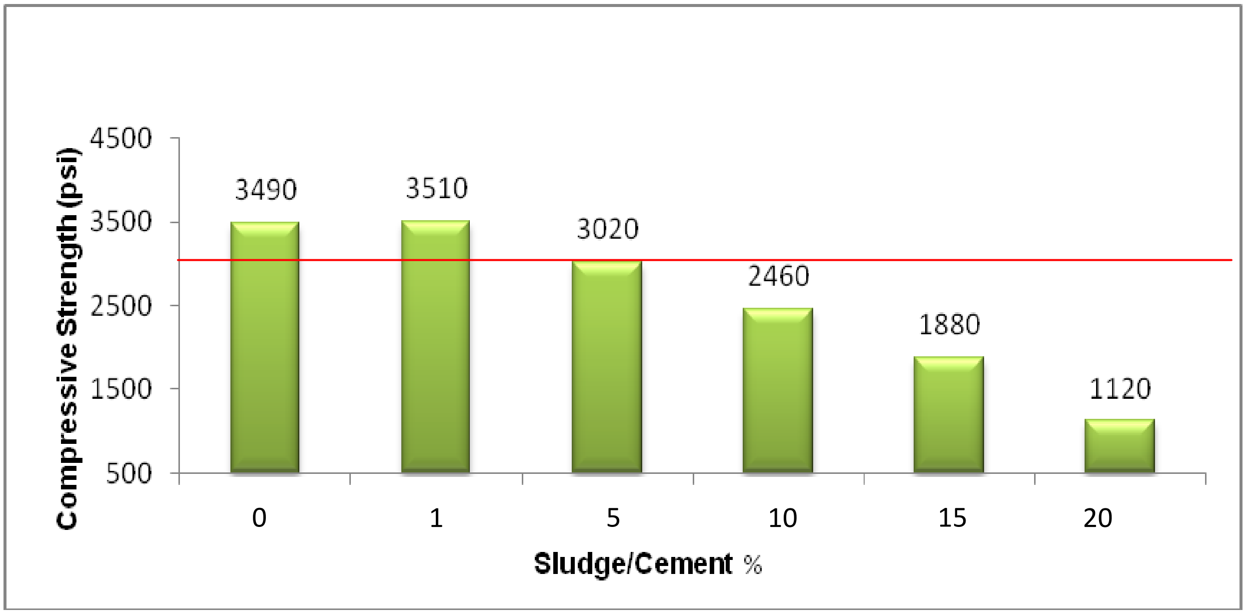

Figure 4.5: 28 days compressive strength of concrete with different sludge/ cement %

It was observed that the 3 days and 7 days compressive strengths gradually decreased with the addition of sludge in concrete. On the other hand, the 28 days compressive strength remained almost same as the sludge free concrete for 1% of sludge addition and then decreased gradually with the increased amount of sludge content. A combined 3 day, 7 day and 28 day compressive strength graph (Fig. 4.6) is better illustrated the deviation of strength for different percentage of sludge addition.

With the hydration reaction in the concrete, forms the calcium silicate hydrate (CaO·SiO2· nH2O, briefed as C–S–H), and Portlandite ($CaOH_2$). CSH is the main constituent that imparts strength to the concrete. Higher strength develops in concrete with the increased amount of CSH formation in concrete. The similar strength in the lower percentage of sludge mixed concrete may have resulted due to negligible effect of sludge in the concrete.

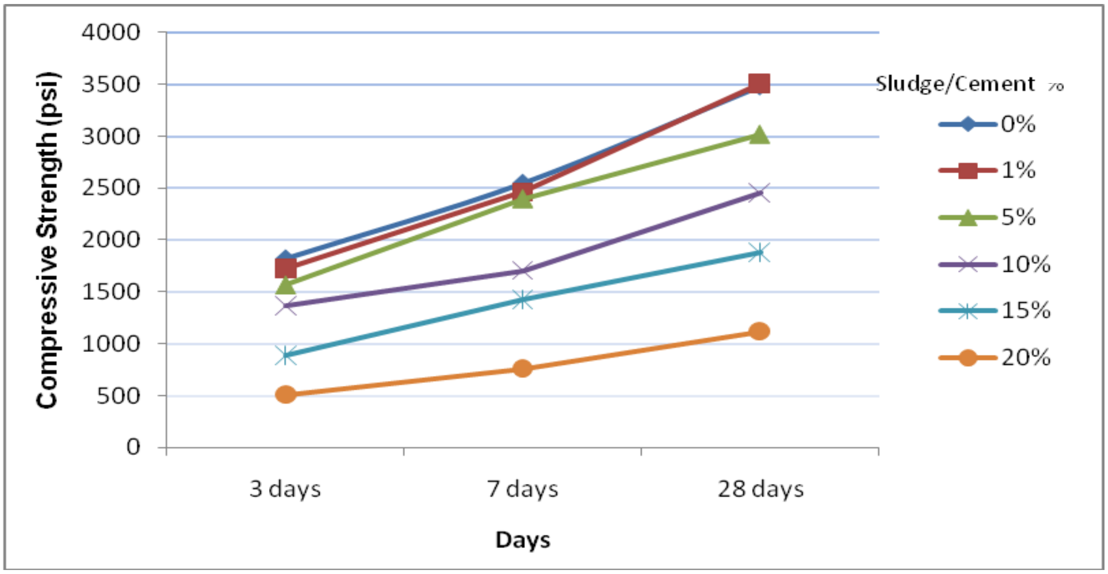

Figure 4.6: Decreased compressive strength of the sludge mixed concrete with the increased sludge / cement percentage

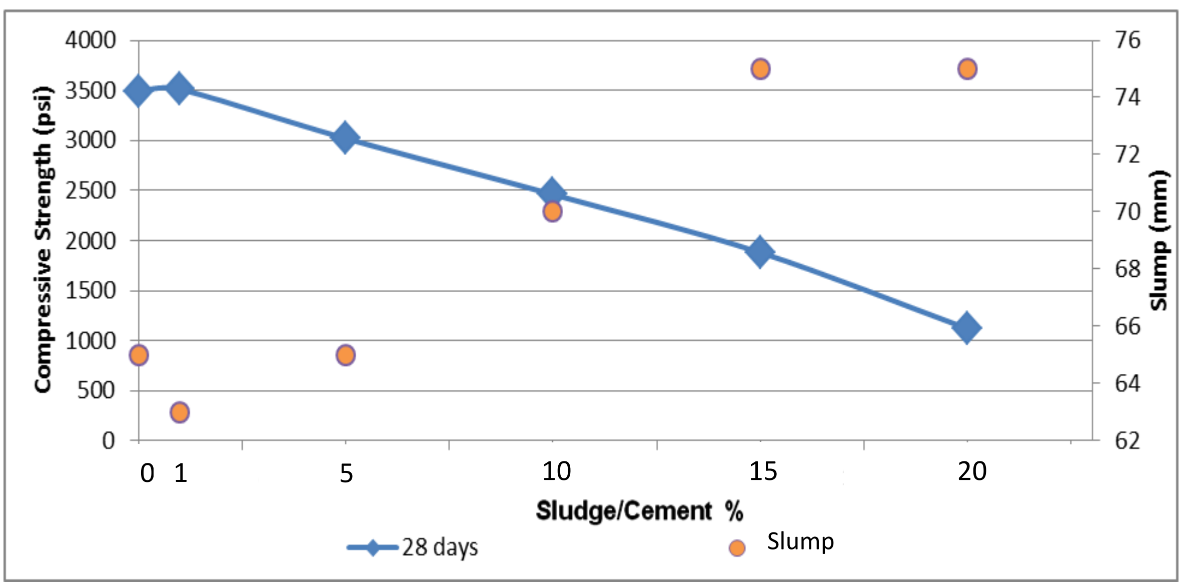

Figure 4.7: Compressive strength and slump of the sludge mixed concrete with w/c ratio of 0.50.

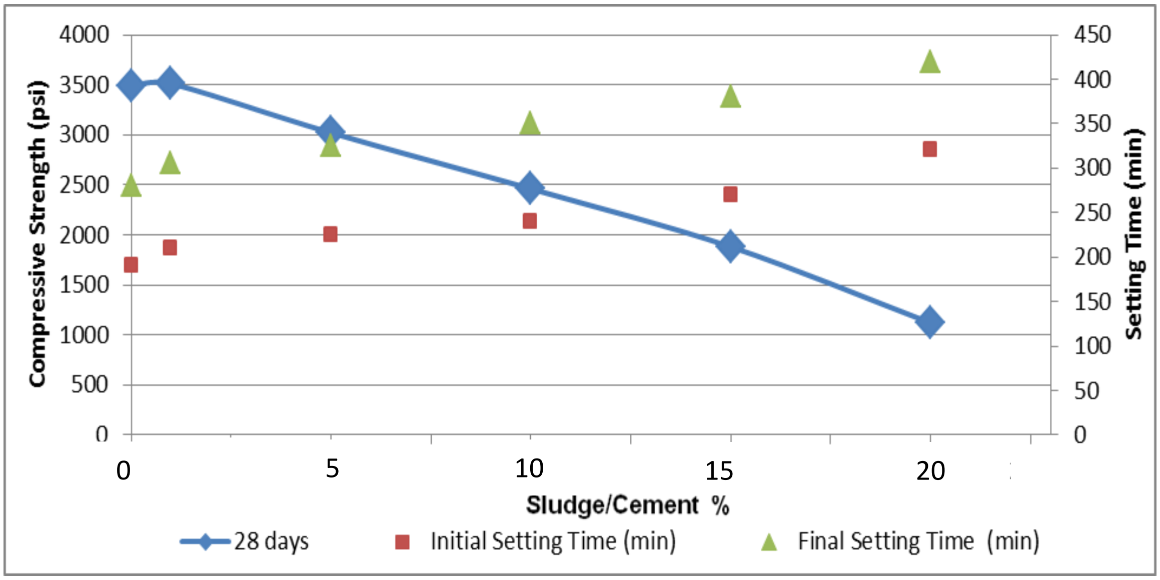

Figure 4.8: Compressive strength and setting time sludge mixed concrete with w/c ratio of 0.50.

The test results showed that up to 5% of sludge/cement addition produced workable structural concrete with compressive strength more that 3000 psi, slump value of 60-70 mm, initial setting time 210-225 min and final setting time 300-325 min (Fig. 4.8 and Fig. 4.9). Hence, this may be an acceptable range to replace the fine aggregate with sludge (by percentage of cement weight) in the concrete. For the next phase of study sludge/ cement of 5% was selected to perform the repeatability test. The compressive strength, slump, setting time and pH was recorded in the repeatability test.

Hossain (2004), in his masters' research studied the stabilization of the heavy metals in the industrial sludge with concrete mix. Sludge from tannery and textile industries were used. The mixing ratio of concrete was 1:1.5:3 with 0.45 water cement ratio. Sludge was used by replacing the fine portion of the concrete with different amount of sludge percentage (by weight of cement). An increase in the strength of the concrete with tannery sludge was observed at low sludge content (3%), the similar trend was also found in this study for 1% use of the sludge. The 28 day strength result of the final product of this study was remarkably higher, which might have resulted due to different mixing proportion and different property of sludge. However, both the study witnessed the strength showed a decreasing trend with increasing amount of sludge.

4.5 Chemical Properties of the Sludge Mixed Concreted

The TCLP test results for the sludge mixed concrete are presented below with the standard specified by USEPA in the Fig.4.9, Fig. 4.10 and Fig. 4.11.

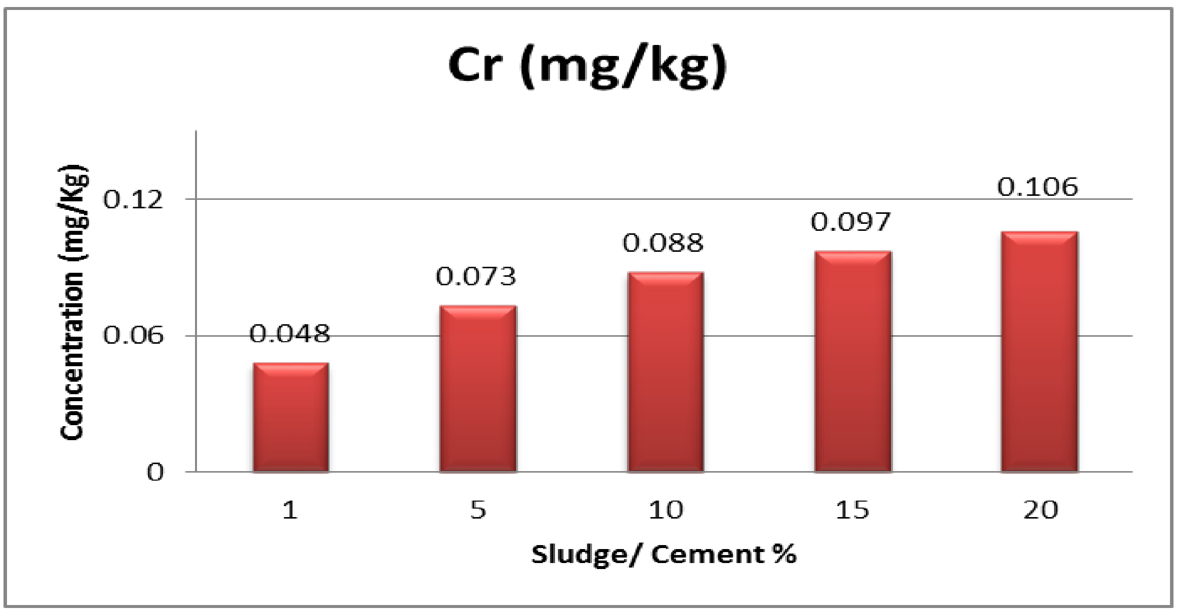

Figure 4.9: TCLP test result for Chromium (Cr)

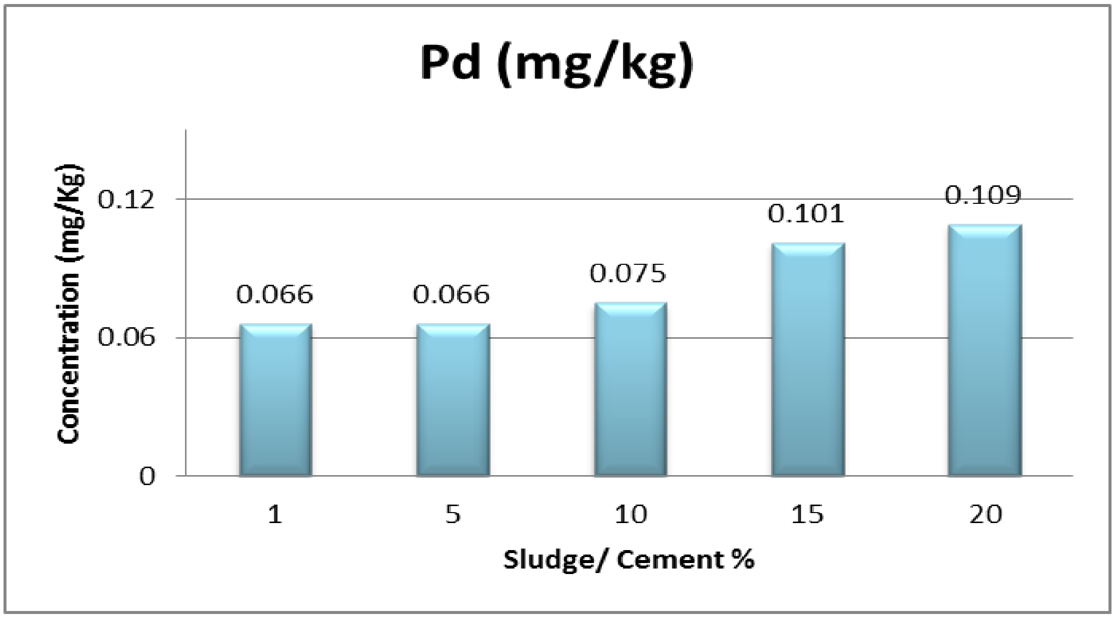

Figure 4.10: TCLP test result for Lead (Pb)

The concentration of chromium (Cr) and lead (Pb) in the TCLP leachates from the crushed concrete are shown in Fig 4.9 and Fig 4.10. The USEPA Land Disposal Restriction limit of concentration of Cr, Pb and Cd in TCLP leachates are 0.60 mg/Kg, 0.75 mg/Kg and 0.11 mg/Kg, respectively (USEPA, 1997). The concentrations of Cr in the leachates from sludge mixed concretes were extremely below the USEPA specified limit (Table 2.1). The concentration of Cr tends to increase with the increased percentage of sludge addition in the concrete mix.

Concrete mixed with 20% of sludge/ cement showed the highest concentration of chromium was 0.106 mg/Kg. This value is significantly lower than the USEPA Land Disposal Restriction Standard of 0.60 mg/Kg.

The Pb concentrations in the sludge mixed concrete were lower than the USEPA specified limit of land disposal restriction. Similar to the Cr concentration, Pb concentration increased with the increased percentage of sludge addition in the concrete mix. Pb concentrations were extremely lower (0.066 mg/Kg) for the concrete mixed with sludge/cement of 5% and below. Concrete mixed with 20% of sludge/ cement showed the highest concentration of Pb (0.109 mg/Kg), which is significantly lower than the USEPA Land Disposal Restriction standard of 0.75 mg/Kg.

The concentration of Cadmium (Cd) found from the TCLP test was undetectable indicating full stabilization of Cd. The leaching of the copper (Cu) was tested for crushed concrete to examine the presence of the metal in the final product. The leaching of copper was founded very low. Up to 5 % addition of sludge/ cement provided undetectable concentration of Cu in the TCLP test of crushed concrete. The concentration was very low for 10% of sludge / cement addition and increased very slowly up to the addition of 20%. This indicated a lower portability of the presence of copper ion in concrete. However, copper is not a set parameter for landfill disposal. Hence, it was tested to determine the potentiality of copper corrosion of concrete in presence of chloride.

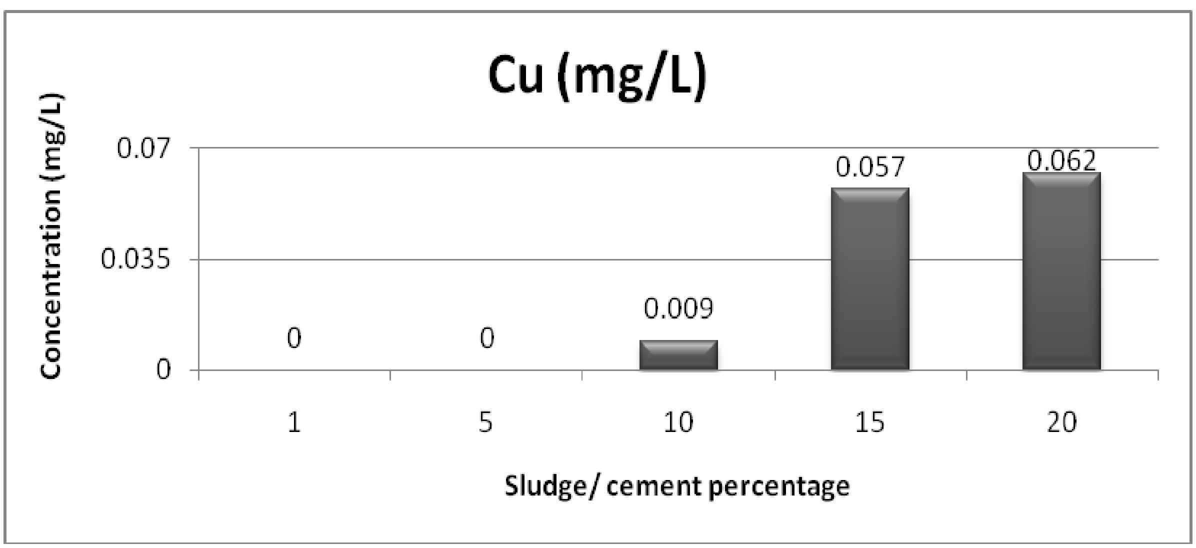

Figure 4.11: TCLP test result for Copper (Cu)

The pH recorded for the sludge free concrete and sludge mixed concrete are illustrated below in Fig: 4.12 to understand the variation of pH occurred during stabilization process. Fresh concrete itself is a highly alkaline material. The concrete casted without sludge and with the addition of different percentage of sludge had high pH range varying from 12.5 to 13.5. Therefore, the stabilization of the heavy metals occurred in a high alkaline system.

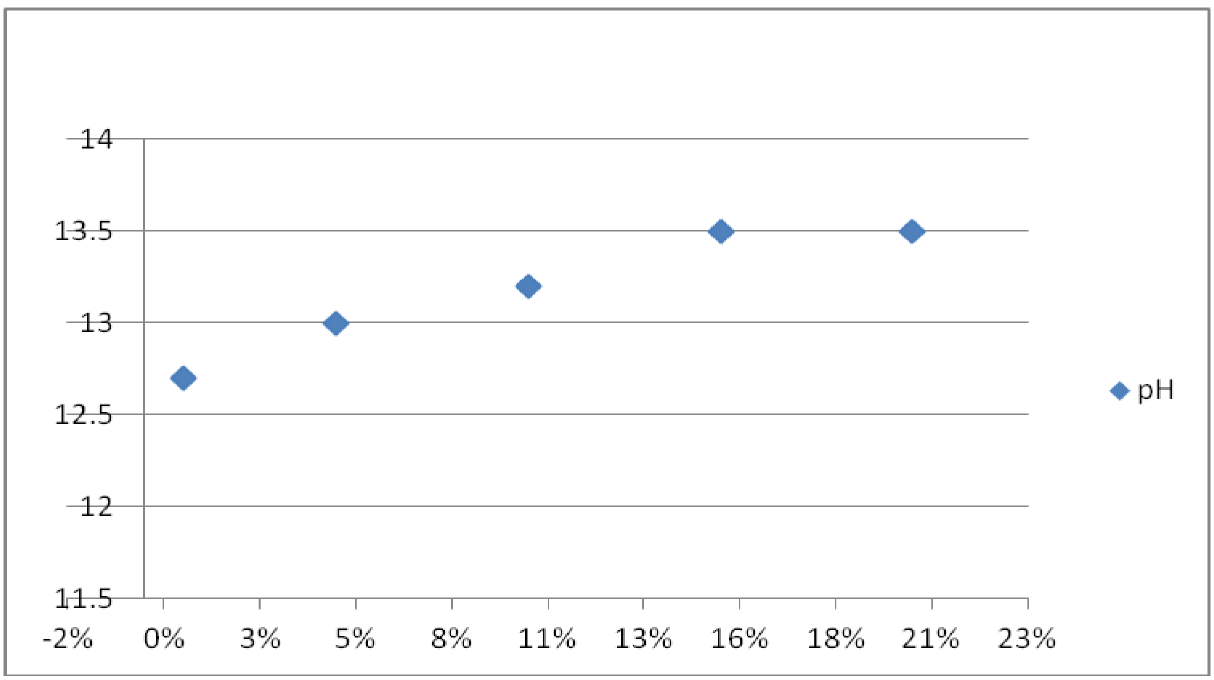

Figure 4.12: The pH of the sludge free and sludge mixed concrete

Portland cement along with the different combination can restrict the mobility of heavy metals due to high pH and capability of cement to precipitate the metals in insoluble form. This stabilization process relies on the formation of calcium silicate hydrate ($CaO \cdot SiO_2 \cdot nH_2O$, briefed as C–S–H), ettringite hydrate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32H_2O$) and monosulphate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) in the matrix, due to the hydration reaction of Portland cement, and thus the heavy metals both chemically fixed in the lattice of hydration production and physically encapsulated in the matrix (Jones, 1990, Fu et al., 2003, Mollah et al., 2000). The above mentioned discussion and the test result obtained in the TCLP test implies that the Ordinary Portland cement had stabilized the chromium and lead content of the tannery sludge to a satisfactory level. The cadmium content was fully stabilized. For this particular tannery sludge, no prior treatment is required for concrete preparation.

4.6 Repeatability Test

Repeatability test was conducted to verify the results obtained from the concrete cylinders casted with 5 % of tannery sludge by weight of cement replacing equal weight of fine aggregate. Three trial mixes of concrete were conducted with similar mixing ratio (1:2:4). The water/ cement ratio of the mixes were 0.50.

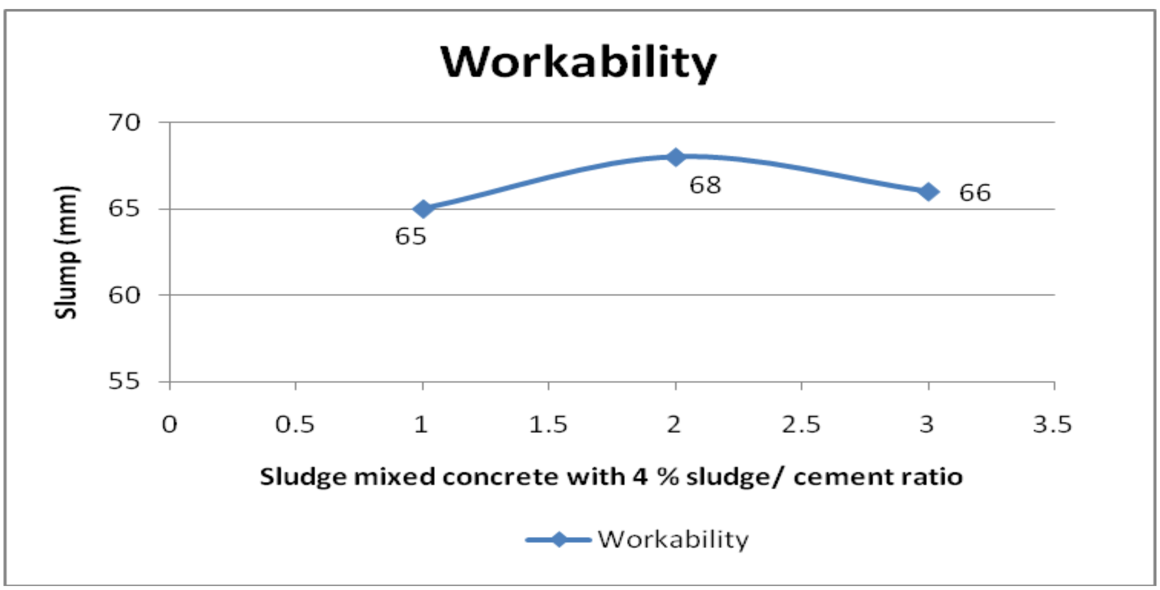

Figure 4.13: Workability of different batches of the concrete mixed with 5% sludge (by wt of cement)

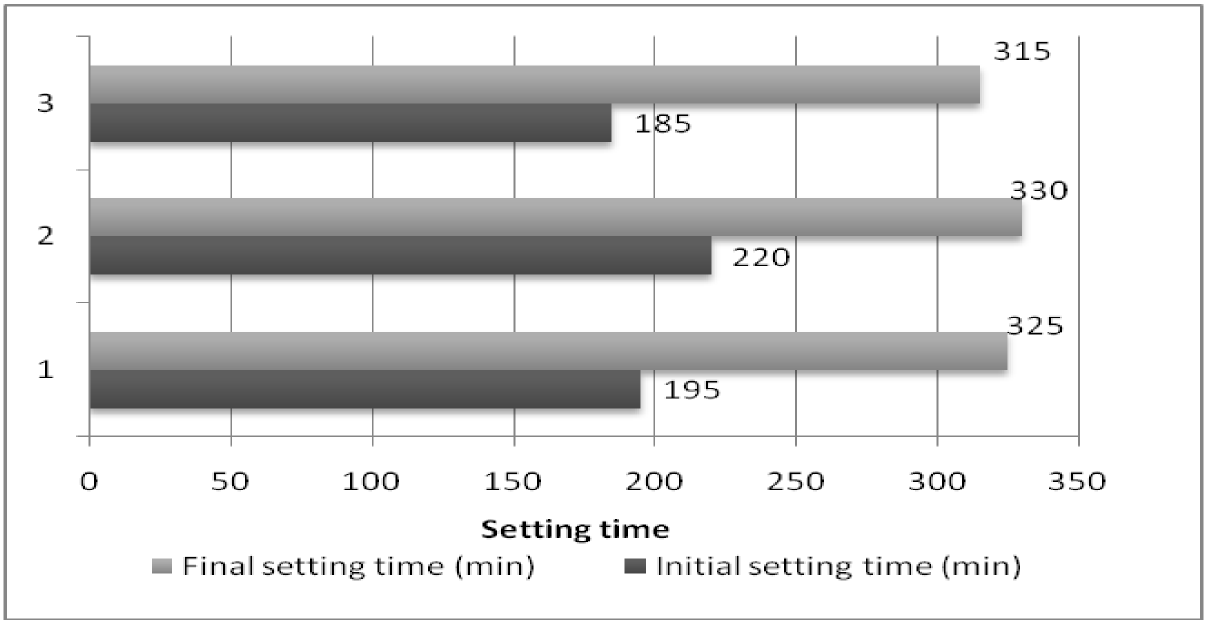

Figure 4.14: Setting time of different batches of the concrete mixed with 5% sludge (by wt of cement)

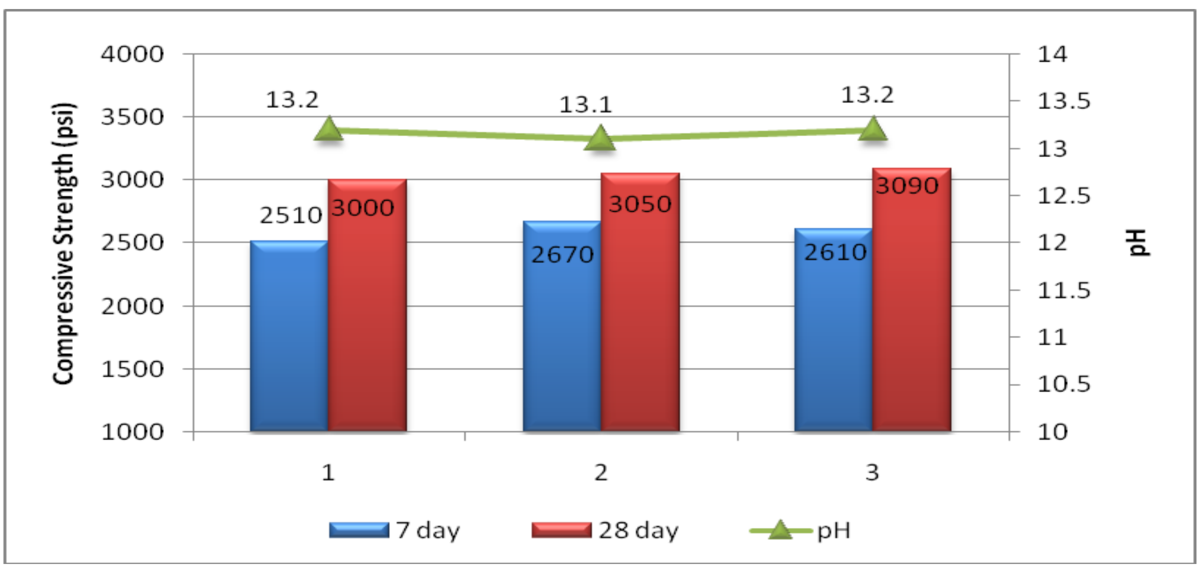

Figure 4.15: Variation of Compressive Strength and pH for different batches of the concrete mixed with 5% sludge (by wt of cement).

The slump (Fig. 4.13) and the setting time (Fig. 4.14) for the concrete specimens were founded in between the desired value. The 28 day compressive strength (Fig. 4.15) of the specimens showed results similar to the result found in the preliminary concrete mix with 5% of sludge/cement addition. pH of the mixes were very high indicting towards high alkaline environment of the concrete. However, there was a significant reduction (15%) of the 28 day strength compared with the strength of the sludge free concrete. Hence, up to 5% of sludge/ cement ratio may be an acceptable range of sludge addition in concrete for heavy metal stabilization process.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Sludge from the Hajaribagh tannery area has been categorized as hazardous waste particularly due to the presence of heavy metals i.e. lead, chromium, cadmium etc. in it. Disposal of this sludge into watercourses, onto land and the concentrated growth of this contaminant have shown how it can cause irreversible damage to the environment in the vicinity. However, the lack of coordination between the between the environmental authorities and the industries regarding the sludge management has resulted the companies to set up their own sludge disposal options. Therefore, the environment is under increasing pressure from this emanating sludge and other wastes of tannery industry. The main objective of this study was to assess the viability of using solidification technology to stabilize and convert the hazardous and toxic heavy metals present in the sludge into an inert, physically stable mass, with very low leachability. The secondary objective of the study was to assess the performance of the sludge added concrete to recommend a suitable concrete mix for minor construction work using sludge partially replacing the fine aggregate in concrete mix.

Laboratory tests and analysis were done to determine the chemical properties of the collected sludge sample and its effect on the properties of the sludge mixed concrete. The sludge was used as a replacement of the fine aggregate by weight of certain cement percentage. Six trial mixes was conducted with different sludge/ cement ratio to evaluate concrete properties and leachability. A suitable sludge/cement ratio was selected by analyzing the result obtained from the test and repeatability test was conducted.

The brief summary of the findings are stated below:

1. For the particular sludge properties, a sludge addition of 1% to 5% by weight of cement replacing equal weight of fine aggregate could be used for concrete mixing considering the overall performance and properties of the concrete. However proper mixing ratio need to be maintained to achieve the compressive strength required for structural concrete (i.e. more than 2500 psi). The average compressive strength obtained from 5% of sludge/ cement addition was 3047 psi in the standard lab condition, which was satisfactory and expected to attain 2500 psi in the field condition for 1:2: 4 mixing ratio.

2. The compressive strength of the concrete decreased gradually with the increased amount of sludge addition. There was a linear relationship between the declining strength with the coefficient of variation of 0.30. For 0%, 5% and 20% of sludge/ cement addition in the concrete mix, the 28 days compressive strength obtained were 3410 Psi, 3510 Psi and 3020 Psi. On the contrary, the slump, setting time and ph of the sludge mixed concrete increased with the increased amount of sludge addition.

3. Laboratory test result demonstrated that the total heavy metal concentration of the sludge was very high for Cr, Pb, Cd and Cu. The TCLP leachates from sludge mixed concrete had very low concentration of chromium. The high concentration of cadmium content of the raw sludge was undetectable in the TCLP test of the sludge mixed concrete. The result implied that the heavy metals were stabilized to a desired level. Hence, the re-use of the tannery sludge in the concrete mixed with suitable proportion may be a feasible option to stabilize the sludge by the solidification process.

4. For non-structural work, concrete strength less than 2500 Psi could be accepted depending on the requirement. In that case, a sludge / cement addition of up to

20% could be used considering the complete stabilization of heavy metals in the sludge. However, a slow setting occurs for the sludge/ cement addition of more 10% by weight of cement.

5.2 Recommendation for Future Study

This study has considered the heavy metal concentration of the sludge sample collected from single tannery industry. Sludge from different tannery industry with extensive analysis of both physical and chemical properties may be include for future study to accumulate a better understanding of its impact and effect on concrete properties.

The present study included single water/ cement ratio to determine the deviation of the compressive strength with the sludge addition. Hence, to achieve more accurate result in the future study, effect of different water / cement ratio may be introduced. Also the same study may be conducted varying the pH range of the concrete to determine the optimum pH value to stabilize the heavy metals of sludge.

This study had covered a conventional mixing ratio to produce structural concrete without any chemical admixture. However, the water content has a huge impact on the compressive strength of the concrete. So the effect of applying water reducer admixture may be considered in future study. In addition volumetric mix design can be considered for mass production.

This study did not include any test of the durability, soundness and permeability and the long term strength test of the concrete. The above mentioned tests of the concrete are important to evaluate the performance of the sludge mixed concrete in the long run which might be included in the scope of the future study.

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Appendix A

A.1 Aqua-regia Method: Extraction Method for Heavy Metals

- 5 gm of sample was taken in a conical flask
- 5 ml distilled water was added to obtain slurry
- 7.5 ml HCL (1:3) and 2.5 ml HNO_3 (1:3) was added to make a 300 ml of sample
- The sample was covered and kept overnight
- Covered sample was then heated for about 2.5 hours at 100º c under reflux condition to reduce the volume to 25 ml.
- The sample was allowed to cool and then mixed with distilled water to obtain 500 ml of sample.
- Filtration was done and the sample was collected.

A.2 Volumetric amount of the materials to produce 1 m^3 of concrete (Converted from 1:2:4 weight basis ratio)

Sludge %	**w/c ratio**	**Cement (Kg/m^3)**	**Coarse aggregate (Kg/m^3)**	**Fine aggregate (Kg/m^3)**	**Sludge (Kg/m^3)**
0	0.50	310	1240	670	0
1	0.50	310	1240	663.3	6.7
5	0.50	310	1240	636.5	33.5
10	0.50	310	1240	603	67.0
15	0.50	310	1240	569.5	100.5
20	0.50	310	1240	536	134

Appendix B

B.1 Leather Processing

Leather tanning is essentially the conversion of raw animal hides (cows, sheep, goats, and buffalo) into leather by a series of chemical reactions that alters the protein structure to preserve the hide. It involves three main stages: the first to produce “wet blue” leather, the second to produce “crust leather,” and the third to produce finished leather.

- **“Wet blue” stage**

Hides are first soaked for one or two days in water, wetting agents and bactericides, to remove the salt. They are then treated in pits or drums with lime and sodium sulfide to remove hair and excess flesh, in processes called liming and unhairing. These two stages are particularly polluting, causing the release of hydrogen sulfide and sulfur dioxide gases (which can cause sulfuric acid in the atmosphere) while the effluent contains calcium hydroxide as well as toxic sulfides and large amounts of suspended solids.

After liming, the hides undergo fleshing, either manually or in a fleshing machine, a process, which strips the remaining flesh and fat from the hide. De-liming then removes the lime from the hides, often by ammonium sulfate or ammonium chloride as well as sodium metabisulfite. Bating, to soften the leather, uses a protein-digesting enzyme.

Pickling then prepares the hide for tanning, often-using salt, sulfuric acid, and formic acid.
Tanning can involve chrome tanning, synthetic tanning or vegetable tanning. Vegetable tanning uses tannins that occur naturally in the leaves and bark of certain plants. Chrome tanning, which is common in Hazaribagh, involves treating the hides with chromium sulfate then sodium carbonate or sodium bicarbonate. Some 60 percent of the chromium is normally discharged as solid or liquid waste.

The hide then undergoes pre-crusting operations. Sammying, pressing the hides through heavy rollers, removes water from the hide. The hide may be split horizontally to adjust the thickness of the leather, the upper part being the most valued leather. In shaving, rotating blades of a machine smooth the rough part of the leather, generating a fine dust of leather particles.

Some tanneries will sell the resulting “wet blue” hides to other tanneries, while others continue further processing (crusting, then finishing) themselves.

- **“Crust leather”**

The leather can be re-chromed in order to increase its density and quality. Chromium sulfate is again used along with sodium carbonate or sodium bicarbonate. Re-tanning spreads tanning agents evenly through the leather. This can involve tanning agents, resin, vegetable tannins and other chemicals. The hide is then ready for dying with acid dyes, alkaline dyes, or various others. Ammonium hydroxide, ammonium chloride, labeling agents, synthetic tanning agents, vegetable extracts, formic acid, and acetic acid are also used.

The hides then undergo fat liquoring, which treats the hides with natural or synthetic oils.

The hides then go through a setting machine to remove the wrinkles in the hide, and then drying (by hanging, in a vacuum machine, or toggling in the sun) before being trimmed and plated (or smoothed out under high pressure and heat).

Some tanneries will sell the resulting “crust leather” to other tanneries, while others continue the finishing process themselves.

3. Finishing

Leather can be finished in a variety of ways. In general, the finishing process gives a decorative and protective surface coating to the leather. Buffing in a machine smoothes the leather, often creating a fine dust. A finishing solution is applied by a spray machine or by padding. Dyes, binders, adhesives, fillers, waxes, resins, polymers, modifiers, fixatives, thinners, oils and preservative may be used in this part of the process.

B.2 : Location Map of Hazaribagh Thana (Banglapedia, 2005)