STABILIZATION OF HEAVY METALS IN INDUSTRIAL SLUDGE WITH CONCRETE MIX

by

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TABLE OF CONTENTS

Page

TITLE PAGE i

CERTIFICATION PAGE ii

DECLARATION iii

DEDICATION iv

LIST OF TABLES viii

LIST OF FIGURES ix

LIST OF ABBREVIATIONS xii

ACKNOWLEDGEMENT xiii

ABSTRACT xiv

CHAPTER 1 INTRODUCTION 1

- 1.1 Background of the Problem 1
- 1.2 Objectives 3
- 1.3 Scope of the Study 3
- 1.4 Organization of the Thesis 4

CHAPTER 2 LITERATURE REVIEW 6

- 2.1 Impacts of Heavy Metals 6
  - 2.1.1 Soils and crops 6
  - 2.1.2 Aquatic plants 8
  - 2.1.3 Invertebrates 9
  - 2.3.4 Fish 10
- 2.2 Health Aspects of Heavy Metals 11
  - 2.2.1 Lead 11
  - 2.2.2 Cadmium 12
  - 2.2.3 Chromium 13
  - 2.2.4 Mercury 13
- 2.3 Leaching from Industrial Sludge 14
- 2.4 Cement Based Stabilization of Industrial Sludge 16

Page
2.5 An Overview of Existing Leaching Tests 18
2.5.1 Static extraction tests 19
2.5.2 Dynamic extraction tests 20
2.5.3 The concepts and applicability of TCLP 21
2.6 Some Past and Current Research on Stabilization with Cement 24

CHAPTER 3 METHODOLOGY 25
3.1 Introduction 25
3.2 Selection of Industries 25
3.3 Sampling Locations 27
3.4 Sample Collection 27
3.5 Sample Preservation and Storage 27
3.6 Preliminary Analyses of Sludge Properties 28
3.7 Analysis of Total Heavy Metal Content of Sludge 30
3.7.1 Extraction methods for chromium, cadmium and lead 30
3.7.2 Extraction method for mercury 30
3.8 Preparation of Concrete with Sludge 31
3.9 Testing of Concrete 32
3.9.1 Test for workability 32
3.9.2 Test for compressive strength 32
3.9.3 Test for durability of concrete 33
3.10 Test for Leaching Potential of Sludge and Concrete 34
3.10.1 Toxicity characteristic leaching procedure 35
3.10.2 Modified leaching test 37
3.11 Preparation and Storage of Standard Metal Solution 38
3.12 Beer – Lambert's Law 38
3.13 Atomic Absorption Spectrometry (AAS) 39

CHAPTER 4 RESULTS AND DISCUSSION 40
4.1 Introduction 40
4.2 Results of Preliminary Analysis for Sludge Constituents 40

Page
4.3 Analysis of Total Heavy Metal Content in Sludge 41
4.4 Analysis of Leachate Results 43
4.5 Analysis of Sludge Mixed Concrete 51
    4.5.1 Results of preliminary analysis of concrete 52
    4.5.2 Results of secondary analysis of concrete 55

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS 65
5.1 Conclusion 65
5.2 Recommendations 66

REFERENCES 68
APPENDIX A HEAVY METALS DIGESTION METHODS FOR SLUDGE 74
APPENDIX B CONCENTRATION PLOTS OF HEAVY METALS IN LEACHATES 77

LIST OF TABLES

Page

Table 2.1. Toxicity Characteristic regulatory standards set forth by the United States Environmental Protection Agency. 23

Table 2.2. Land Disposal Restrictions–Universal Treatment Standards set forth by the United States Environmental Protection Agency. 23

Table 4.1. Results of preliminary analysis of sludge. 41

Table 4.2. Concentration of total Pb, Cr, Cd and Hg in mg/kg of sludge for sludge S-A and S-B. 42

LIST OF FIGURES

		Page
Figure 3.1.	Flowchart of the activities performed in the study.	26
Figure 4.1.	Concentrations of total Pb, Cr and Cd in mg/kg of sludge for sludge S-A and S-B.	42
Figure 4.2.	Results of average concentrations of Pb, Cr and Cd in standard TCLP and modified leaching test leachates from sludge S-A.	44
Figure 4.3.	Results of average concentrations of Pb, Cr and Cd in standard TCLP and modified leaching test leachates from sludge S-B.	44
Figure 4.4.	Results of normalized average concentration of Pb in standard TCLP leachates from crushed concrete sample for sludge S-A.	45
Figure 4.5.	Results of normalized average concentration of Pb in standard TCLP leachates from crushed concrete sample for sludge S-B.	45
Figure 4.6.	Results of normalized average concentration of Pb in modified leaching test leachates from crushed concrete sample for sludge S-A.	46
Figure 4.7.	Results of normalized average concentration of Pb in modified leaching test leachates from crushed concrete sample for sludge S-B.	46
Figure 4.8.	Results of normalized average concentration of Cr in standard TCLP leachates from crushed concrete sample for sludge S-A.	48
Figure 4.9.	Results of normalized average concentration of Cr in standard TCLP leachates from crushed concrete sample for sludge S-B.	48
Figure 4.10.	Results of normalized average concentration of Cr in modified leaching test leachates from crushed concrete sample for sludge S-A.	49
Figure 4.11.	Results of normalized average concentration of Cr in modified leaching test leachates from crushed concrete sample for sludge S-B.	49

Page

Figure 4.12. Variation of slump of fresh concrete with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.45. 52

Figure 4.13. Variation of average 7-day cylinder compressive strength of concrete at with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.45. 53

Figure 4.14. Variation of average 28-day cylinder compressive strength of concrete with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.45. 53

Figure 4.15. Variation of slump and average 28-day cylinder compressive strength of concrete with increase in sludge content at water-cement ratio of 0.45. 55

Figure 4.16. Variation of slump of fresh concrete at different water-cement ratio with increase in sludge content for sludge S-A and S-B. 56

Figure 4.17. Variation of average 28-day cylinder compressive strength of concrete at different water-cement ratio with increase in sludge content for sludge S-A and S-B. 57

Figure 4.18. Observed average changes in initial volume of concrete with increase in sludge content for sludge S-A and S-B at different water cement ratio after immersion in 1.0% $MgSO_4$ solution for 140 days. 59

Figure 4.19. Observed average changes in initial volume of concrete with increase in sludge content for sludge S-A and S-B at different water cement ratio after immersion in 2.5% $MgSO_4$ solution for 140 days. 59

Figure 4.20. Observed average changes in initial volume of concrete with increase in sludge content for sludge S-A and S-B at water cement ratio of 0.40 after immersion in $MgSO_4$ solution of different concentrations for 140 days. 60

Page

Figure 4.21. Observed average changes in initial volume of concrete with increase in sludge content for sludge S-A and S-B at water cement ratio of 0.45 after immersion in $MgSO_4$ solution of different concentrations for 140 days. 60

Figure 4.22. Reduction in average compressive strength of concrete with increase in sludge content for sludge S-A and S-B at different water cement ratio after immersion in 1 % $MgSO_4$ solution for 140 days. 62

Figure 4.23. Reduction in average compressive strength of concrete with increase in sludge content for sludge S-A and S-B at different water cement ratio after immersion in 2.5 % $MgSO_4$ solution for 140 days. 62

Figure 4.24. Reduction in average compressive strength of concrete with increase in sludge content for sludge S-A and S-B at water cement ratio of 0.45 after immersion in $MgSO_4$ solution of different concentrations for 140 days. 63

Figure 4.25. Reduction in average compressive strength of concrete with increase in sludge content for sludge S-A and S-B at water cement ratio of 0.45 after immersion in $MgSO_4$ solution of different concentrations for 140 days. 63

LIST OF ABBREVIATIONS

ACI	American Concrete Institute
ASTM	American Society for Testing and Materials
DEPZ	Dhaka Export Processing Zone
ECA'95	Environmental Conservation Act 1995
ECR'97	Environmental Conservation Rules 1997
LDR	Land Disposal Restrictions
NIST	National Institute of Standards and Technology
NWMP	National Water Management Plan
OPC	Ordinary Portland Cement
SPLP	Synthetic Precipitation Leaching Procedure
TC	Toxicity Characteristic
TCLP	Toxicity Characteristic Leaching Procedure

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ABSTRACT

Leaching from industrial sludge is a growing problem worldwide, especially in developing countries like Bangladesh where the industrial sludge is usually highly polluted with persistent toxic heavy metals and bio-organics. Limitations in treatment facilities combined with the lack of environmentally friendly disposal options is posing a potential threat of contaminating surface and ground water resources of the country with leachates from mismanaged sludge. The primary objective of this study was to assess the viability of stabilization of the heavy metals present in industrial sludge with concrete mix from environmental perspective, to assess the strength and usability of the resultant concrete and to propose a stable mix that can be used for minor construction.

Dry sludge samples from two industries at the Dhaka EPZ were collected and analyzed for various pre-selected physical properties and chemical constituents that are likely to affect the properties and behavior as well as leaching from resultant concrete. The heavy metal contents of the sludge samples in terms of total Cadmium (Cd), Lead (Pb), Chromium (Cr) and Mercury (Hg) were determined following standard USEPA methods.

The air-dried sludge samples were powdered prior to use in concrete mix. The sludge samples were used in different proportions in concrete mix replacing equal weight of finer portion of the fine aggregates. In the preliminary phase, sludge content varied from 3 to 10% by weight of cement in the concrete mix. Based on the cylinder compressive strength test results and slump results on concrete, a relatively narrow range of sludge content was selected for secondary analysis at different water-cement ratio. The durability of sludge-mixed concrete under sulfate laden environment at different water-cement ratio and sludge content were analyzed.

The Toxicity Characteristic Leaching Procedure (EPA Method 1311) was performed on the raw sludge and crushed concrete samples for analyzing the long-term leaching potential of the sludges and concrete in terms of the heavy metals of concern for this study. A modified leaching test was performed on the same samples in an effort to simulate the scenario of open environment exposure expected for the stabilized sludge.

The TCLP leachates from raw sludge showed significant concentration of Pb and Cr. The concentrations of heavy metals in leachates from crushed concrete samples were very low. In most cases, the concentrations were within the standard deviations of that observed in raw sludge leachates. If the background contamination of concrete is excluded, then the concentrations become negligible and can be attributed to standard experimental errors. The sludge-mixed concrete samples showed little difference in durability compared to the sludge free samples. However, noticeable change in durability was observed with change in water-cement ratio.

The concrete based stabilization of heavy metals seemed successful. The water-cement ratio seems to play a significant role in workability and strength and possibly the major role in durability in case of sludge-mixed concrete. Water-cement ratio should be kept in the range near 0.40. The test results of concrete suggest that the sludge amount is better to be limited within 5 to 6% by weight of cement from the conservative standpoint of possible presence of high amount organics in sludge in the fields. At 5% sludge content and water-cement ratio of 0.40, the 28-day average compressive strength of sludge-mixed concrete for the low organic sludge and the organic-rich sludge were observed to be 5050 psi and 4850 psi, respectively; which can be regarded as acceptable for structural purpose.

CHAPTER 1
INTRODUCTION

1.1 Background of the Problem

Leaching from industrial sludge is a growing problem for both the developed and developing countries. The problem is acute in developing countries due to limitations in treatment facilities at the first hand and lack of cost-effective and environmentally friendly disposal options on the other. The industrial sludge in Bangladesh is generally highly polluted with persistent toxic heavy metals and bio-organics and the resulting leachates often has significant amount of toxic heavy metals. Physio-graphically almost the entire country is a flood plain where over-population and extensive agriculture has made the country's land resource a scarce one. Due to severe scarcity of suitable land for disposal, surface water or on-land disposal is often practiced by industries located near rivers, canals, etc. which results in contamination of the soil and surface water sources. Wastes disposed on land get to the open waters with flooding and runoff from monsoon rainfall. As the country has a large inter-linking river network, anything that reaches the open waters is transported downstream in a short time. Pollution of soils and vegetables grown in locations far away from any industries and in mostly agricultural areas is a sufficient evidence of such pollution (Hossain & Badruzzaman, 2002). Underneath the flood plains, the country has vast unconfined aquifers having ground water table at shallow depth, which is often within a few meters during the monsoon. These aquifers are the primary source of drinking water and a major source of irrigation water in Bangladesh. Hence, degradation of ground water quality is of major concern.

Bangladesh presently has Environmental Conservation Act (ECA'95) and Environmental Conservation Rules (ECR'97) in effect since 1995 and 1997, respectively. The accompanying environmental quality standards and discharge quality standards of ECR'97 cover only the treatment of effluents to meet definite discharge quality standards. There are neither any regulatory guidelines regarding leaching from sludge nor there any guideline for disposal of industrial solid or semi-solid sludge. The concept of leaching from hazardous industrial wastes can be termed 'alien' in the present environmental guidelines of the country. The industries are virtually on their own in setting up course of action regarding disposal of sludge. The industries having proper treatment facilities (i.e. meeting effluent quality standards) meeting the standards and guidelines often face the problem with the disposal of the dry solid sludge. The sludge has high levels of the contaminants, especially heavy metals. The notable heavy metals of concern in Bangladesh are lead (Pb), chromium (Cr), cadmium (Cd), aluminium (Al), mercury (Hg), etc. Disposal of sludge on-land poses a potential threat as it is may lead to leaching and subsequent contamination of aquifers..

In the draft National Water Management Plan (dNWMP) of Bangladesh, concern over heavy metal contamination of groundwater and surface water resources (Cd, Cr, Pb, Hg, etc.) due to unregulated disposal of industrial wastes has been stressed as these heavy metals tend to persist in the environment and may have adverse effects on the food chain (Halcrow, Mott MacDonald and Associates, 2000). However, the relocation plans prescribed by the Department of Environment (DoE) for some sensitive industries have been negated in that study considering the huge costs involved and the fear of diffusing the problem to other places from the hot-spots rather than solving the problem. Emphasis was on mitigating problems locally. It was further stressed that study on characterizing industrial wastes and heavy metal contamination of surface and ground water resources is needed.

Stabilization of the industrial wastes prior to disposal is presently advocated. This is because; reclamation of contaminated water bodies and soils is extremely difficult if not impossible. It often is an expensive and requires time intensive techniques that may not be feasible even for the developed countries. Concrete based stabilization of industrial sludge has been practiced in some countries as an effective solution in reducing leachability of heavy metal containing wastes by solidification. This approach may also serve as an economically viable and environmentally friendly option for Bangladesh. However, detailed study in waste stabilization in concrete mix has not been performed in Bangladesh. Detailed research seems necessary for determining a proper mix design and methodology concerning stabilization of industrial sludge with concrete without significantly sacrificing its strength. Thus, the present study plans to focus on the above issues.

1.2 Objectives

The objectives of the study are;

- To assess the viability of stabilization of heavy metals present in industrial sludge with concrete mix from environmental perspective.
- To assess the effect of the above option on the compressive strength of concrete.
- To assess the effect of the option on the workability and durability of the resultant concrete.
- To propose a stable concrete mix to be used for construction using sludge partially replacing the fine aggregates in the concrete mix.

1.3 Scope of the Study

The characterization of the industrial sludge is required for prescribing a stabilization technique as the sludge constituents play a vital role in both leaching and strength of concrete. For better evaluation, a large number of samples from different category of industries have to be analysed. In this study, sludge samples from the Textile and Dying industries from Dhaka Export Processing Zone (DEPZ) have been used. In case of replicability of the method for other industrial sludge, modification may be required.

The sludge samples considered were dry sludge. The study does not cover the stabilization of untreated semi-solid sludge or liquid industrial wastes. The heavy metals of concern for this study were Lead (Pb), Chromium (Cr), Mercury (Hg) and Cadmium (Cd).

The primary purpose of the study is stabilization. Hence, the concrete mix to be proposed is not aimed at large scale production for commercial purposes but for small scale development activities undertaken by the industries concerned as well for some public facilities that do not demand high strength. In addition, area for use of such concrete mix has been proposed considering only the leaching of heavy metals of concern for this study, not the potential risk of leaching of other pollutants that have not been monitored in this study.

1.4 Organization of the Thesis

The thesis consists of five chapters. Apart from this chapter, the remainder of the thesis has been divided into four chapters.

Chapter 2 includes literature review covering impacts of heavy metals, especially Lead, Cadmium, Chromium and Mercury. Brief description of the kinetics of leaching, the theoretical background of concrete based stabilization, reviews of different leaching tests, and the reviews of relevant literature regarding stabilization of heavy metals in sludge are also presented in this chapter.

Chapter 3 describes in detail the methodology adopted in the work. The sample collection, preservation and storage are discussed together with sample preparation and analysis. Preparation and Methodology adopted in casting concrete and analysis of its properties has been stated in detail. The preparation and methods of analysis of leachates from sludge and concrete have been described in this chapter.

Chapter 4 presents the analysis of the constituents of the sludge samples, heavy metals leachability of the sludge samples, the performance of concrete based stabilization in terms of leachate reduction, the analysis of the strength, workability and durability of sludge-mixed concrete at different sludge content and water-cement ratio.

Finally, Chapter 5 provides a summary of the findings and recommendations for further studies in this field.

CHAPTER 2
LITERATURE REVIEW

2.1 Environmental Impacts of Heavy Metals

The impacts of heavy metals on the environment are manifold. The impacts are either direct or indirect affecting various components of the environment, which are often interlinked. However, the impacts of heavy metals on the environment can be discussed by considering the impacts component wise separately as presented briefly in the subsequent sub-sections.

2.1.1 Soils and Crops

Heavy metals such as Zn, Cd, Cu, Pb, Ni and Cr are present in all soils but are usually found at low concentrations. Baseline concentration of the heavy metals is usually in the range from 0.1-200 mg/kg (Chilton and Kinniburgh, 2003). Higher concentration usually occurs in soils below or near landfills and in agricultural lands that have been irrigated with contaminated water and which has use of metal rich pesticides. The major activity in soil systems occurs in the upper 300 mm (12 inch) of the soil mantle. Heavy metals are removed by adsorption on soil particles. Adsorption of phosphates and heavy metals may occur at deeper levels as the capacity of the upper layer is exhausted. While no clear limit to the capacity is evident, the adsorptive capacity is thought to exceed the tolerance limit of plants. Hence, the first effect would be on the crop and not on the groundwater (McGhee, 1991).

The relationship between soil contamination and crop contamination is complicated and depends on many soil and plant factors. Chilton and Kinniburgh (2003) suggested some critical factors such as the ability of the soil to adsorb the heavy metals 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 metals such as Zn and Cu. Soil pH strongly affects the amount of adsorption. Adsorption of most trace metals is much lower under acidic conditions potentially resulting in greater plant uptake and greater toxicity. Most heavy metals are reported to be very strongly bound by natural organic matter and so tend to be at high concentrations where organic contents are high. Ashfaque (1999) while working with sediment of Dhanmondi Lake observed the same phenomenon.

Simmons (2002) suggested that the availability of the heavy metals (e.g. Cd, As, etc.) to the plants is dependent on the pH as well as the redox condition of the soil in the cultivated land, which affects the phytoavailability of the heavy metals. During flooding, the pH of the soil increases and the availability of Cd reduces as it is in the form of CdS adsorbed on the soil particle surfaces. However, during the dry season subsequent re-aeration increases the soil acidity and lowers the pH. Cadmium is transformed to Cd^{+2}, which is highly phytoavailable, and results in accumulation in food grains (e.g. rice grains).

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

Somashekar 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 study suggested that concentrations of heavy metals in crops have a positive correlation with the amount of metal present in soil while the rate of accumulation is dependent on the availability of the metals in soil to plants. The concentration of heavy metals in soil was found to be dependent on the effluent characteristics, i.e. whether acidic or alkali, and it was concluded that moderately acidic soil favours greater accumulation of metal ions

According to Chilton and Kinniburgh (2003), soils contaminated with heavy metals pose a threat in two ways: (i) directly through their toxic effect on the growth of crops thereby reducing crop yields, and (ii) indirectly by entering the animal and human food chain could adversely impact human health. Heavy metals may have deleterious effect on the microbial functioning of soils with long-term consequences. However, some metals (e.g. cadmium) can be taken up by crops in sufficient quantities to be of concern for human health before it has any noticeable impact on crop growth.

2.1.2 Aquatic Plants

The leachates from industrial wastes that reach the waters may induce changes in the physical condition of the receiving water. These include alterations in particle size and organic content of the substrate and pH of the water. Aquatic plants usually respond to such perturbations by a decrease in density, species composition, and diversity. But the effect of heavy metal contamination on aquatic plants is highly variable.

Cairns et al. (1972) suggested that characteristic responses such as decreased diversity and density of populations generally occur in highly contaminated areas. However, in moderately or lightly polluted areas the effect is much more inconsistent. Rushforth et al. (1981) observed that population response to heavy metals is significantly influenced by variations in natural environmental parameters, such as light and temperature. The response of different plant species to heavy metals contamination differ by wide margins. The presence of plants in potentially polluted waters may simply reflect adaptation to harsh environmental conditions. Based on these data, it was concluded that demonstrable impacts on the communities varied seasonally, no species could be designated as indicators of heavy metal contamination, and diversity indices were not reliable indicators of mildly contaminated sediments. Yan (1979) investigated the combined effects of heavy metals and low pH on the density and species composition of phytoplankton in several lakes contaminated with mine wastes. Although copper and nickel concentrations in water were relatively high, there was only a weak correlation between biomass and heavy metal levels.

2.1.3 Invertebrates

Heavy metals are accumulated in sediments through formation of organic complexes with the organic substances present in bottom sediments. Invertebrates are usually most likely to be affected by this high concentration of heavy metals as heavy metals may readily desorb from sediments into interstitial water, thus influencing invertebrate survival. But the invertebrates form a diverse group and it is often difficult to establish or predict a consistent response to heavy metals.

In case of unicellular invertebrates, lack of knowledge of their natural life and ecology combined with the ability of some species to adapt to heavy metal contamination, limit one's ability to distinguish natural variability from that induced by metals. Toxic effects of metals on multicellular invertebrates depend on a number of intrinsic factors such as age, size, sex, reproductive state, and nutritional status. These factors, combined with poor knowledge of natural life-history, limit the usefulness of population-oriented data. In addition, aquatic insects show marked differences in abundance and diversity due to emergence of adults (Slobodchikoff and Parrot, 1977; de March, 1976).

Moore (1979) investigated the effects of contaminated sediments on the density, diversity, and species composition of benthic invertebrates in part of Great Slave Lake. Although benthic invertebrate densities were inversely related with metal levels, there was no apparent effect on diversity or species composition. These data possibly implied that population estimates provided a good assessment of the impact of the waste disposal method. A similar conclusion was reached by Moorc ct al. (1979).

2.1.4 Fish

Fish species subject to 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 amounts in various parts of fish. Maximum copper concentration of 7.44 mg/kg was found in the stomach. Lead, cadmium and mercury contamination of fish is common (Friberg et al., 1974). The bottom feeding species are more likely to be affected by contamination due to the presence of heavy metals in bottom sediments of polluted water bodies in very high concentrations.

In order to assess the impact of the metals, long-term detailed investigations 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 effects of major industrial projects on aquatic environments.

Reduced growth and fecundity are often taken as a measure of the response of fish to metals. Even though such data are relatively easy to obtain, it may be difficult to distinguish the influence of reduced food supply from the toxic effects of heavy metals in impacted waters. For example, a possible scenario would be the elimination of invertebrates from contaminated sediments despite innocuous metal levels in the water. This situation might indicate to the unwary that metal pollution caused the reduction in growth and fecundity. Another complicating factor is the increase in acidification of water which often accompanies waste discharge. Once again fecundity and growth can be affected, either directly through pH stress or indirectly through reduction in food supply. The same can be said about the effects on fish of siltation and destruction of other components of the habitat.

Hagen and Langeland (1973) investigated the impacts of polluted snow on the water quality and organisms in Norwegian lakes. Elevated concentration of zinc and lead levels in lake water 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 effects of low pH and oxygen levels from those of metals.

2.2 Health Aspects of Heavy Metals

Heavy metals even at trace amount are usually toxic to humans. Some of the heavy metals are labeled as cumulative toxins due to their ability to cumulate. The cumulative toxins such as arsenic, cadmium, lead and mercury are particularly hazardous. These metals are concentrated by the food chain, thereby posing the greatest danger to organisms near the top of the chain (Peavy et al., 1985). The health aspects of the heavy metals of concern in this study (i.e. Pb, Cd, Cr and Hg) are briefly discussed below:

2.2.1 Lead

Many environmentally important lead compounds such as halides, sulfates, phosphates, and hydroxides are insoluble and thus are of relatively low toxicity in aquatic systems. By contrast, soluble lead compounds are intermediate between hard and soft acids in their 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 humans lead resembles calcium in deposition and transport, accounting for the high concentrations 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 to 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 mutagenic using the Ames *(Salmonella)* test. By contrast, inorganic lead compounds induce renal carcinoma in rats and mice. Similarly, primary hamster embryo cells treated with lead acetate underwent transformation (Dipaolo et al., 1978). When transformed cells were injected into hamsters, fibrosarcomas were produced.

2.2.2 Cadmium

There are few recorded instances of cadmium poisoning in humans following consumption of contaminated water, fish and grains. The most significant example of intoxication, Itai-itai disease, was diagnosed in residents of Toyama Prefecture (Japan) from the 1940's to the 1960's. Untreated metal mine wastes had been discharged into local rivers (Friberg et al., 1974). Potable water was heavily contaminated, and was also used to irrigate rice fields, which in turn became heavily contaminated. Patients suffering from Itai-itai disease showed signs of osteomalacia in bones and calcification and pyelonephritis in kidneys. This resulted in skeletal deformation and renal dysfunction. However, cadmium-induced kidney damage was not reported in any other sector of the population (Yosumura et al., 1980). Cadmium induced renal dysfunction in individuals dietarily exposed to cadmium is irreversible and progressive despite decreased exposure (Kido et al. 1988). Several studies have suggested that Cd- induced renal dysfunction interferes with Vitamin D metabolism, with consequential reduction in calcium absorption resulting in osteoporosis particularly in multiparous women (Kido et al., 1990; Simmons, 2002)

Because cadmium accumulates in organs and has a long half-life (10-30 years), the ingestion of small amounts of contaminated fish over long periods may lead to some form of cadmium intoxication. Consequently, regulatory standards restrict consumption of fish with residues of greater than 0.5 mg/kg wet weight.

2.2.3 Chromium

Chromium appears to be necessary for glucose and lipid metabolism and for utilization of amino acids in several systems. It also appears to be important in the prevention of mild diabetes and atherosclerosis in humans (Towill, 1978). The harmful effects of waterborne chromium in man are associated with hexavalent chromium; trivalent chromium, which is regarded as a form of chromium essential to man, is considered practically non-toxic and no local or systemic effects appear to have been reported. People living in areas of the world where atherosclerosis is mild or virtually absent tend to have higher chromium levels in tissues than people from areas where the disease is endemic (Schroeder, 1968).

Hexavalent chromium doses has been implicated as the cause of digestive tract cancers in man (Ministry of Supply and Services, 1979), and there is firm evidence that there is an increased risk of lung cancer for workers who are exposed to high levels of chromium (Ministry of Supply and Services, 1979 and Commission of the European Communities, 1979). Kaufman (1970) reported that hexavalent chromium at concentration greater than 10 mg/kg of body weight will result in liver necrosis, nephritis, and death in man while lower doses are likely to cause irritation of the gastrointestinal mucosa. Exposure to a mixture of chromium (VI) compounds of different solubilities (astound in the chromate production industry) carries the greatest risk for human beings.

2.2.4 Mercury

Organic mercury compounds may induce a toxicity which is commonly referred to as Minamata disease. Clinical signs of intoxication include ataxia, depressed peripheral sensation, and gait and limb reflex dysfunction (National Research Council of Canada, 1979). Sorbed methylmercury is transported by the blood stream, and accumulates in tissues such as liver, kidney, and brain. It can cause severe neurological damage to humans and wildlife. Furthermore, Hg can be transferred to human fetus during pregnancy and might interfere with the brain development of the embryo.

The whole body half-life of methylmercury is generally less than 70 days and may range from 35-189 days, depending on subject and method of analysis (Vaidehi et al., 1997). The Food and Drug Administration of US has established acceptable maximum concentration of methylmercury in fish as 1 mg/kg of wet wt (FDA, 1994).

2.3 Leaching from Industrial Sludge

Leaching is the process of release of contaminants from within the waste to the percolating water in soluble or suspended form (Peavy et al., 1985). Poon et al. (1985) defined leaching as the process by which a component of the waste is removed mechanically or chemically into solution from the solidified matrix by passage of a 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 contaminants is termed 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 has entered the landfill from external sources, such as surface drainage, rainfall, groundwater and water from springs (Peavy et al., 1985).

The leachability of a particular waste type depends on the physical and chemical properties of both the waste and the leachant as well as on the conditions of the ambient environment it is subjected to. The leachablity of inorganic or organic constituents from a waste differs for different disposal scenario (e.g. co-disposal in municipal landfill, mono disposal of mining waste, etc.) and type of leachant. The factors affecting the leaching of contaminants from waste may be contaminant specific and the magnitude and scale of their influence may differ widely (Batchelor, 1999; Rixey, 1999; Kimmel, 1999).

In case of organic constituents, the factors affecting the leaching potential are partitioning or solubility, presence of organic carbon which will impact the concentration of the organic, constituents in the aqueous phase, liquid-to-solid ratio and non-aqueous phase extraction (Murarka, 1999 and Rixey, 1999). Organic compounds are rarely available in the landfill as crystalline solids, partitioning is the predominant consideration over solubility (Murarka, 1999).

The common factors that affect the leaching potential of inorganic constituents at the disposal site include pH, redox conditions, liquid-to-solid ratio at the disposal site after degradation and solubility of the contaminants (Murarka, 1999). Batchelor (1999), however, suggested some additional factors that can play a role in leachability of a waste, such as presence or absence of surface area (e.g., particle size considerations), the presence or absence of ligands (e.g., citrate) within the waste and the leaching fluid and the presence of other metals in the leachant. It was also reported that while leaching the acids and bases within the wastes also leach into the leachant causing alteration of the pH of the waste. Among all the factors listed above, pH is the single most important one as it controls the leaching of many inorganic contaminants, as well as affecting the speciation of many metals (Murarka, 1999). In most solidified wastes, after pre-treatment prior to disposal, the contaminants are usually held physically in the solidified matrix and subject to leaching by percolating liquids (Hills et al., 1994).

In general, after disposal of the waste in landfills the organic portion of the waste readily undergoes aerobic decomposition. But in short span of time, after the entrapped air is exhausted, the anaerobic decomposition of the waste begins. This results in organic acid formation. The intermediate formation of organic acids can lead to toxicity problems because of either depression of the pH or the cations associated with the acids. Additionally, heavy metals may exhibit toxicity since they may be solubilized under the chemically reduced conditions which exist in anaerobic system (McGhee, 1991). Batchelor (1999) reported that at low pH condition, as in landfills, most heavy metals are likely to leach significantly by forming soluble forms through chemical reaction with the leachant, while at high pH leachability reduces as the metals are precipitated as metal hydroxides and adsorbed on the particle surfaces. However, for some metal hydroxides (e.g. lead), there are maxima in the concentration plots at both high and low pH values, with a minimum in the middle of the pH range. This behavior is due to the amphoteric nature of some metal hydroxides, and it can be predicted from first principles. The particle size is the controlling factor determining the extent of surface area available for leachant to interact to desorb the contaminants and bring those to solution. In case of very small size of waste particle, a possible way out may be higher particle size which can be achieved through solidification.

The leachability of the industrial sludge, when mismanaged by disposal in a landfill together with municipal solid having usually high concentration of carbonaceous organics, is likely to be high and poses great danger by contaminating the groundwater aquifers (Kimmel, 1999). The assessment of the leachabilty of hazardous constituents like heavy metals in industrial sludge subject to such adverse situation is essential for regulatory purposes. However, there are well documented leaching test procedures (e.g. TCLP, SPLP, etc.) that can effectively mimic site conditions as well as characterize the waste in terms of the leaching potential of the contaminants.

2.4 Cement Based Stabilization of Industrial Sludge

Traditional waste water treatment facilities usually cause precipitation and aims to concentrate the pollutants in sludge. The sludge produced at the end of treatment usually has high concentration of toxic substances requiring treatment. Many toxic materials and heavy metals have been found to be concentrated in sludge and such contaminants may severely restrict the disposal options open to the community. It is therefore preferable to exclude such contaminants through pre-treatment of industrial sludge (McGhee, 1991). The only option is to stabilize the sludge prior to disposal to reduce the availability of the contaminants to the environment. For the wastes to be of any use, some form of solidification should accompany stabilization.

Stabilization is defined as a process where additives are mixed to minimize the rate of contaminant migration from the waste and to reduce the toxicity of the waste. Thus, stabilization can be described as a process by which contaminants are fully or partially bound by addition of supporting media, binders or other modifiers. Likewise solidification is a process employing additives by which the physical nature of the waste, measured by the engineering properties of strength, compressibility and/or permeability, is altered during the process. Thus objectives of stabilization and solidification would encompass both the reduction in waste toxicity and mobility as well as an improvement in the engineering properties of the stabilized material (La Grega et al., 1994). McGhee (1991) defined stabilization as the process through which the nuisance potential of the waste is reduced or eliminated, and defined solidification as the process in which the liquid portion of the waste is reduced substantially and the solid portion compacted to provide a stable solid matrix. In case of industrial solid and semi-solid sludge, the term stabilization implies the reduction of leachability of the contaminants (e.g., heavy metals) within the sludge prior to disposal.

Chemical stabilization and physical encapsulation are the two controlling factors in reducing metal mobility in the stabilized/solidified waste forms (Hills et al., 1992). At elevated pH most metals are reported to form metal hydroxides of low solubility (Batchelor, 1999). The concrete based stabilization of sludge is based on this principle.

Within the concrete calcium hydroxide is produced as a byproduct of cement hydration. This calcium hydroxide raises the pH within the concrete provides the majority of acid neutralizing capacity in the cement paste (Poon et al., 1985). The alkaline environment causes formation of insoluble metal hydroxides. The metal hydroxides are then precipitated and adsorbed on the surfaces of the cement-aggregate matrix (Hills et al., 1992). However, the amphoteric nature of some metal hydroxides may present difficulties at high pH existing during stabilization process.

The use and effectiveness of calcium hydroxide as a stabilization agent in lime based stabilization of industrial liquid and semi-solid sludge is reported in the literature (McGhee, 1991). The primary goal of lime based stabilization is to raise the pH of the waste so that the precipitation of the heavy metals as metal hydroxides and subsequent adsorption on the surfaces takes place. The prescribed pH of the waste at the beginning of stabilization is above 12 and the pH of the stabilized waste is required to be maintained above 11 all the time prior to disposal (McGhee, 1991). However, the lime based stabilization fails to provide physical stability of stabilized materials which is essential if it is to be used for other purposes. In contrast concrete based stabilization offers both chemical stabilization and physical encapsulation (Hills et al., 1992).

2.5 An Overview of Existing Leaching Tests

Leaching tests are designed to determine the leachability of a waste type subject to a particular idealized disposal scenario. Leaching tests have been developed and still developing in different countries. Hartwell (1999) noted that batteries of leaching tests have been proposed or promulgated not only by the US, but by France, the Netherlands, Germany, Sweden, Denmark, the European Union and Canada. Both the government and private sector have developed and incorporated leaching methods into their programs. Within the US, standardized leaching protocols have been published by a number of concerned authorities like the 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 concepts and assumptions. Tests have been developed to account for the variability in the ratio of volume of leachant to solid waste (i.e. liquid/solid ratio), chemical composition of the leaching fluid, testing of monolithic and granular wastes, as well as stabilized and solidified wastes (Hartwell, 1999 and Batchelor, 1999).

Leaching test methods can be divided into two general categories: static extraction tests and dynamic extraction tests. In static extraction protocols, leaching takes place with a single, specified volume of leaching fluid. In dynamic extraction protocols, the leaching fluid is renewed throughout the test.

2.5.1 Static extraction tests

In static extraction protocols, a specific amount of leaching fluid is placed in contact with a specific amount of waste for a specified length of time, with no replacement of or addition to, the leaching fluid. The leachate from the test is removed at specified times, usually the end of the test, for analysis. Static extraction protocols assume that a steady state condition is achieved by the end of the test. Types of static extraction tests include agitated and non-agitated extraction tests, sequential chemical extraction tests, and concentration buildup tests.

In agitated extraction tests, the waste and leachant are co-mingled and agitated, so the test reaches steady-state conditions as quickly as possible. Test protocols frequently incorporate particle size reduction steps to increase the amount of surface area available for contact, thereby reducing the amount of time required to reach a steady state condition. Agitated extraction tests measure the chemical properties of a waste/leachant system rather than the physical, rate-limiting mechanisms. Hence, this type of test may over-estimate the short-term release of constituents. Examples of agitated extraction tests include the TCLP (EPA method 1311), EP Tox, California's WET, and the SPLP (USEPA, 1992a and Hartwell, 1999). This type of tests are suitable for risk assessment programme and consequently aid in setting regulatory standards for different waste management scenario (Hartwell, 1999 and Murarka, 1999).

Non-agitated extraction tests measure the physical, rate-limiting mechanisms, rather than the chemical properties of a waste/leachant system. This type of test is based on the assumption that the physical integrity of the waste matrix affects how much material can be leached out of the matrix. Examples of non-agitated extraction tests include the Strategic Leach test and High Temperature Static Leach test. (Hartwell, 1999 and Murarka, 1999)

A sequential chemical extraction test is a series of agitated extraction tests, using increasingly aggressive leaching fluids. The hypothesis is that increasing chemical aggressiveness will result in increasing amounts of extracted contaminants. An example of a sequential chemical extraction test is ASTM's Sequential Batch Extraction of Wastes with Acidic Extraction Fluid (Hartwell, 1999).

Concentration build-up tests call for aliquots of the waste to be contacted repeatedly with the same leachate, at a very low liquid to solid ratio. This type of test models a volume of fluid flowing through a body of waste, with the concentration of extracted contaminants building up in the leachate as it progress through the system. An example of concentration build-up test is Wisconsin's Standard Leach Test (Hartwell, 1999).

2.5.2 Dynamic extraction tests

In dynamic extraction protocols, the leaching fluid is renewed, either continuously or intermittently, for driving the leaching process. Because the physical integrity of the waste is usually maintained during the test, and the information is generated as a function of time, dynamic extraction tests provide information about the kinetics of contaminant mobilization. In general, dynamic extraction tests can be categorized as: serial batch tests, flow-around tests, flow-through tests, and Soxhlet tests.

In a serial batch test, a portion of a crushed, granular sample is mixed with leachant and agitated for a specified time period. At the end of the time period, the leachate is separated, fresh leachant added, and the process repeated until the desired number of leaching periods has been completed. Examples include the Multiple Extraction Procedure: EPA method 1320 (USEPA, 1992a), the US Army's Graded Serial Batch test (Hartwell, 1999).

Flow-around tests are used for either monolithic samples, or samples that are somehow contained and the leachant flows around the sample. Examples of flow around tests include the ISO Leach Test 6961, ANSI 16-1, the Monolithic Diffusion test from the Netherlands, and ASTM's Static Leaching of Monolithic Waste Forms for disposal of Radioactive Wastes (Hartwell, 1999; Murarka, 1999).

Flow-through tests are applicable to porous samples, rather than monolithic and can be set up to mimic site-specific conditions. Examples include Canada's Waste Interface Leach test, NVN 7344 Column Test, and ASTM's Column Test (Hartwell, 1999).

In Soxhlet tests, a Soxhlet extractor is employed and the leachant is continuously renewed with "recycled" leachant from which previously extracted contaminants have been removed. However, it is limited to relatively low boiling solvents as leachants, and hence, not suitable for use with volatile contaminants. Canada's Soxhlet Test (MCC-5s) is a good example of this type of test (Hartwell, 1999).

2.5.3 The concepts and applicability of TCLP

The Toxicity Characteristic Leaching Procedure or TCLP is a standard leaching test of USEPA, EPA SW-846 method 1311 (USEPA, 1992a). This is a mandatory test in the US for analyzing the leaching potential of industrial waste prior to disposal. The test was developed as part of a set of second generation of leaching tests replacing the old Extraction Procedure (EP) at EPA, in response to the 1984 Hazardous and

Solid Waste Amendments (HSWA). The primary objective was to accurately predict leaching potential of wastes when mismanaged. The TCLP was developed to cover a wide range of contaminants, including hazardous organics, which were not adequately addressed in past procedures like EP (Kimmel, 1999).

The Resource Conservation and Recovery Act (RCRA) directed EPA to establish characteristics that identify wastes that pose a threat when improperly managed. One of the characteristics established was the Toxicity Characteristic (TC), which was developed to identify those wastes which might result in contamination of ground water if improperly managed. Among several mismanagement scenarios, co-disposal in a municipal waste landfill was chosen as the single scenario to be applied to all wastes. This scenario was believed to be the most appropriate reasonable worst case (Kimmel, 1999). The TCLP was intended to be a laboratory test designed to simulate leaching in a municipal landfill (Murarka, 1999; Kimmel, 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 conditions than column leaching tests. The leaching fluid used was to be designed to simulate the result of rainwater infiltrating the landfill, reacting with the municipal solid waste, and then leaching through the waste being tested. For this 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 characteristic (TC) were derived using the same scenario and were set at levels that would prevent the groundwater contamination from reaching levels that poses potential environmental and health effects. A fraction of the table of TC regulatory standards covering major heavy metals is provided in Table 2.1. A fraction of the Land Disposal Restrictions (LDR) 'Universal Treatment Standards' of USEPA for non-wastewaters (e.g., sludge) is presented in Table 2.2.

There has been considerable debate on the suitability of the method for all types of waste and waste disposal scenario. However, no other leaching test has been reported so far to have coverage for such wide variety wastes as TCLP. The method is simple, easy, well documented and reproducible (Rahmat, 2001). The toxicity characteristic (TC) regulatory levels of TCLP are explicit and easy for regulatory interpretation. The method is equally applicable to wastes having monolithic structure and wastes with smaller particle size making it suitable for assessing the leachability of solidified stabilized waste as well as raw untreated waste. So, TCLP can be used to evaluate the stabilization performance of different treatment options.

However, the TCLP is not designed to address specific monodisposal scenario like disposal of mineral mining wastes. In such case, the appropriate method would be EPA method 1312: Synthetic Precipitation Leaching Procedure (SPLP), which offers slightly more flexibility than TCLP (Batchelor, 1999; USEPA, 1992a).

Table 2.1. Toxicity Characteristic regulatory standards set forth by the United States Environmental Protection Agency.

Heavy Metal	Concentration in TCLP leachate (mg/L)
Lead (Pb)	5.0
Chromium (Cr)	5.0
Cadmium (Cd)	1.0
Mercury (Hg)	0.2

†Source: 40 CFR, Part 261.31 (USEPA, 1992b)

Table 2.2. Land Disposal Restrictions–Universal Treatment Standards set forth by the United States Environmental Protection Agency.

Heavy Metal	Concentration in TCLP leachate (mg/L)
Lead (Pb)	0.75
Chromium (Cr)	0.60
Cadmium (Cd)	0.11
Mercury (Hg)	0.20

†Source: 40 CFR, Part 268.48 (USEPA, 1997)

2.6 Some Past and Current Research on Stabilization with Cement

The stabilization of industrial sludge through solidification with concrete has been practiced in some other countries for well over a decade.

Poon et al. (1985) studied the mechanisms of metal stabilization by cement based fixation processes. The study aimed at the chemical aspects of stabilization from mostly environmental perspective. However, the structural integrity of the stabilized wastes did not receive much attention.

Tay and Show (1991) focused mostly on the engineering properties of the cement made from sludge. The study suggested that virtually any form of sludge or waste can be used for making cement and aggregates if the cost and energy requirements can be complied 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 sludge. Hills et al. (1994) observed reduced leaching from cyanide rich wastes after solidification with cement. The mechanical properties of the resultant 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 heavy metals was successful. Marked decrease in the strength was observed with increase in sludge content. However, testing for changes in durability of concrete with increase in sludge was not included.

CHAPTER 3
METHODOLOGY

3.1 Introduction

The methodologies adopted in the study can be divided into definite steps which included selection of industries for sludge collection, selection of sampling locations, sample collection and preservation schemes, procedures for analysis of the sludge samples for pre-selected physical and chemical parameters, procedures for digestion of sludge to determine total concentration of heavy metals, methodology for casting concrete with sludge, test procedures for testing properties of sludge-mixed concrete to assess the usability of such concrete and procedures for analysis of leaching of raw and stabilized sludge to assess the performance stabilization. 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 Selection of Industries

To ensure that the sludge has significant amount of heavy metals of interest certain industries were targeted. The textile-dyeing industries and leather industries are the major industries in our country and industries of both categories have use of substances containing significant amount of heavy metals as evident from current literature. However, leather processing industries cover only a fraction of heavy metals of interest whilst the textile-dyeing industries employ a wide range of toxic heavy metals in all phases of production. The textile industries are more likely to cover the targeted heavy metals as per current literature (Shenai, 1997, 1979; Srivastva, 1979; Tchobanoglous et al., 1993). Moreover, very few leather industries possess effluent treatment plants and hence generation of dry solid or semi-solid sludge, which is of concern for this study, is limited. So, sludge samples from textile-dyeing industries were considered for the present study.

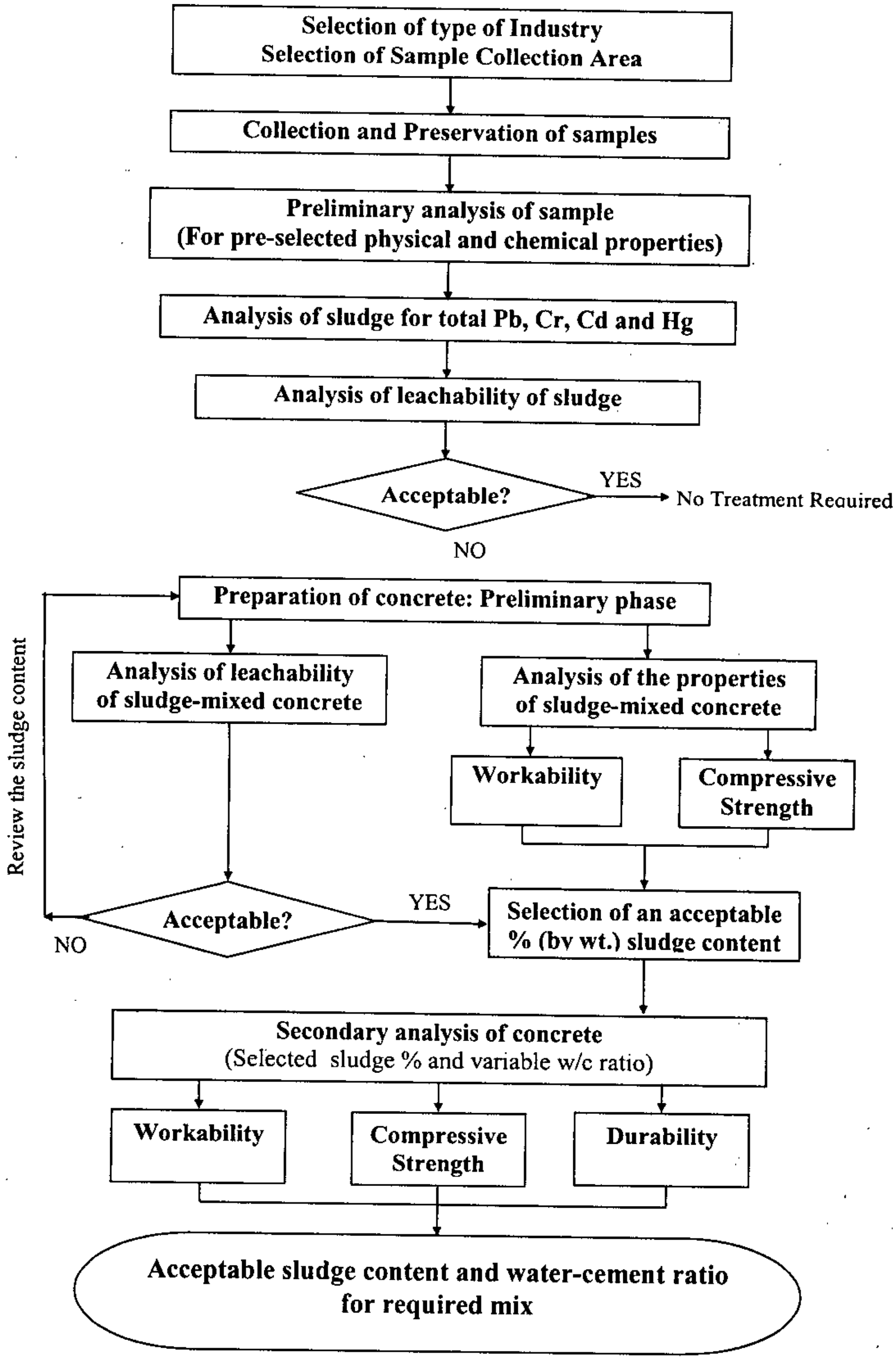

Figure 3.1. Flowchart of the activities performed in the study.

3.3 Sampling Locations

Collection of sludge sample from industries is often very difficult task due to the unwillingness of the industries to handover the sludge to external personnel. However, collection of sludge samples from the point of generation (i.e. end point of the treatment plant of the industry) is essential to label the sludge as authentic and to ensure that it had not undergone significant changes after generation. The Dhaka Export Processing Zone (DEPZ) was selected as the location to collect sludge samples as the industries there are more likely to have functioning effluent treatment plants and consequently having regular generation and disposal of sludge.

3.4 Sample Collection

With the assistance of the EPZ authorities sludge samples from two industries, one knitwear industry and one dyeing industry, were collected with prior approval of the management. Both the industries had functional treatment plants and a fixed sludge disposal system in operation. The sludge samples were collected at the point of generation. Both the industries asked to remain anonymous throughout this study. Thus the samples were labeled S-A and S-B, respectively.

3.5 Sample Preservation and Storage

Plastic containers were selected for storing sludge samples because of low possibility of reaction with the sludge compared to glass containers. The containers were sealed to prohibit loss of moisture. The digested sludge samples were preserved in disposable small plastic bottles and kept in cool dry place before analyses. The leachate samples were also preserved in plastic bottles. The preservation periods prior to analysis did not exceed the recommended maximum preservation periods as outlined in the relevant methods of preparation.

3.6 Preliminary Analyses of Sludge Properties

The sludge samples were analyzed for pre-selected physical and chemical parameters which are likely to influence the leaching characteristics of the sludge in the open environment and/or influence the workability, strength and durability of the resultant sludge-mixed concrete as indicated in the literature. The properties analyzed include pH, alkalinity, organic content and certain anions, namely, chloride, sulfate, sulfide, silica, nitrate, etc. The methodologies applied for analyzing sludge were the same as the standard methodologies applicable for soils and sediments (USEPA, 1992a; Alam et al., 1991). Analyses of the anions were done on the standard extract from sludge (Alam et al., 1991). Apart from chloride, all others were performed with HACH DR/2010 spectrophotometer and the results were verified with HACH DR/4000U spectrophotometer and NIST standards. The concentrations of the constituents were expressed in mg/kg of sludge. The methods are briefly stated below:

pH: The pH of the sludge samples were analyzed following standard procedure adopted for soils and sediments (Alam et al., 1991; FPCO, 1995). The analysis was done with platinum electrode pH meter, HACH Senssion1, with 1: 2.5 (W:V) soil-water suspension. About 20 gram sludge sample was mixed with 50 mL distilled water and stirred thoroughly for 30 minutes and then allowed to settle for a few minutes. The supernatant liquid was used for analyzing the pH of the sludge.

Alkalinity: The pH of the sludge samples were analyzed following standard procedure adopted for soils and sediments (Alam et al., 1991; FPCO, 1995). Sludge and water was mixed 1: 2.5 (W:V) 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 50mL of the extract was then titrated with (0.02N) 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 of 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 overnight at 100°C (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°C ~ 450°C 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.

$$\% \text{ Organic Content} = (W_1 - W_2) \times 100 / W_1 \qquad (3.1)$$

Chloride: Sludge and water were mixed at 1: 5 (W:V) ratio. The mixture was stirred vigorously with a magnetic stirrer for 30 minutes. It was allowed to settle for an hour. 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 to 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 HACH DR/2010 spectrophotometer through *SulfaVer 4 Method* (Range: 0 ~ 70.0 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, stirred vigorously for 30 minutes and then the slurry was allowed to settle for an hour. The supernatant liquid was filtered through filter paper. The extract was then analyzed with spectrophotometer through *Silicomolybdate Method* (High range: 0 ~ 100.0 mg/L).

Sulfide: Sludge and water were mixed at 1: 5 (W:V) ratio, stirred vigorously for 30 minutes and then the slurry was allowed to settle for an hour. 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 is 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 allowed to settle for an hour. The supernatant liquid was then filtered through filter paper. The extract was then analyzed with HACH DR/2010 spectrophotometer through *Cadmium Reduction Method* (High range: 0 ~ 30.0 mg/L NO_3-N).

3.7 Analysis of Total Heavy Metal Content of Sludge

The digestion techniques adopted for extracting total metal for chromium, cadmium and lead were the same whereas a different digestion technique was followed for digestion of sludge samples for mercury. The digested samples were later analyzed with Atomic Absorption Spectrophotometer using flame emission technique. The Atomic Absorption Spectrophotometer for the purpose was Shimadzu AA-6800.

3.7.1 Extraction methods for chromium, cadmium and lead

For digestion of sludge samples the USEPA prescribed method, EPA *3050B*, for sediment, sludge and soils (USEPA, 1992a), which is popularly termed as 'acid-peroxide digestion', has been adopted. As the digestion of sludge and soils has been traditionally done with aqua-regia technique, a separate set of digested sludge samples were prepared using the technique for comparison. Both the methods are briefly described in the Appendix A.

3.7.2 Extraction method for mercury

The USEPA Method 7471 (USEPA, 1992a) is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom sediments and sludge-type materials. This technique has been adopted for this study for digestion of raw sludge samples. The method is briefly described in the Appendix A.

3.8 Preparation of Concrete with Sludge

The sludge samples were air dried and powdered. The mix proportion selected for the study was 1: 1.5 : 3 (cement: sand: coarse aggregate) in weight basis. The sand selected for the mix was medium sand having fineness modulus (FM) of 2.70 and having specific gravity of 2.65. The coarse aggregate used was crushed stone aggregates of 19 mm (0.75 inch) size having specific gravity of 2.74 and dry-rodded density of 1580 kg/m^3. Ordinary Portland cement having specific gravity 3.15 was used for the mix.

The sludge was to replace the fine aggregate (i.e. sand) by equal weight as certain percentage of cement in the mix. As the sludge samples were much lighter compared to the sand used for the study, there some change in the volume composition is expected with the introduction of sludge in mix. To minimize the effect the finer portion of the sand was replaced by sludge of equal weight.

It was decided to cast concrete in two phases. In the first phase the concrete was cast to assess the reduction in strength and change in workability with increase in sludge content. Bosunia and Choudhury (2001) evaluated the current concrete practices in Bangladesh, and recommended a water-cement ratio of not more than 0.45 for producing dense impermeable concrete. Moreover, trial mixes done prior to casting, resulted in too high slump values at water-cement ratio above 0.45. Hence, the water-cement ratio was kept at the recommended maximum 0.45 for all the batches. The sludge content was varied from 3 to 10% by weight of cement in the mix for both the sludge S-A and S-B. A sludge free batch of concrete was cast for comparison.

From the preliminary assessment of changes in strength and workability in the first phase, a range of sludge content was selected for further analysis. In the second phase two different water-cement ratio, 0.40 and 0.45, were used to see the influence of water-cement ratio. A sludge-free batch of concrete was cast for each water-cement ratio for comparison. The durability of resultant concrete was analyzed along with strength and workability for different sludge content and water-cement ratio.

3.9 Testing of Concrete

The tests of concrete included standard tests for compressive strength and workability and tests of durability.

3.9.1 Test for workability

The workability is an essential property of any concrete mix to be used conveniently during construction. There have been a wide range of tests formulated so far for measurement of the workability of a concrete mix. Unfortunately, there is no single acceptable test which will directly measure the workability of a mix (Neville, 1996). The slump test, defined in ASTM C 143-90a and BS 1881: Part 102: 1983, was chosen as a measure of workability of a mix as it is the prescribed test for measuring workability in most of the guidelines in different countries including Bangladesh. This test was performed for each batch of concrete. The slump was measured and recorded, just before casting, to the nearest one-fourth of an inch in line with ASTM C 143-90a.

3.9.2 Test for compressive strength

The compressive strength of concrete is the major property of concern in design with concrete. The compressive strength test was performed following guidelines of ASTM C 192-90a on standard cylinders (as defined in the method) to measure the 7 day and 28 day cylinder compressive strengths of concrete. The test was performed for each batch including fresh (i.e. sludge-free) concrete and recorded to the nearest 50 psi. The equipment used for the purpose was Universal Testing Machine (UTM).

3.9.3 Test for durability of concrete

Durability of sludge mixed concrete is of concern together with strength and workability. Introducing alien materials can sometime significantly affect the durability of the concrete. Concrete having acceptable strength can become undesirable if it is not durable against severe weathering conditions. Hence, a test of durability is essential. Among the various aspects, durability of concrete against sulfate is the most crucial one. However, there is no standard test in ASTM or other guidelines which is readily applicable for concrete. For the present case, durability of concrete to sulfate condition was analyzed by observing volume changes (expansion or swelling) occurring over time and also by observing the reduction in strength of concrete after prolonged exposure to sulfate environment.

Cylinders were immersed in 1% and 2.5% sulfate solutions after hardening and expansion in volume was measured regularly through changes in the dimensions. The volume changes of sludge-free concrete and sludge-mixed concrete at different water-cement ratio is compared. The formula for calculating expansion in volume is given in Eq. 3.2.

$$\% \Delta V = \frac{V_{Final} - V_{Initial}}{V_{Initial}} \times 100 \qquad (3.2)$$

Where,

$\% \Delta V$ = Change in volume of concrete (percentage of $V_{Initial}$),

V_{Final} = Volume of concrete at the end of exposure period, and

$V_{Initial}$ = Volume prior to immersion in sulfate solutions.

The compressive strength test was performed on cylinders immersed in sulfate solutions and cylinders cured under sulfate free environment after a specified period of curing (140 days) and the reduction in average strength due to sulfate exposure was calculated for every batch of concrete. The reduction in strength was expressed in percentage of average strength of concrete cured in sulfate free water. The percentage reduction in strength at different water-cement ratio and sulfate exposure was compared for every batch. The formula for calculating reduction in compressive strength is given in Eq. 3.3.

$$\%\Delta f_c' = \frac{f_{c(\mathrm{SE})}' - f_{c(\mathrm{SF})}'}{f_{c(\mathrm{SF})}'} \times 100 \qquad (3.3)$$

Where,

$\%\Delta f_c'$ = % reduction in compressive strength in concrete exposed to sulfate,

$f_{c(\mathrm{SE})}'$ = Compressive strength of concrete at the end of exposure period, and

$f_{c(\mathrm{SF})}'$ = Compressive strength of concrete at sulfate-free environment.

3.10 Test for Leaching Potential of Sludge and Concrete

The test for leaching from sludge is essential to assess the initial condition of sludge prior to stabilization. The test for leaching from sludge-mixed concrete is required to assess the performance of the stabilization through comparison with the initial leaching potential of the sludge. To test the leaching potential of the sludge and concrete the USEPA method, EPA 1311, popularly known as toxicity characteristic leaching procedure or TCLP was selected. Moreover, a slightly modified leaching procedure formulated in line with the TCLP procedure but using different extraction fluid than TCLP was also applied on the samples to compare the leachability of samples under this procedure to standard TCLP. The method is termed 'Modified Leaching Test'. The fresh or sludge-free concrete had also undergone leaching procedures as it acts as a control for comparing the leachates from other batches. The leachates produced through the above procedures were analyzed for heavy metal concentrations with Shimadzu AA-6800 by flame emission Atomic Absorption Spectrophotometry (Sec. 3.13).

3.10.1 Toxicity characteristic leaching procedure

The Toxicity Characteristic 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 infiltrating the landfill, reacting with the municipal solid waste, and then leaching through the waste being tested (EPA, 2002). So 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). The test is essential US for meeting land disposal restrictions

The procedure may be summarized in the following steps:

1) *Initial evaluation of the sample*

   a. Determination of percent solids in the waste. If the percent solid exceeds 0.5% separation of solid and liquid phase is necessary for separate analyses. The liquid phase is filtered through a 0.6 to 0.8 μm glass fiber filter and considered the extract. The solid phase undergoes extraction.
   b. Reduction of particle size (if necessary) to meet the maximum size limit set for TCLP. The waste particles for TCLP should not exceed 1 cm.
   c. Evaluation of the total metal concentration within the waste is performed to assess whether the waste is likely to leach significantly or whether the regulatory limits can be exceeded. The USEPA recommended formula (EPA, 2002) for assessing maximum theoretical concentration in TCLP leachate from waste is illustrated in (Eq. 3.4).

$$\frac{(A \times B) + (C \times D)}{B + [20(L/kg) \times D]} = \mathrm{E} \qquad (3.4)$$

Where,

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

In this study TCLP was performed on both the sludge and crushed concrete samples and the samples consisted of 100% solid as per TCLP. The only extract of concern was the extract from the solid phase. Particle size reduction had to be performed for both raw sludge and crushed concrete samples.

2) Determination of the appropriate extraction fluid

The next step is 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 a pH of 4.93±0.05 and extraction fluid II (EF-II) is specified to have a pH of 2.88±0.05. The extraction fluid employed is a function of the alkalinity of the 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:

a. 5.0 gram of sample having particle size <1 mm (reduced) is taken and mixed thoroughly with 96.5 mL of de-ionized (DI) water and stirred vigorously for 5 minutes with a magnetic stirrer and allowed to settle. The pH is then measured and recorded.
b. If pH < 5.0, extraction fluid-I (EF-I) is selected immediately and step 3 is followed.
c. 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 50°C and kept at 50°C for 10 minutes. The sample is then allowed to cool and pH is measured.
d. 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

a. 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 the solid phase and sealed.

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

For the present study the extraction vessels permit 25.0 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 μm glass fiber filter with pressure not exceeding 50 psi. The pH of the extract is maintained at less than 2.0 for metal analyses.

A more elaborate description of the procedure can be found in EPA method 1311 (USEPA, 1992a). Badruzzaman (2003) has a detail description of the TCLP system employed in this study.

3.10.2 Modified leaching test

All the steps for this test apart from the selection of the appropriate extraction fluid are essentially the same as TCLP (Sec. 3.10.1). Here, rainwater is chosen as the extraction fluid instead of going through with the lengthy process of pH evaluation. As it is intended that, if successful, the sludge stabilized concrete will be used in constructing road pavements or for open air construction, it is likely to be exposed to prolonged rain throughout the design life. Thus, leaching under a natural condition may provide a different result. The test was designed to address this issue.

3.11 Preparation and Storage of Standard Metal Solution

Standard metal solutions of different metals (Cr, Cd and Pb) 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 HNO_3 per litre was used. For mercury (Hg) standard metal solutions were prepared on the day of testing using the procedure as described in EPA Method 7471A (Appendix A).

3.12 Beer – Lambert's Law

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

$$A = \varepsilon c l \tag{3.5}$$

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 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.

3.13 Atomic Absorption Spectrometry (AAS)

In this method, a light beam of appropriate wavelength for a 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 visible and ultraviolet radiation (*i.e* Beer-Lambert's law, Eq. 3.5). 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 4
RESULTS AND DISCUSSION

4.1 Introduction

The analysis section of this study begins with the analysis of sludge samples for pre-selected sludge constituents and their possible influence on the properties of sludge-mixed concrete. The subsequent sections include the analysis of total heavy metal content in sludge samples, assessing the leachability of the sludge samples and evaluation of the performance of concrete based stabilization through analysis of the leachate results, and analyzing the concrete properties for selecting a proper mix design. The analysis of properties of sludge-mixed concrete can be separated in two phases. The preliminary analysis involved relatively wide range of sludge content. The secondary analysis a narrow range of sludge content selected from the preliminary stage but focused on selecting a stable mix proportion from in depth analysis of sludge-mixed concrete.

4.2 Results of Preliminary Analysis for Sludge Constituents

The sludge samples S-A and S-B were analyzed for determining sludge characteristics in terms of their physical properties and chemical constituents. The parameters analyzed included pH, alkalinity, percent organic, sulfate, sulfide, nitrate, chloride and silica. The parameters analyzed are reported to have bearing on strength and durability of concrete as well as on the leaching potential of sludge. The test results are presented in Table 4.1.

The pH results indicate that the sludge S-A is slightly alkaline while S-B slightly acidic in nature. The alkalinity of the both the sludge was low. The observed concentrations of chloride and sulfide were low in both the sludge. Concentration of nitrate and silica in both the sludge can be termed moderate. However, the concentration of sulfate was very high in both the sludge samples. Among the anions sulfate has the most significant impact on durability of concrete. High concentration of sulfate in sludge is likely to influence the durability of the sludge-mixed concrete.

The percent organics in two sludge samples differed significantly. The sample S-A is observed to possess moderate concentration of organic carbon ($\approx$8%) whereas S-B seemed very rich ($\approx$70%) in organic carbon. The presence of organic substances in the mix is likely to reduce the strength of concrete. Hence, difference of strength is expected for the same sludge content in the mix in case of organic-rich sludge S-B and sludge S-A

Table 4.1. Results of preliminary analysis of sludge

Parameters	Units	Sludge A (S-A)	Sludge B (S-B)
pH*	-	7.82 (±0.00, n=3)	6.25 (±0.02, n=3)
Alkalinity (as $CaCO_3$)	mg/kg	106.67 (±2.36, n=3)	93.33 (±2.36, n=3)
Organic Content (%)	-	7.85 (±0.15, n=3)	69.30 (±0.76, n=3)
Chloride	mg/kg	121.67 (±2.36, n=3)	109 (±0.94, n=3)
Sulfate	mg/kg	6750 (±40.82, n=3)	4590 (±9.43, n=3)
Sulfide	mg/kg	0.21 (±0.01, n=3)	0.54 (±0.00, n=3)
Nitrate	mg/kg	162.47 (±2.32, n=3)	298.33 (±3.77, n=3)
Silica	mg/kg	207.33 (±0.94, n=3)	177.33 (±0.94, n=3)

*Note: n stands for number of samples; * pH is dimensionless quantity.*

4.3 Analysis of Total Heavy Metal Content in Sludge

The sludge samples were digested for analysis of total metal content with AAS. The digestion techniques adopted were acid-peroxide digestion and aqua-regia digestion (Sec. 3.6). There were six samples from each sludge type for a particular digestion procedure. The acid-peroxide digested samples showed higher extraction compared to aqua-regia digestion in all the samples digested. Hence, the results based on acid-peroxide digested samples were accepted. The results of concentration of total Pb, Cr, Cd and Hg for both S-A and S-B are listed in Table 4.2. The average concentration of total Pb, Cr and Cd are graphically presented in Fig.4.1.

Table 4.2. Concentrations of total Pb, Cr, Cd and Hg in mg/kg of sludge for sludge S-A and S-B.

Heavy Metal	**Concentration (mg/kg)**	
	Sludge A (S-A)	**Sludge B (S-B)**
Lead (Pb)	105 (±3.0, n=6)	107 (±1.8, n=6)
Chromium (Cr)	322 (± 22.7, n=6)	390 (±3.0, n=6)
Cadmium (Cd)	9.5 (±0.9, n=6)	12.8 (±0.8, n=6)
Mercury (Hg)	Not detected	Not detected

Note: n stands for number of samples.

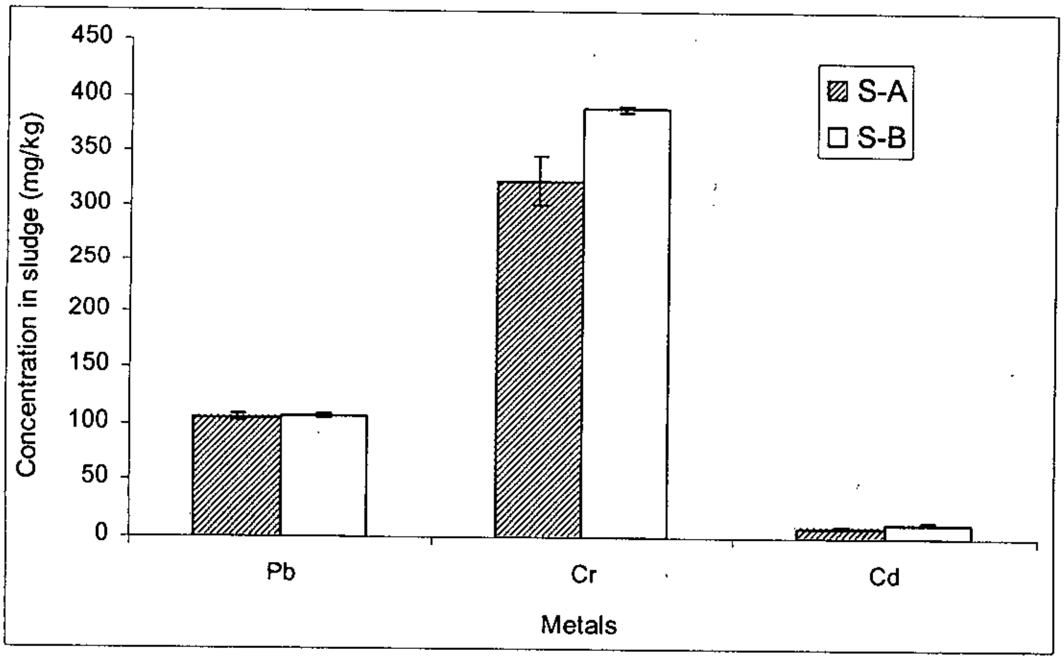

Figure 4.1. Concentrations of total Pb, Cr and Cd in mg/kg of sludge for sludge S-A and S-B.

The average total metal concentration of Pb and Cr was very high in both S-A and S-B. They had high potential for significant leaching of Pb and Cr. The concentration of Cd was moderate. The theoretical maximum possible concentration of the heavy metals in TCLP leachates were calculated from the total metal concentration results with the USEPA prescribed formula (Eq. 3.4). The results indicated that, in case of 100% leachate, there is possibility of exceeding the USEPA toxicity regulatory limits for Pb and Cr (Table 2.1). The concentrations of Pb, Cr and Cd in 100% leachate would exceed the USEPA land disposal regulatory limits (Table 2.2).

However, to analyze the performance of stabilization after solidification with concrete, the concentration of all the metals of concern in leachates from raw sludge is essential. These would act as baseline information regarding the leachability of the sludge prior to stabilization. So, the TCLP leachates from raw sludge samples were analyzed to determine concentrations of Pb, Cr and Cd.

4.4 Analysis of Leachate Results

The standard TCLP (USEPA method 1311) and modified leaching test, which employs rainwater as leaching fluid in place of the TCLP prescribed leaching fluids, were performed on raw sludge samples and on crushed concrete samples from every batch of concrete. There were six standard TCLP leachate samples from each batch of sludge-mixed concrete. In case of modified leaching the number of leachate samples were three from the same batches. The leaching test was also performed on crushed sludge-free (i.e., 0% sludge) concrete which acts as control.

The TCLP leachates from raw sludge showed significant concentrations of Pb and Cr while showing low concentration of Cd. The average concentration of heavy metals in the leachates from sludge S-A and S-B are presented in Fig. 4.2 and Fig. 4.3, respectively. The USEPA-LDR 'Universal Treatment Standards' limit the concentrations of Pb, Cr and Cd in TCLP leachates below 0.75 mg/L, 0.60 mg/L and 0.11 mg/L, respectively (USEPA, 1997).

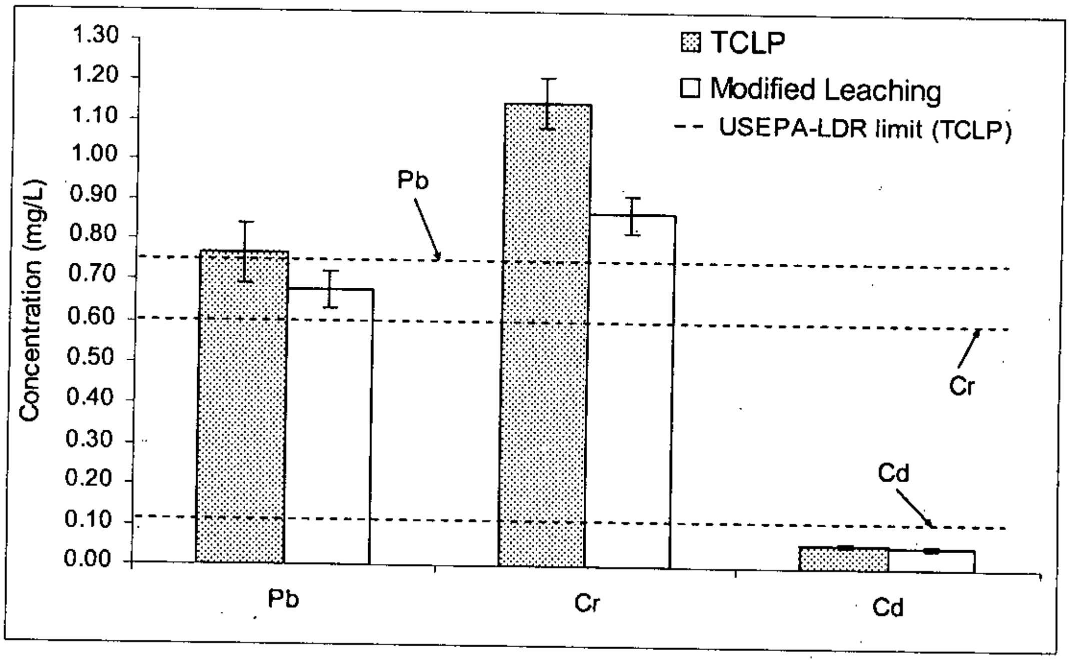

Figure 4.2. Results of average concentrations of Pb, Cr and Cd in standard TCLP and modified leaching test leachates from sludge S-A.

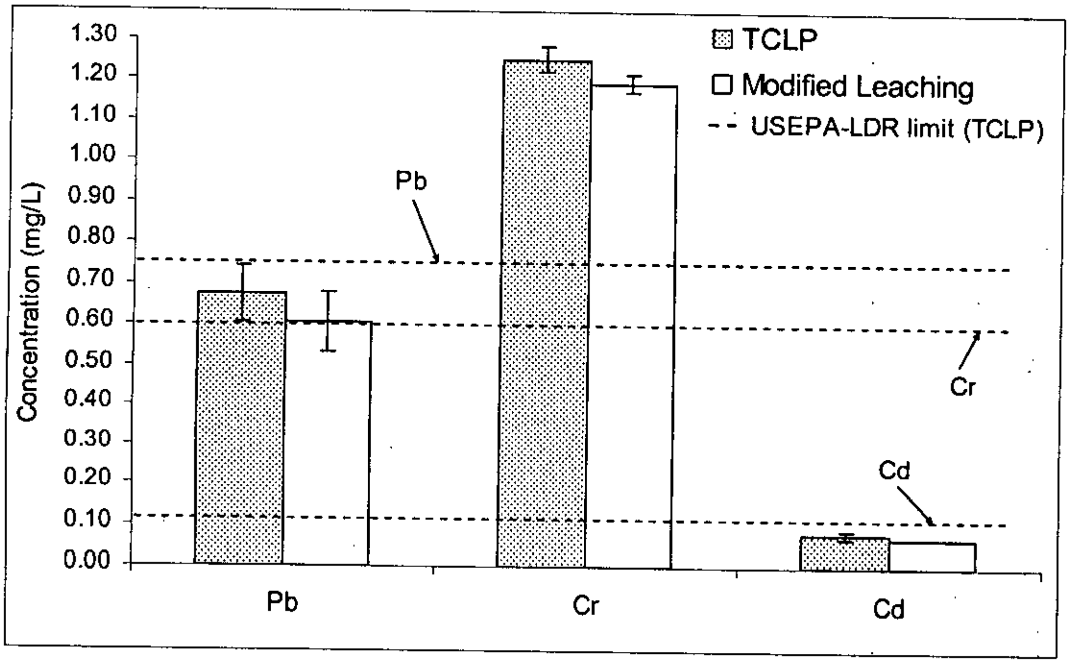

Figure 4.3. Results of average concentrations of Pb, Cr and Cd in standard TCLP and modified leaching test leachates from sludge S-B.

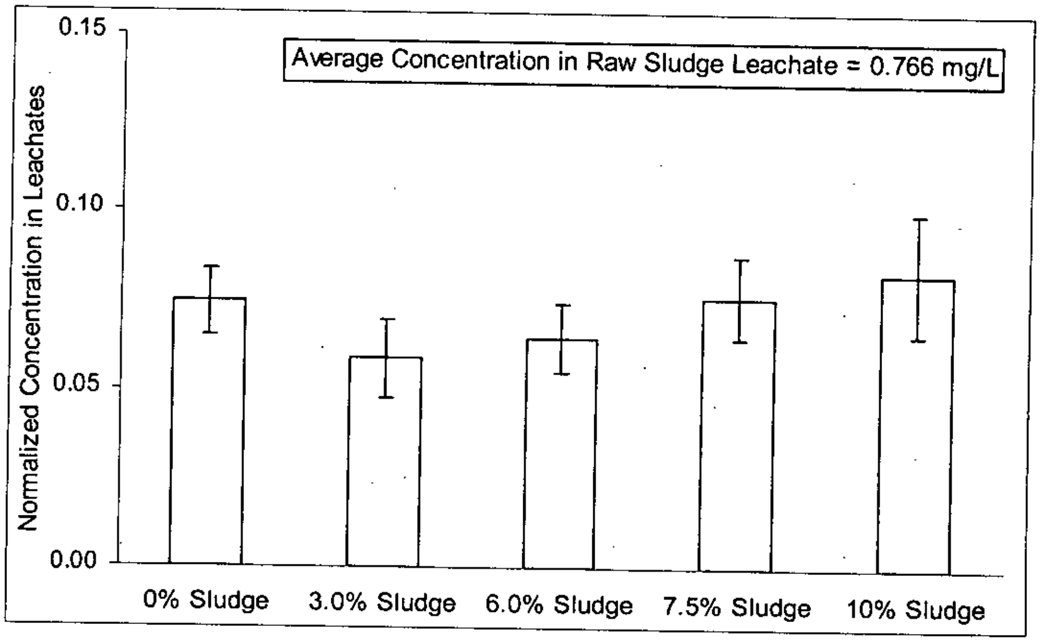

Figure 4.4. Results of normalized average concentration of Pb in standard TCLP leachates from crushed concrete sample for sludge S-A.

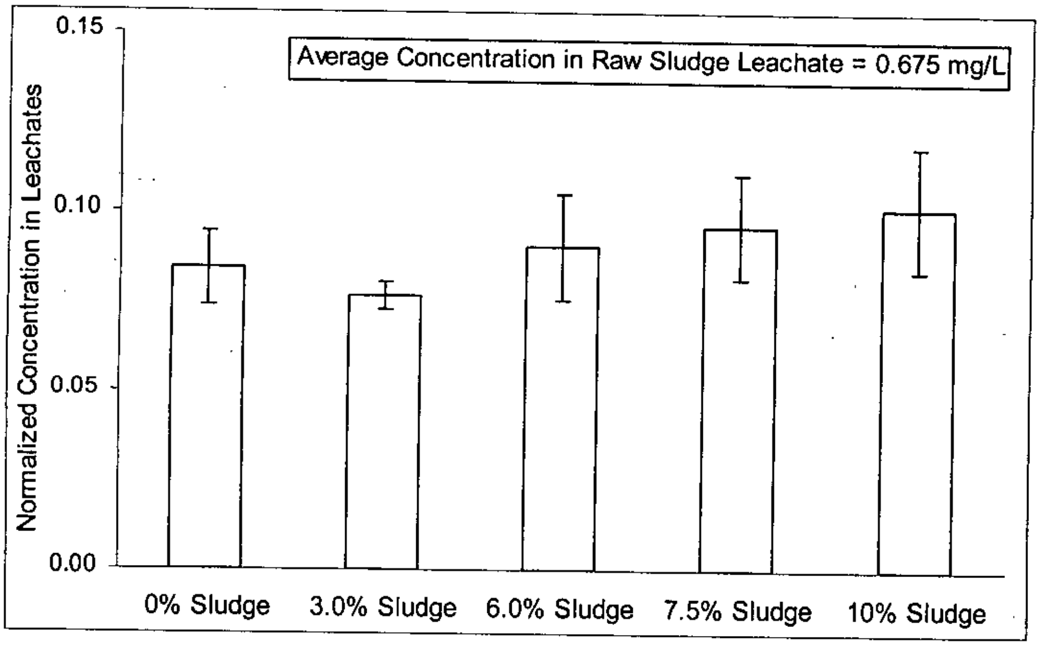

Figure 4.5. Results of normalized average concentration of Pb in standard TCLP leachates from crushed concrete sample for sludge S-B.

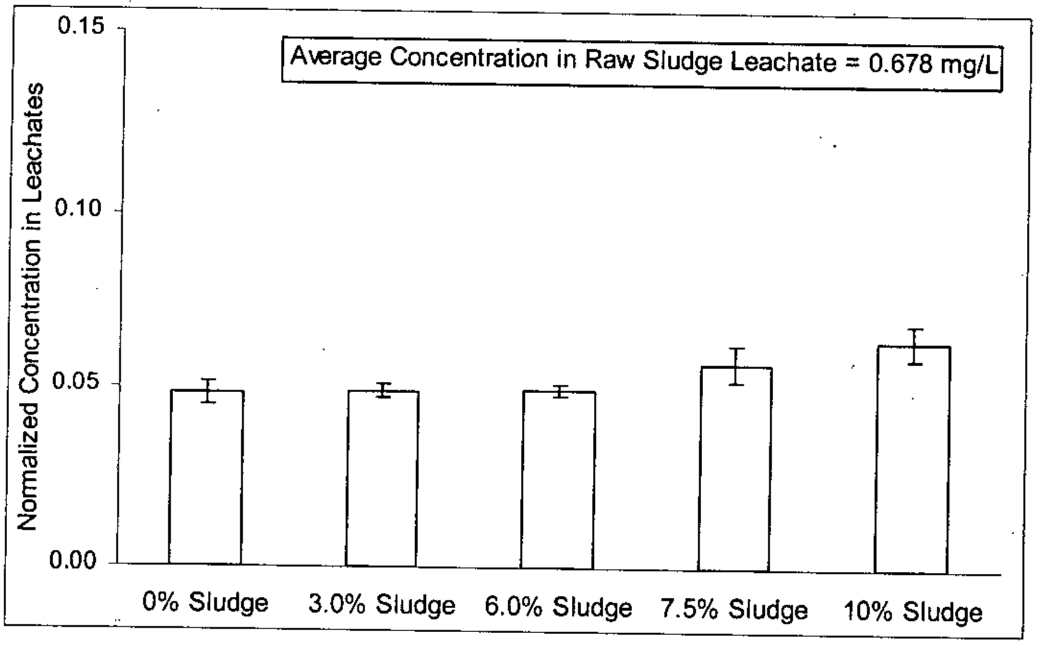

Figure 4.6. Results of normalized average concentration of Pb in modified leaching test leachates from crushed concrete sample for sludge S-A.

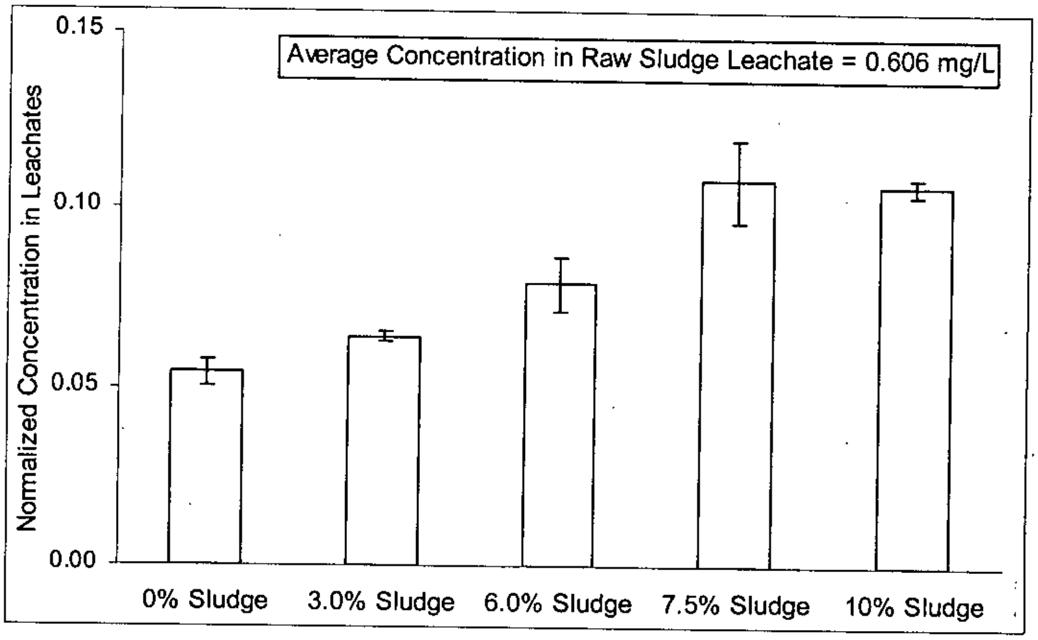

Figure 4.7. Results of normalized average concentration of Pb in modified leaching test leachates from crushed concrete sample for sludge S-B.

The average concentration of Cr in TCLP leachates exceed the regulatory limits for both sludge S-A and S-B; whereas the average concentration of Pb in TCLP leachates exceed the regulatory limits for sludge S-A, and likely to exceed for sludge S-B (Fig 4.2-Fig.4.3). This suggests the need for treatment prior to disposal. The modified leaching test leachates from raw sludge consistently showed lower concentrations of the heavy metals than those in the TCLP leachates, which indicated lower leaching potential in open environment compared to landfill environment.

The concentration results of heavy metals in leachates from crushed concrete were normalized by expressing the concentrations as fractions of corresponding average concentration in raw sludge to assess the reduction in leachability. The concentration results for Pb and Cr in crushed concrete leachates are presented in Fig. 4.4 through Fig. 4.11.

The normalized average concentrations of lead (Pb) in TCLP leachates from crushed concrete with different sludge content for sludge S-A and sludge S-B are presented in Fig. 4.4 and Fig.4.5, respectively. The results of modified leaching for the above case are presented in Fig. 4.6 and Fig.4.7. It was observed that the concentrations of Pb in leachates from sludge-mixed concrete were far below the concentration in leachates from raw sludge marking a significant reduction of leachability after solidification with concrete mix. In all cases the concentrations were within the standard deviations of the concentrations in leachates from raw sludge. The concentration of Pb in leachates from sludge-mixed concrete differed little from that of sludge-free concrete. An increasing trend in the concentrations of Pb in leachates is observed with an increase in sludge in the mix.

Maximum average concentration of Pb in TCLP leachates from crushed concrete with sludge S-A and S-B were 0.063 mg/L and 0.068 mg/L, respectively; which is significantly lower (< 10%) than the recommended USEPA land disposal restriction universal treatment standard of 0.75 mg/L (in TCLP) for Pb.

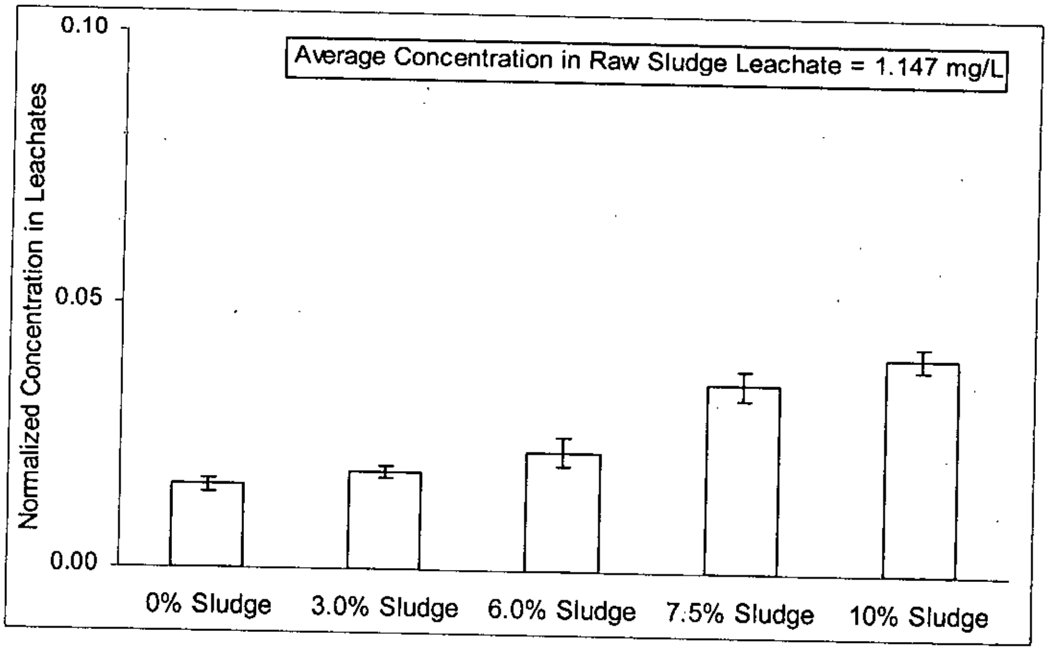

Figure 4.8. Results of normalized average concentration of Cr in standard TCLP leachates from crushed concrete sample for sludge S-A.

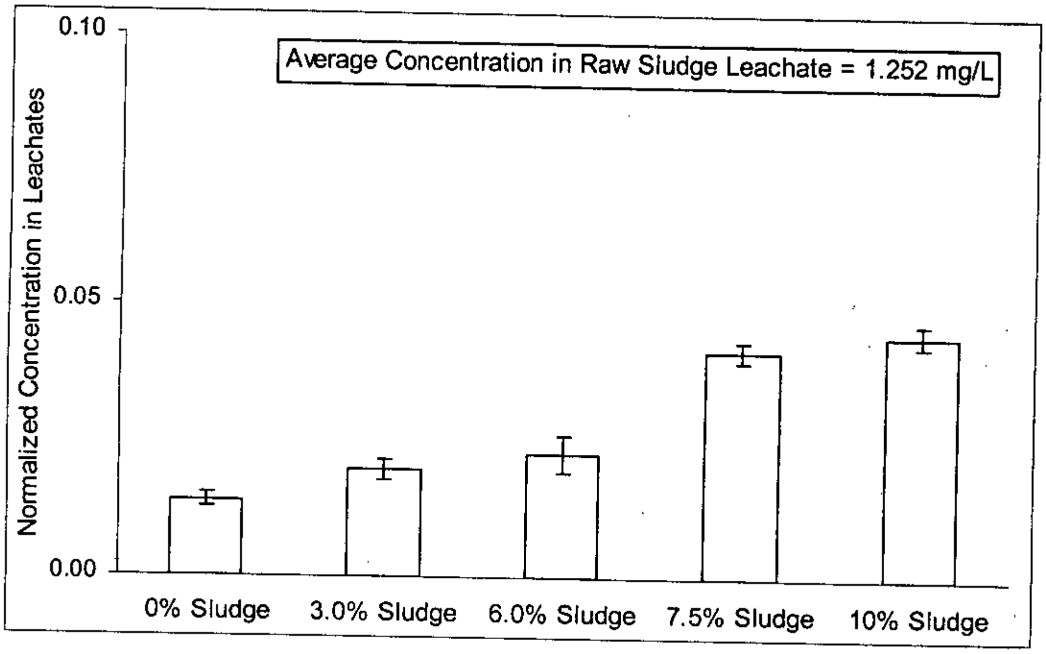

Figure 4.9. Results of normalized average concentration of Cr in standard TCLP leachates from crushed concrete sample for sludge S-B.

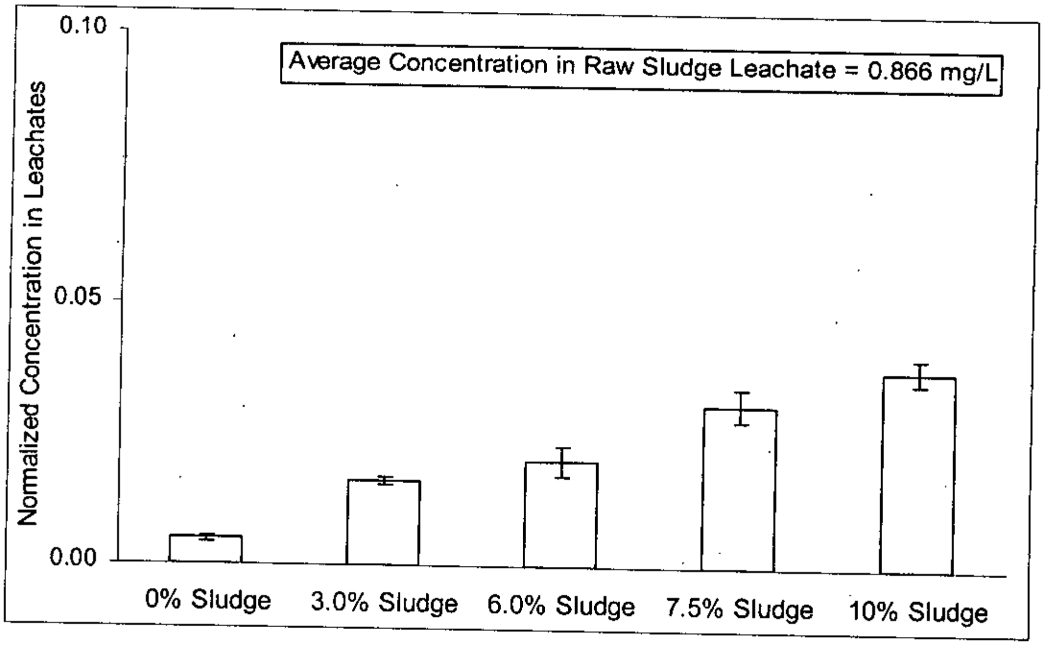

Figure 4.10. Results of normalized average concentration of Cr in modified leaching test leachates from crushed concrete sample for sludge S-A.

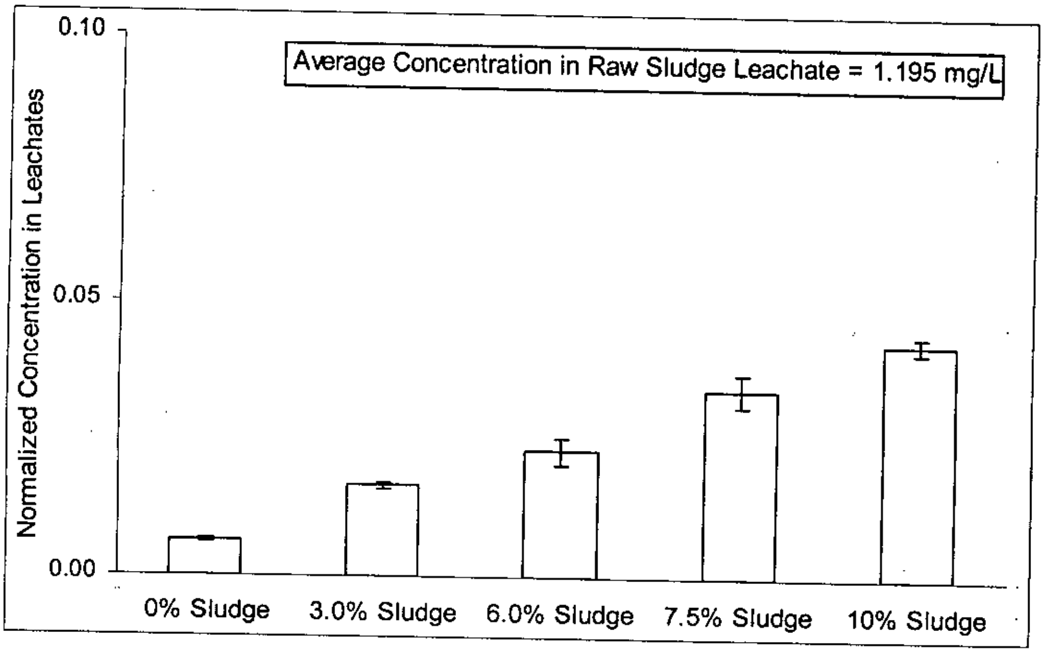

Figure 4.11. Results of normalized average concentration of Cr in modified leaching test leachates from crushed concrete sample for sludge S-B.

The normalized average concentrations of chromium (Cr) in TCLP leachates from raw sludge and crushed concrete with different sludge content for sludge S-A and sludge S-B are presented in Fig. 4.8 and Fig.4.9, respectively. The results of modified leaching for the above case are presented in Fig. 4.10 and Fig.4.11. The concentrations of Cr in leachates from sludge-mixed concrete were far below the Cr concentrations in the leachates from raw sludge (i.e., < 5%). In most cases the concentrations were within the standard deviations of the concentrations in leachates from raw sludge. Presence of Cr was observed in leachates from sludge-free concrete. An increasing trend in concentration of Cr is observed in leachates with increase in sludge in concrete mix.

Maximum average concentration of Cr in TCLP leachate from crushed concrete with sludge S-A and S-B were 0.047 mg/L and 0.056 mg/L, respectively; which is significantly lower (< 10%) than the recommended USEPA land disposal restriction universal treatment standard of 0.60 mg/L (in TCLP) for Cr.

Cadmium was undetected in leachates from crushed concrete, for both TCLP and modified leaching. It may be said that the Cd was properly stabilized.

The presence of Pb and Cr leachates from sludge-free concrete, as evident from leachate results presented in Fig. 4.4 through Fig.4.11, is an indication of presence of lead and chromium in the aggregates especially sand and stone aggregates. However, the Pb in leachates from sludge-free concrete may also be due to unaccounted contamination of the filter media.

Both Pb and Cr are usually present in soils and rocks in trace amounts (Chilton and Kinniburgh, 2003; McGhee, 1991). The concentration of Pb in natural soils usually ranges from 2 mg/kg to 200 mg/kg with average background concentration of 10 mg/kg. The concentration of Cr in natural soils usually ranges from 1 mg/kg to 2000 mg/kg with an average background concentration of 100 mg/kg (USEPA, 1983). The average concentrations of Pb and Cr observed in TCLP leachates from sludge-free concrete were 0.057 mg/L and 0.018 mg/L, respectively. In case of modified leaching test leachates the corresponding concentrations were 0.033 mg/L and 0.006 mg/L. Such low concentration can be regarded as well within the expected leachability from materials employing earth materials (e.g., sand, stone, etc.). However, the aggregates used for all the batches of concrete were from a single source. Hence, the residual concentrations of Pb and Cr may be more or less the same for all the batches of concrete.

The low concentrations of the heavy metals (i.e., Cd, Cr and Pb) in leachates from solidified sludge (i.e., sludge-mixed concrete) suggest that the heavy metals were immobilized through chemical stabilization in highly alkaline environment provided by cement in concrete. It is evident from the final pH of TCLP and modified leaching test leachates (from concrete) that ranged between 11.72 to 11.78 and 11.91 to 11.94, respectively indicating a highly alkaline environment suitable for amphoteric precipitation of heavy metals as metal hydroxides or silicates.

4.5 Analysis of Sludge Mixed Concrete

The sludge-mixed concrete was cast in two phases. At the first phase, sludge content of sludge-mixed concrete varied from 3 to 10 percent by the weight of cement (wet wt.) in the mix for both sludge S-A and organic-rich sludge S-B. Cylinder compressive strength test and slump test was performed. The results were compared with sludge-free concrete to assess the reduction of strength and change in workability at different sludge content. A range of sludge to cement ratio was selected for further analysis. At the second phase, sludge content of concrete varied within the selected range and two different water-cement ratios (0.40 and 0.45) were adopted. The durability test was included along with compressive strength test and slump test. The results were compared with those for sludge-free concrete at different water-cement ratio.

4.5.1 Results of preliminary analysis of concrete

The preliminary analysis of concrete include analysis of workability based on slump test results on sludge-free concrete and analysis of compressive strength based on standard cylinder compressive test results.

Workability results

The results of slump test for each batch of concrete of the first phase is presented in Fig. 4.12. As comprehended the slump had a steady increasing trend for increasing sludge content in concrete for both S-A and S-B. The concrete with organic-rich S-B had a greater slump compared to concrete with S-A at the same sludge content. The limiting slump was taken as 2.0 inch (i.e. ≈5.0 cm) as this is the maximum allowable slump recommended by the United States Department of the Interior (USDI) for most structures (USDI, 1965). The slump at 10% sludge content for concrete with organic-rich S-B exceeds the limiting range.

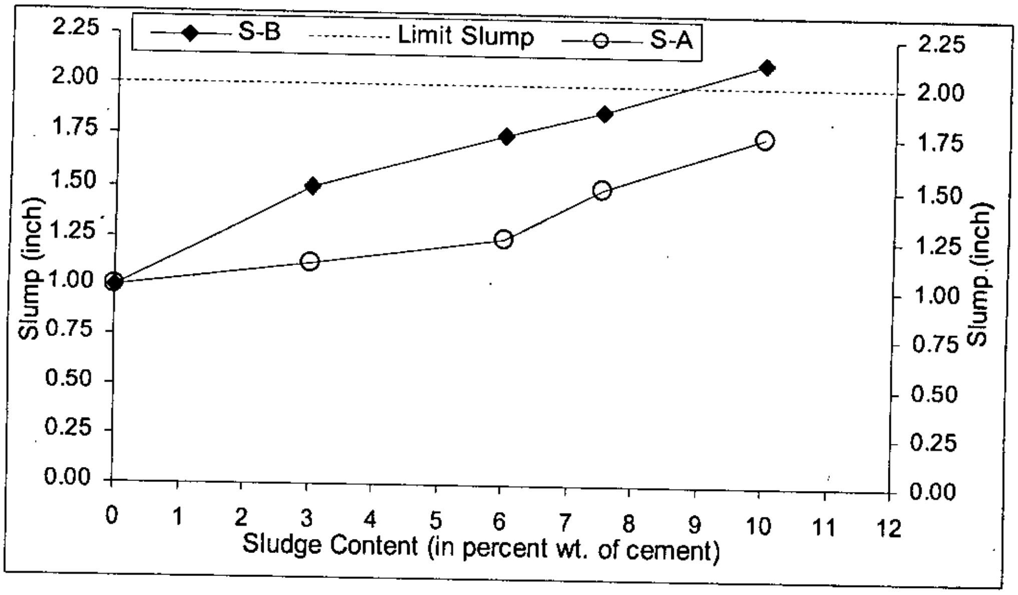

Figure 4.12. Variation of slump of fresh concrete with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.45.

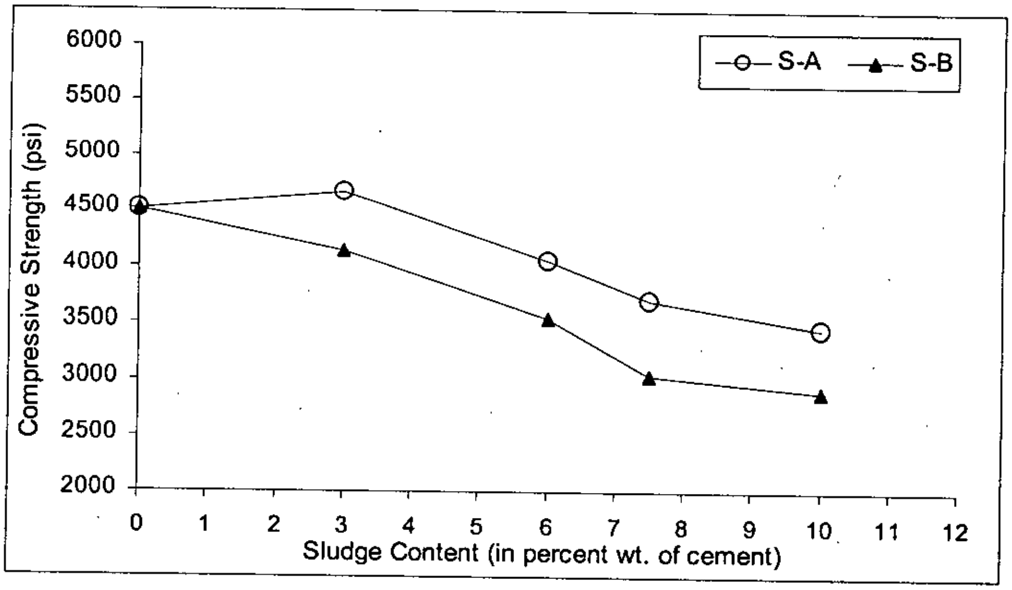

Figure 4.13. Variation of average 7-day cylinder compressive strength of concrete at with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.45.

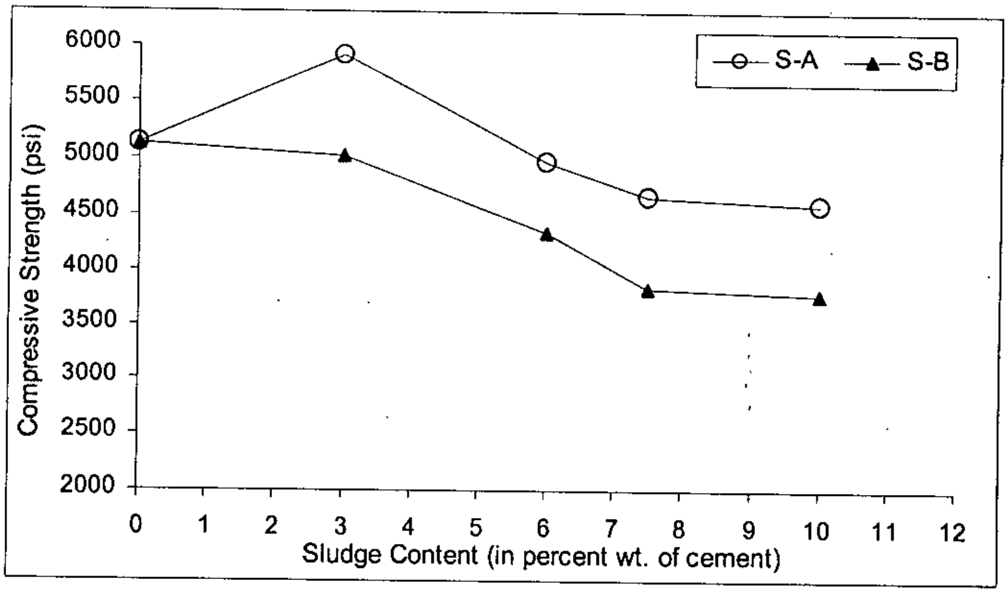

Figure 4.14. Variation of average 28-day cylinder compressive strength of concrete with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.45.

Compressive strength results

Compressive test on standard cylinders were performed for each batch of concrete. The 7-day and 28-day compressive strength test results are presented in Fig.4.13 and Fig.4.14 respectively. The 7-day and 28-day compressive strength of sludge-mixed concrete decreased with increasing sludge content for sludge S-B. However, strength results of concrete with S-A showed increase in compressive strength at low sludge content (3%) for both 7-day and 28-day strengths. At higher sludge content the strength pattern was similar to concrete with S-B. The reduction of compressive strength with increasing sludge content, considering the strength of sludge-free concrete as base strength, was observed to be much higher for S-B than with S-A.

Sludge S-A had low organic content while organic content of sludge S-B was very high (Table 4.1). Organic substances, even at low concentrations, are reported to cause significant reduction in strength of concrete. The higher reduction in strength in case of concrete with sludge S-B may be attributed to high organic content of the sludge. The increase in strength of concrete with sludge S-A at low sludge content may be termed indicative, and hence, demands further investigation. Both the sludge samples S-A and S-B were rich in sulfate (Table 4.1). Sulfate salts, when mixed up to a certain threshold concentration in specially manufactured cements (i.g., $CaSO_4$ in case of Supersulfated cement), are reported to increase concrete strength during the initial periods (Neville, 1996). No such information, however, is available for Ordinary Portland Cement, which is used for this study. The increase in strength of concrete, therefore, may be due to presence of substances in the sludge having cementitious characteristics. But no definite conclusion can be reached without thorough knowledge on all the chemical species present in sludge.

The American Concrete Institute (ACI) recommends a minimum compressive strength of 2500 psi for structural concrete (ACI, 2002). It is also recommended that at the 28-day cylinder compressive strength of concrete, which is cast and tested at controlled laboratory environment, be sufficiently higher (i.e., about 1000 psi or more) than the design strength

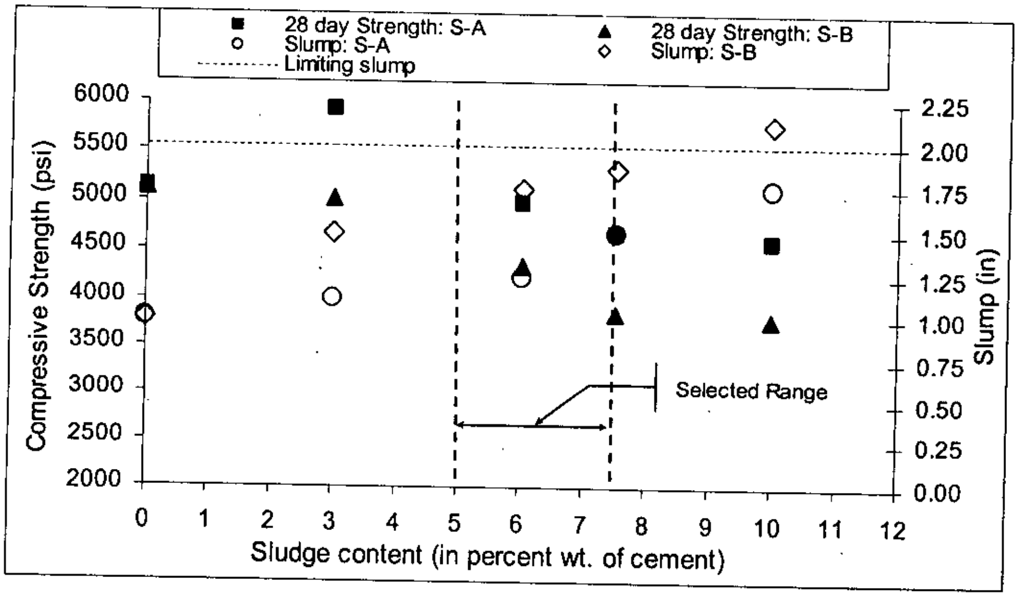

Figure 4.15. Variation of slump and average 28-day cylinder compressive strength of concrete with increase in sludge content at water-cement ratio of 0.45.

A maximum of 30 percent reduction in 28-day cylinder compressive strength of sludge-free concrete was allowed in case of concrete with sludge so that the recommended conditions are met. It was observed that a range of sludge to cement ratio of 5.0 to 7.5 % may be an acceptable range of sludge content. The slump at this range did not exceed the maximum limiting slump of 2.0 inch (Fig.4.15). Hence, the range of 5 to 7.5% sludge content was selected for further analysis.

4.5.2 Results of secondary analysis of concrete

The secondary analysis of concrete consists of analysis of workability based on slump test results at different water-cement ratio, analysis of standard cylinder compressive strength test results at different water-cement ratio, and durability of sludge-mixed concrete under sulfated condition at different water-cement ratio. The sludge content varied within the range pre-selected in the preliminary phase.

Workability results

The results of slump test on performed on fresh concrete cast in the second phase are presented in Fig. 4.16. The slump was observed to have a steady increasing trend for increasing sludge content in concrete with sludge S-A and slightly higher slump was observed at water-cement ratio of 0.45 than at water-cement ratio of 0.40. The slump of concrete with organic-rich sludge S-B had similar pattern except at water-cement ratio of 0.40 and 5% sludge content. Moreover, the slump of concrete with organic-rich sludge S-B is lower than concrete with sludge S-A at water-cement ratio of 0.40, which is in contrast to what is observed at water-cement ratio of 0.45. May be the high organic content in sludge S-B was a possible reason for such behavior. The decrease in slump at lower water-cement ratio was noticeable. However, slump was below the limiting slump of 2.0 inch for all batches.

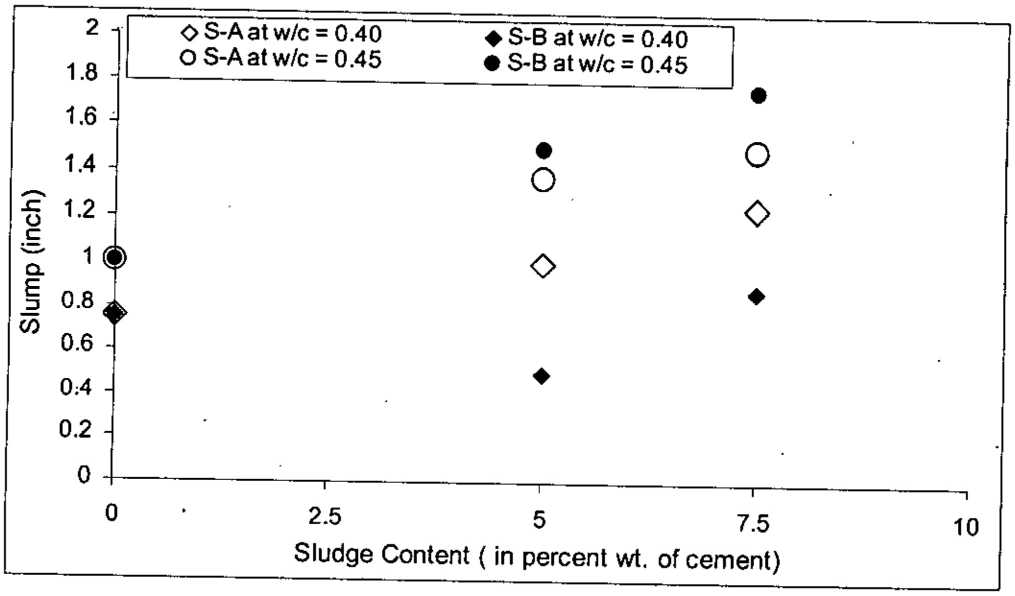

Figure 4.16. Variation of slump of fresh concrete at different water-cement ratio with increase in sludge content for sludge S-A and S-B.

Compressive strength results

Compressive strength test on standard cylinders were performed for each batch of concrete. The 28-day compressive strength test results are presented in Fig.4.17. The maximum observed reduction in 28-day compressive strength in sludge-mixed concrete was below 25% of the compressive strength of sludge-free concrete. The reduction of compressive strength with increase in sludge content showed the same pattern, observed earlier at the preliminary stage. The phenomenon of increased compressive strength for sludge S-A, was repeated with 5% (by wt. of cement) sludge content at both the water-cement ratio. The reduction in compressive strength was higher at water-cement ratio of 0.45 than that at water-cement ratio of 0.40. The case was more severe in case of concrete with organic-rich sludge S-B.

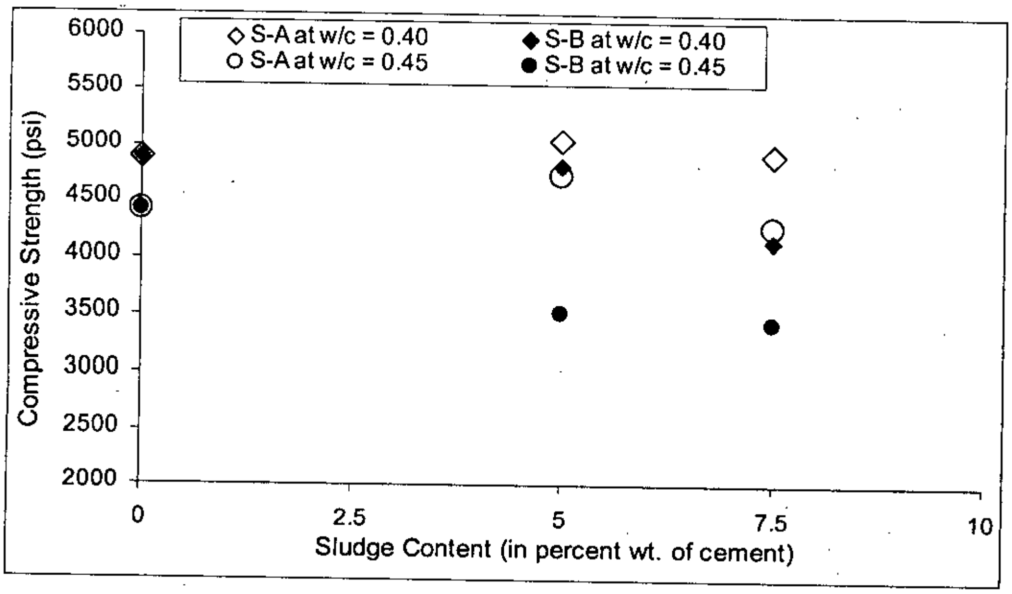

Figure 4.17. Variation of average 28-day cylinder compressive strength of concrete at different water-cement ratio with increase in sludge content for sludge S-A and S-B.

Durability test results of concrete

The durability of sludge-mixed concrete in sulfate environment was analyzed in this study by observing volume changes (expansion or swelling) occurring over time of concrete cylinders immersed in 1% and 2.5% $MgSO_4$ solutions following hardening, and also by observing the reduction of strength of those cylinders from corresponding strength in sulfate-free concrete after a period of 140 days.

Analysis of volume expansion in concrete

The volume was measured regularly through measurement of the diameters and lengths of cylinder and the percent expansion of volume was calculated using the formula outlined in Eq. 3.2. There was no standard guideline on the period of exposure for the test. The major portion of the expansion in the volume occurred during the first few weeks and after ten weeks time there was insignificant changes. Considering the lab space required for curing large number of cylinders in sulfate laden environment and the relatively slow changes in dimensions, a time period longer than 140 days seemed little fruitful. Hence, final measurements were taken after 140 days of exposure. The results of average volume expansion (expressed in percentage of initial volume) occurring in concrete cylinders immersed in 1.0% and 2.5% $MgSO_4$ solutions are presented in Fig. 4.18 and Fig. 4.19, respectively. The volume changes occurring at water-cement ratio of 0.40 and 0.45 are presented in Fig.4.20 and Fig.4.21, respectively.

In case of 1% $MgSO_4$ solutions, the maximum increase in initial volume was below 2 percent of initial volume for all the batches (Fig.4.18) while in case of 2.5 % $MgSO_4$ it was below 2.5 percent (Fig.4.19). At water-cement ratio of 0.40 maximum volume change occurred in sludge-free concrete and the changes in volume showed a decreasing trend with increase in sludge content (Fig.4.20). At water-cement ratio of 0.45 there was an increasing trend with increase in sludge content (Fig.4.21).

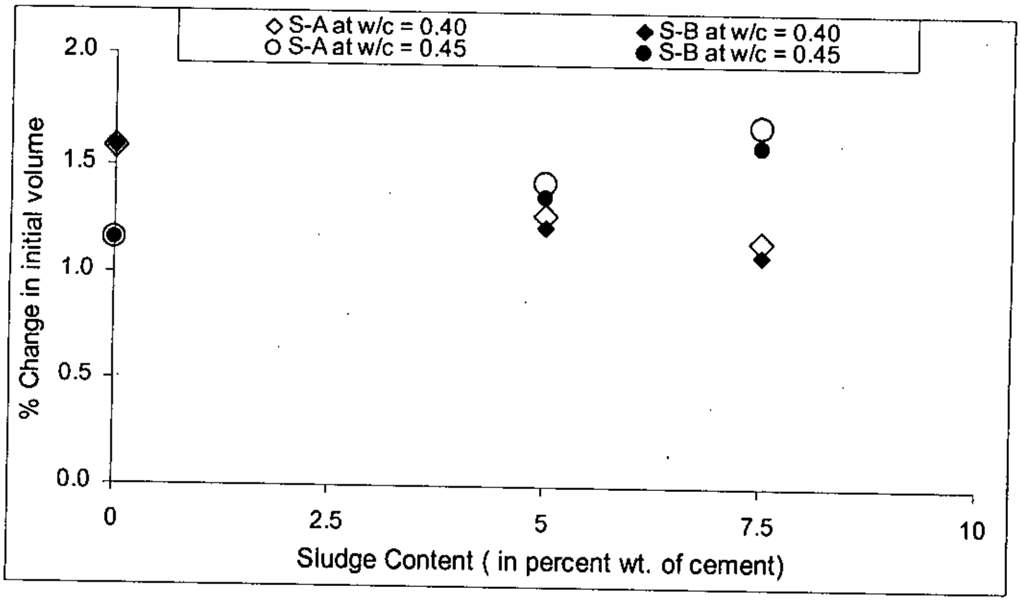

Figure 4.18. Observed average changes in initial volume of concrete with increase in sludge content for sludge S-A and S-B at different water-cement ratio after immersion in 1.0% $MgSO_4$ solution for 140 days.

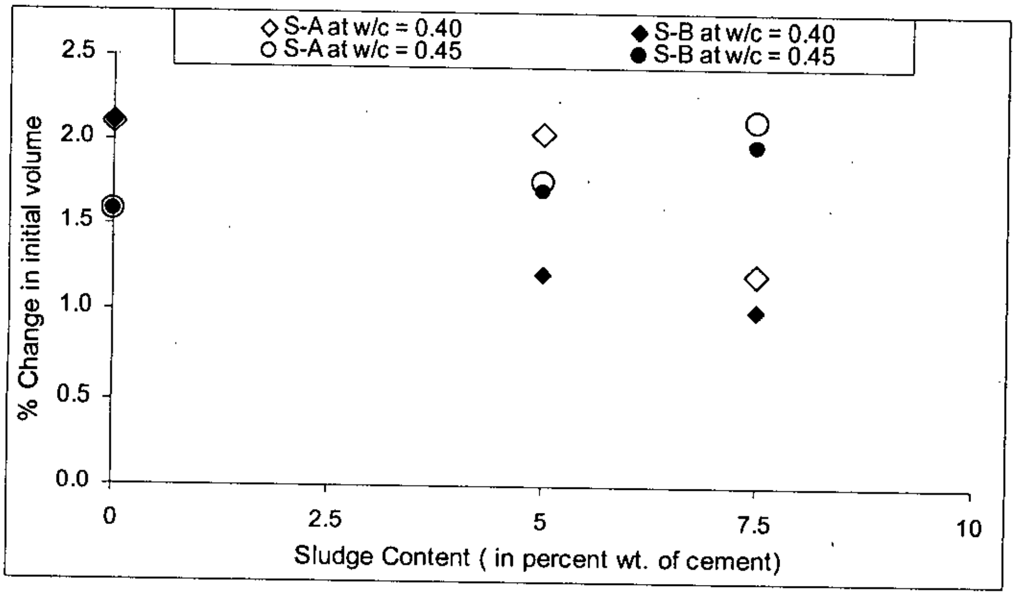

Figure 4.19. Observed average changes in initial volume of concrete with increase in sludge content for sludge S-A and S-B at different water-cement ratio after immersion in 2.5% $MgSO_4$ solution for 140 days.

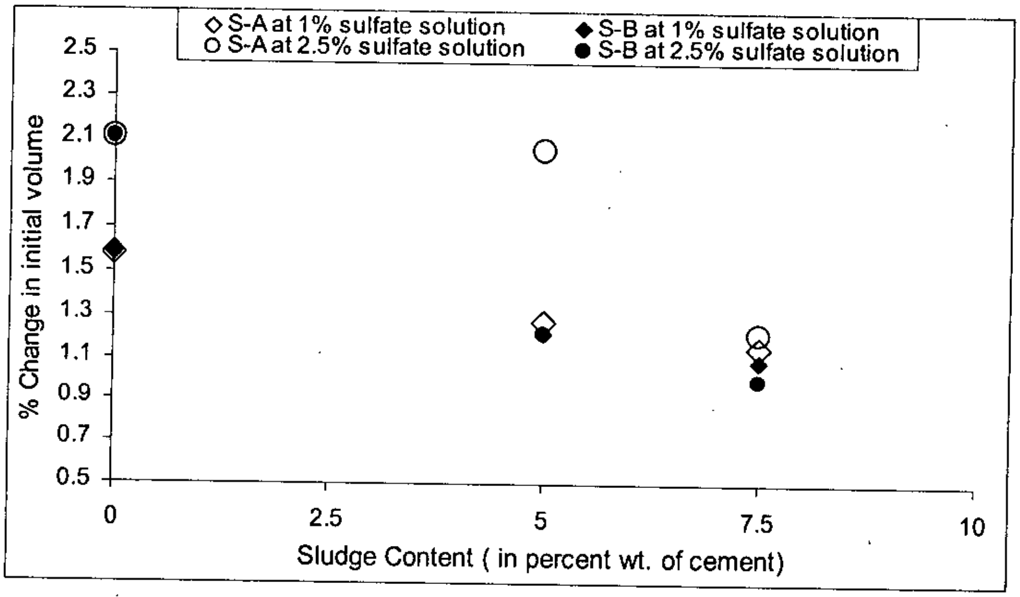

Figure 4.20. Observed average changes in initial volume of concrete with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.40 after immersion in $MgSO_4$ solution of different concentrations for 140 days.

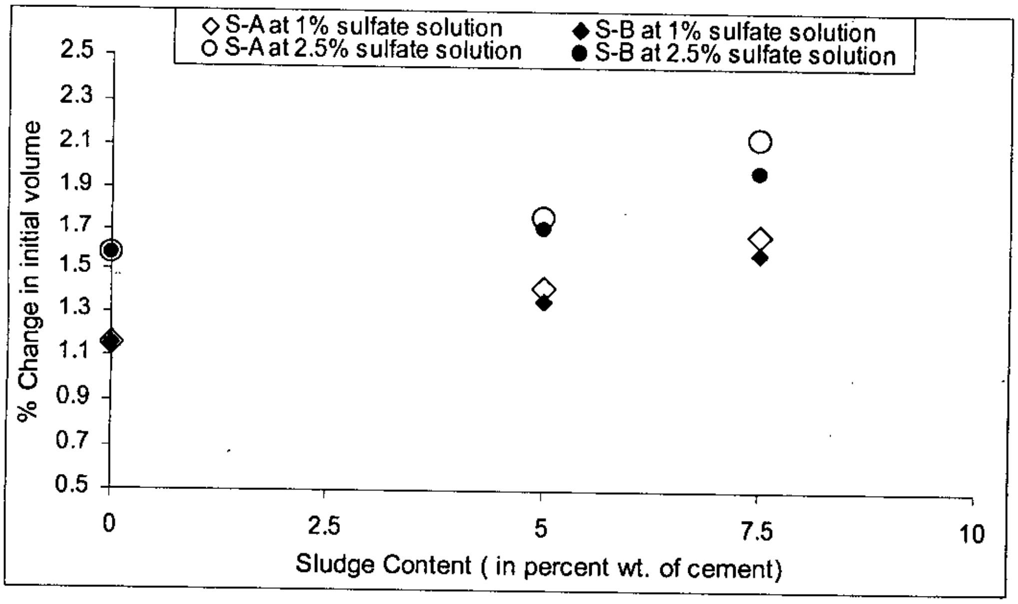

Figure 4.21. Observed average changes in initial volume of concrete with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.45 after immersion in $MgSO_4$ solution of different concentrations for 140 days.

In general, larger volume changes occurred in higher sulfate exposure (Fig.4.20-Fig.4.21)) and in case of higher water-cement ratio (Fig.4.18-Fig.4.19). Concrete with sludge S-A underwent slightly higher expansion in volume than concrete with sludge S-B. It is known that the extent of the influence of sulfate is dependent on the level of penetration of sulfate ions into the cement-aggregate matrix within the concrete (Neville, 1996; Shetty, 1996). The level of penetration is, however, dependent on the porosity of the concrete as well as on the concentration of sulfate in the ambient environment (Neville, 1996). A higher water-cement ratio usually results in a larger amount of pores within the concrete for a particular mix and thus, permits higher level of penetration of sulfate. So, relatively greater volume expansion at higher water-cement ratio is expected. In this study, the pore-size distribution of hardened concrete could not be analyzed due to lack of laboratory facility. Hence, it was not possible to assess the extent of sulfate penetration within concrete.

The shift in the response of sludge-mixed concrete to sulfate environment with difference in water-cement ratio can be termed indicative, and hence, demands further investigation. It may be argued that the porosity of sludge-mixed concrete have somewhat different relationship with water-cement ratio than that of sludge-free concrete. However, before reaching any conclusion, analysis of the pore-size distribution and porosity of the sludge-mixed concrete at different sludge-content and water-cement ratio is essential. Hence, no final conclusion could be reached in explaining this shift.

However, the change in volume was very low (< 2.5 % of initial volume) and volume changes of sludge-mixed concrete did not vary much from that of sludge-free concrete for the range of sludge content (i.e. 5-7.5%) used in this phase.

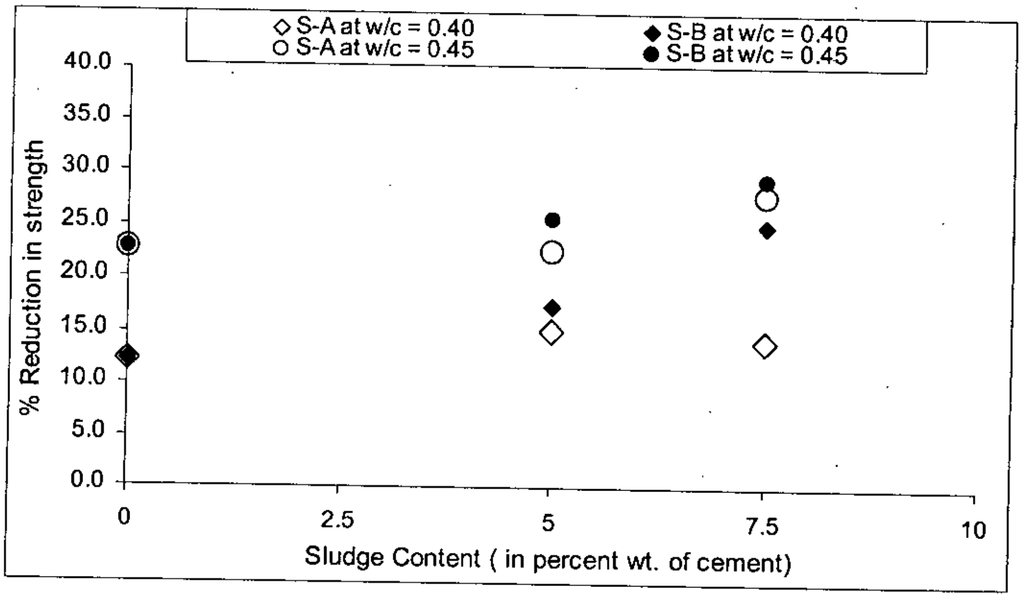

Figure 4.22. Reduction in average compressive strength of concrete with increase in sludge content for sludge S-A and S-B at different water-cement ratio after immersion in 1 % $MgSO_4$ solution for 140 days.

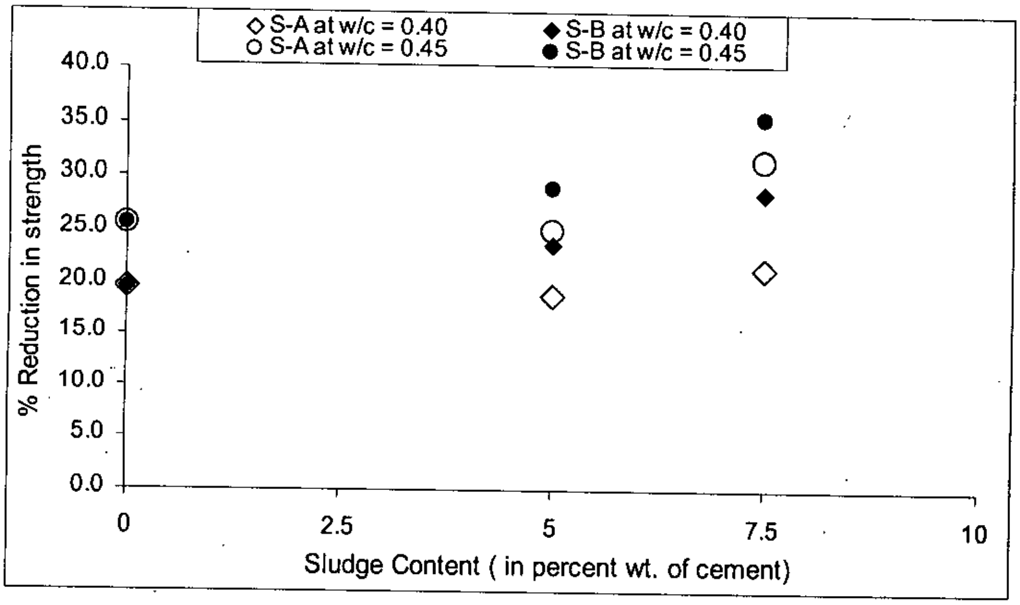

Figure 4.23. Reduction in average compressive strength of concrete with increase in sludge content for sludge S-A and S-B at different water-cement ratio after immersion in 2.5 % $MgSO_4$ solution for 140 days.

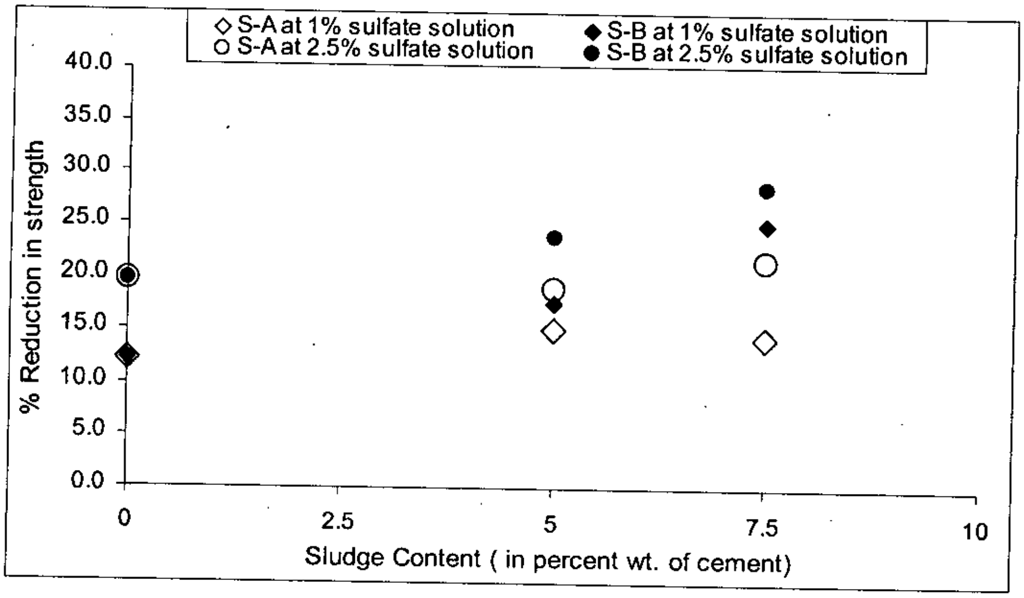

Figure 4.24. Reduction in average compressive strength of concrete with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.40 after immersion in $MgSO_4$ solution of different concentrations for 140 days.

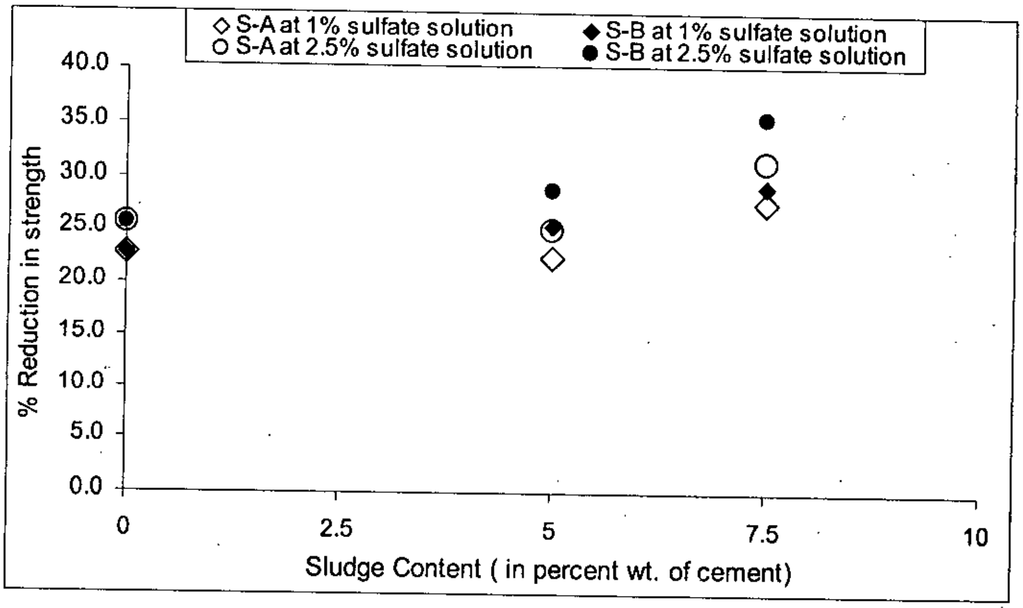

Figure 4.25. Reduction in average compressive strength of concrete with increase in sludge content for sludge S-A and S-B at water-cement ratio of 0.45 after immersion in $MgSO_4$ solution of different concentrations for 140 days.

Analysis of reduction in compressive strength

The compressive strength of cylinders of every batch after 140 days of sulfate exposure was determined. The percent reduction of average compressive strength from the corresponding average compressive strength of cylinders in sulfate-free environment were calculated using formula outlined in Eq. 3.3.

The results of reduction in strength after 140 days in concrete immersed in 1.0% and 2.5% $MgSO_4$ solutions are presented in Fig. 4.22 and Fig. 4.23, respectively. The reduction in strength occurring at water-cement ratio of 0.40 and 0.45 are presented Fig.4.24 and Fig.4.25, respectively.

In general, the reduction in strength was higher at 2.5% $MgSO_4$ than at 1% $MgSO_4$ (Fig.4.24-Fig.4.25); and higher reduction was observed at water-cement ratio of 0.45 than water-cement ratio of 0.40 (Fig.4.22-4.23). There seemed to be a steady increase in the magnitude of reduction of strength with increased sludge content. The reduction of strength was higher in case of concrete with organic-rich sludge S-B than concrete with S-A containing relatively lower amount of organics (Fig. 4.22-Fig.4.25).

Comparing the variations in reduction in compressive strength between sludge-free and sludge-mixed concrete, it is observed that at sludge content of about 5% the reduction of strength in sludge-mixed concrete differ little from that of sludge-free concrete The sulfate durability in terms of reduction in strength can be termed acceptable at low sludge content (nearly 5%) and low water-cement ratio (0.40) for both sludge samples.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

The industrial sludge produced at the end of treatment is usually highly contaminated with heavy metals and bio-organics. Due to lack of coordination between environmental authorities and industries regarding management of sludge, the companies are on their own to set up sludge disposal options. As a result, the common practice is open water disposal or on-land disposal without treatment. The heavy metals leaching from such mismanaged sludge is posing potential threat to both groundwater and surface water with long-term consequences. Stabilization combined with possible significant improvement in the engineering properties of the stabilized material may provide sustainability to the sludge management system. The primary objective of this study was to assess the performance of stabilization of heavy metals (Pb, Cd, Cr and Hg) in industrial sludge with concrete mix. Secondary objectives included assessment of the effect of addition of sludge on compressive strength, workability and durability of resultant concrete at different scenarios, and to recommend a stable concrete mix to be used for construction using sludge partially replacing the fine aggregates in the concrete mix.

The TCLP leachates from sludge-mixed concrete had very low concentrations of lead and chromium compared to the leachates from raw sludge indicating almost complete stabilization of major portion of the leachable heavy metals in sludge. Cadmium, which was at low concentration in the sludge, was completely stabilized. Thus, the stabilization of the sludge with concrete mix may be possible if proper control measures and mix proportions are maintained.

The modified leaching test results implied that, if sludge-mixed concrete is used for minor construction and is exposed to open air environment, the concentration of the metals in leachates would be environmentally insignificant and the leaching of heavy metals would be lower compared to the leaching under aggressive conditions.

In general, there was a decrease in compressive strength with increase in sludge content in the mix. The decrease was more pronounced in case of organic-rich sludge. The durability of sludge-mixed concrete under sulfate-laden environment, in terms of volume expansion or swelling and reduction in strength, did not differ significantly from that of sludge-free concrete at low sludge level.

The water-cement ratio in the mix seems to play an important role in the strength and workability, and possibly the major role in durability of sludge-mixed concrete. From durability perspective of sludge-mixed concrete, the water-cement ratio is recommended to be near 0.40.

Considering the compressive strength, workability and changes in the durability of concrete, a sludge content of 5 to 6% by weight of cement may be an acceptable sludge content for both organic-rich sludge and sludge having low organic. A relatively higher sludge content may be adopted for low-organic sludge. However, it is not expected that the differentiation of sludge on organic content would be possible in the fields. Hence, the conservative mix ratio prescribed above may be a safe choice. At 5% sludge content and water-cement ratio of 0.40, the 28-day average cylinder compressive strength of sludge-mixed concrete with low organic sludge (i.e. S-A) and organic-rich sludge (i.e., S-B) were observed to be 5050 psi and 4850 psi, respectively. The strength of the sludge-mixed concrete can be termed acceptable for construction. .

5.2 Recommendations for Future Studies

The present study generated leachates considering two different disposal scenarios, disposal in municipal landfill and open air environment covered by TCLP and the modified leaching test, respectively. Other scenarios like acid rain, nitrate-rich and phosphate-rich environment may be considered in future studies if the concrete is to be exposed to such situations.

In this study, the aim was to observe the changes in compressive strength of concrete with the increase in sludge content in the mix. The mix design followed was an arbitrary one. For the concrete to be used regularly in construction, a mix targeting a specified minimum strength should be adopted.

The present study included only two sludge samples, which is too low to propose a reliable mix. Future studies should aim at increasing the number of samples and may focus on sludge from industries not covered in this study.

The industrial sludge in Bangladesh is usually rich in organics. Hence, study is required to thoroughly investigate on the limiting range of sludge content in case of organic-rich sludge.

The present study analyzed the sulfate durability of concrete by employing $MgSO_4$ solution. However, durability testing with $MgSO_4$ is relatively slow and thus the test may miss some aspects of long-term exposure of concrete to sulfate conditions. The rapid assessment tests employing sulfuric acids maybe a suitable alternative for future studies. The durability of concrete subject to impurities other than sulfate may also be included.

The present study did not include analysis of the porosity or permeability of sludge-mixed concrete. However, the permeability of concrete usually dictates the extent of access of the impurities (e.g., silicate, chloride, sulfate, sulfide, etc.) to the hydrated cement paste within the cement-aggregate matrix, and thereby, has a direct bearing on the durability. Without information on permeability, the assessment is strictly limited to the experimental observations, and long-term predictions regarding durability are not possible. Future studies should focus on analyzing the pore-size distribution within the concrete and the permeability of the concrete.

REFERENCES

ACI (2002), Building Code Requirements for Structural Concrete (318-02) and Commentary (318R-02), American Concrete Institute (ACI), Farmington Hills, MI, USA, 2002.

Alam, M. D. U., Huq, S. M. I., Rahman, M. S., and Anam K. (1991), A Handbook on Chemical Analysis of Soil, Plant and Water,(1st Ed.), Published by Ahmed Parvez Shamsuddin.

Ali, A., Ahsanuzzaman, A. N. M., Badruzzaman, A. B. M. and Rahman, M. M. (1998), Lead Pollution of Dhanmondi Lake in Dhaka, Aqua, volume 7, no.6, December 1998.

Ashfaque, K. N. (1999), Analysis of Heavy Metals in Bed Sediments of Dhanmondi Lake, M.Sc. Thesis, Department of Civil Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh.

Badruzzaman, A. B. M. (2002), Leaching of Arsenic from Wastes of Arsenic Removal Systems, Proceedings of BUET-UNU International Symposium on Fate of Arsenic in the Environment, Dhaka, February 2003, 'Fate of Arsenic in the Environment', ISBN: 984-32-0507-3, pp. 161-179.

Batchelor, W. (1999), Inorganic Leaching Science, Proceedings of the Environmental Protection Agency, Public Meeting on Waste Leaching-Session III : Leaching Science, USEPA, USA, July 22-23, 1999.

Bosunia, S. Z., Choudhury, J. R. (2001), Durability of Concrete in Coastal Areas of Bangladesh, Journal of Civil Engineering, The Institution of Engineers, Bangladesh, Vol.CE 29, No.1, June 2001, pp. 41-53.

Cairns, J. Jr., Lanza, G. R., and Parker, B. C. (1972), Pollution Related Structural and Functional Algae and Protozoa, Proceedings of the Academy of Natural Sciences of Philadelphia.

Chilton, J. and Kinniburgh, D. (2003), Soil and Groundwater Protection in the South-East Asia Region, Water Resources Journal, ESCAP, UN, December 2003, Vol.215, pp.87-94.

Commission of the European Communities (CEC) (1979), Trace Metals: Exposure and Health Effects, Oxford, Pergamon Press.

Cooper, W. C. (1976), Cancer Mortality Patterns in the Lead Industry, Annals of the New York Academy of Sciences, 1976, New York, USA.

de March, B. G. E., (1976), Spatial and Temporal Patterns in Macrobenthic Stream Diversity, Journal of the Fisheries Research Board of Canada.

Dipaolo, J. A., Nelson, R. L. and Casto, B. C. (1978), In Vitro Neoplastic Transformation of Syrian Hamster Cells by Lead Acetate and Its Relevance to Environmental Carcinogenesis, British Journal of Cancer.

EPA (2002), Frequently Asked Questions: TCLP Questions, From: http://www.epa.gov/epaoswer/hazwaste/test/faqs_tclp.htm, [Last Updated: November 4, 2002], [Accessed: February 17 2004].

FPCO (1995), FAP16: A Study of Sedimentation in the Brahmaputra-Jamuna Floodplain, Environmental Study, Bangladesh Flood Action Plan, Ministry of Water Resources, Flood Plan Coordination Organization, 1995, pp.1-11.

FDA (1994), Mercury in Fish: Cause For Concern?, FDA Consumer, U.S. Food and Drug Administration, USA, November, 1994.

Friberg, L., Piscator, M., Nordberg, G. F., Kjellstrom, T. and Boston, P. (1974), Cadmium in the Environment, 2nd edition, CRC Press, Cleveland, Ohio, USA.

Hafiz, A. (1998), Comparative Study of Copper Contamination in the Water and Sediment Column of the Ramna Lake and Dhanmondi Lake, M.Sc. Engg. Thesis, Department of Civil Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh.

Hagen A., and Langeland, A. (1973), Polluted Snow in Southern Norway and the Effect of the Meltwater on Freshwater and Aquatic Organisms, Environmental Pollution.

Halcrow, Mott MacDonald and Associates (2000), Draft Development Strategy, Annex G: Environment, National Water Management Plan (NWMP) Project, Ministry of Water Resources, WARPO, August 2000, pp.24-49, 59-65.

Hartwell, S. (1999), Overview of Current Approaches, Proceedings of the Environmental Protection Agency, Public Meeting on Waste Leaching-Session III: Leaching Science, USEPA, USA, July 22-23, 1999.

Hills, S. D., Sollars, C. J. and Perry, R. (1992), Ordinary Portland Cement Based Solidification of Toxic Wastes: The Role of OPC reviewed, Cement and Concrete Research, Vol. 23(1), pp.196-211.

Hills, S. D., Sollars, C. J. and Perry, R. (1994), Solidification of Hazardous Waste Containing Cyanide, Cement and Concrete Research, Vol. 24(4), pp.267-276.

Hossain, M. A. and Badruzzaman, A. B. M. (2002), Analysis of Heavy Metals in Vegetable Samples Sold in Some Local Bazaars, Proceedings of 2nd International Conference on Bangladesh Environment (ICBEN 2002), Dhaka, Bangladesh, 19-21 December 2002, 'Bangladesh Environment 2002', ISBN: 984-32-0443-3, Vol.1, pp. 558-570.

Kaufman, D. B. (1970), Acute Potassium Dichromate Poisoning in Man, American Journal of Diseases of Children.

Kido, T., Honda, R., Tsuritani, I., Yamaya, H., Ishizaki, M., Yamada, Y. and Nogawa, K. (1988), Progress of Renal Dysfunction and Osteopenia in Inhibitants Environmentally Exposed to Cadmium, Archives of Environmental Health, , Vol.43, pp. 213-217.

Kido, T., Nogawa, K., , Honda, R., Tsuritani, I., Ishizaki, M., Yamada, Y. and Nakagawa, H. (1988), The Association Between Renal Dysfunction and Osteopenia in Environmental Cadmium Exposed Subjects, Environmental Research, , Vol.51, pp. 71-82.

Kimmel, T. (1999), Background of Toxicity Characteristic Leaching Procedure (TCLP), Proceedings of the Environmental Protection Agency, Public Meeting on Waste Leaching-Session I: Introduction and Overview, USEPA, USA, July 22-23, 1999.

LaGrega, M. D., Buckingham, P. L., and Evans, J. C. (1994), Hazardous Waste Management, McGraw-Hill, Inc., pp. 641-698.

Mathur, K. C., Shukla U. M., Shukhla A. K. and Mathur S. (1998), Effect of Fly Ash Containing Heavy Metals On Plants Species Ipomea carnea, Typha angustata and Calotropis procera, Pollution Research, Vol. 17, pp.1-3.

McGhee, T. J. (1991), Water Supply and Sewerage, 6th Edition, McGraw-Hill Book Co., Singapore, ISBN: 0-07-100823-3. pp. 401-402, 491-492, 514,547.

Ministry of Supply and Services (1979), Guidelines for Canadian Drinking Water Quality, 1978, Quebec, Canada.

Moore, J. W. (1979), Diversity and Indicator Species as Measures of Water Pollution in a Subarctic Lake, Hydrobiologia.

Moore, J. W., Beaubien, V. A. and Sutherland, D. J. (1979), Comparative Effects of Sediment and Water Contamination on Benthic Invertebrates in Four Lakes, Bulletin of Environmental Contamination and Toxicology.

Murarka, I. (1999), Importance of Leachate Tests in the Assessment Process, Proceedings of the Environmental Protection Agency, Public Meeting on Waste Leaching-Session II: Modeling and Risk Assessment, USEPA, USA, July 22-23, 1999.

Neville, A. M. (1996), Properties of Concrete, Fourth Edition, ELBS and Addison Wesley Longman Limited, England, ISBN: 0-582-279380, pp. 482-586.

National Research Council of Canada (1979), Effects of Mercury in the Canadian Environment, Associate Committee on Scientific Criteria for Environmental Quality, Ottawa, Canada, NRC Publication, No. 16739

Peavy, H. S., Rowe, D. R. and Tchobanoglous, G. (1985), Environmental Engineering, International Edition, McGraw-Hill Publications, ISBN: 0-07-100231-6, pp. 37-38, 436-437, 633.

Poon, C., Clark, A., Peters, C. and Perry, R. (1985), Mechanisms of Metals Stabilization by Cement Based Fixation Process, The Science of the Total Environment, pp. 55-71.

Rahmat, M. N. (2001), Development of Environmentally Friendly Building Material: An Analysis of The Use of Solidified Industrial Waste, Proceedings of the Brunei International Conference on Engineering and Technology - 2001 (BICET 2001), Institut Teknologi Brunei, Bandar Sari Begawan, Brunei, October 9th-11th 2001, pp. 121-130.

Rixey, W. (1999), Organic Leaching Science, Proceedings of the Environmental Protection Agency, Public Meeting on Waste Leaching-Session III: Leaching Science, USEPA, USA, July 22-23, 1999.

Rushforth, S. R., Brotherson, J. D., Fungladda, N. and Evenson, W. E. (1981), The Effects of Dissolved Heavy Metals on Attached Diatoms in the Uintah Basin of Utah, USA, Hydrobiologia, 1981.

Schroeder, H. A. (1968), The Role of Chromium in Mammalian Nutrition, American Journal of Clinical Nutrition.

Shenai, V. A. (1997), Technology of Textile Processing -Volume VI: Technology of Dyeing, 8th Ed., Sevak Publications, Mumbai, India, pp. 30, 143, 373-385.

Shenai, V. A. (1979), Technology of Textile Processing -Volume IV: Technology of Printing, 2nd Ed., Sevak Publications, Mumbai, India, pp. 93-224, 324-403.

Shetty, M. S. (1996), Concrete Technology-Theory and Practice, Fourth Edition, S. Chand and CompanyLimited, New Delhi, India, ISBN: 81-219-0348-3.

Simmons, R. W. (2002), Accumulation of Arsenic and Cadmium in Rice Grain: Implications for Human Health, Water Resources Journal, ESCAP-UN, December 2002, Vol. 213, pp. 27-34.

Slobodchikoff, C. N., and Parrott, J. E. (1977), Seasonal Diversity in Aquatic Insect Communities in an All-year Stream System, Hydrobiologia.

Srivastva, S. B. (1979), Recent Processes of Textile Dyeing, Bleaching and Finishing, S. B. Publications, Delhi, India. pp. 52-82.

Somashekar, R. K. and Siddaramaiah (1997), Heavy Metal Concentrations in Soil and Crops Grown with Metal Rich Industrial Waste Waters, Journal of Industrial Pollution Control, Vol. 13(1).

Tay, J. H., and Show, K. Y. (1991), Properties of Cement Made from Sludge, Journal of Environmental Engineering, Vol. 117(2), pp. 236-246.

Towill, L. E. (1978), Reviews of the Environmental Effects of Pollutants III: Chromium, Cincinnati, US Department of Commerce, National Technical Information Service.

Tchobanoglous, G., Theisen, H. and Vigil, S. A. (1993), Integrated Solid Waste Management: Engineering Principles and Management Issues, Intl. Edition, McGraw-Hill Book Co., Singapore, ISBN: 0-07-112865-4, pp. 107-108.

USDI (1965), Concrete Manual, 7th Edition, United States Department of the Interior- Bureau of Reclamation, USA, pp.145.

USEPA (1983), SW-874: Hazardous Waste Land Treatment, Office of Solid Waste and Emergency Response, US Environmental Protection Agency, USA, April 1983, pp.273.

USEPA (1992a), SW-846: Solid Waste Physical and Chemical Test Methods, Office of Solid Waste and Emergency Response, US Environmental Protection Agency, USA, July 1992.

USEPA (1992b), 40 Code of Regulations, Part 261.31, US Environmental Protection Agency, USA, July 1992.

USEPA (1997), 40 Code of Regulations, Part 268.48, US Environmental Protection Agency, USA, February 1997.

Vaidehi, J., Rao, A. P., Sinha, N., Dave, H. B. and Sood, P. P., (1997), Elimination of Methyl Mercury from Fish Tissues During Gluathione & Vitamin B Complex therapy, Pollution Research **16:**183-187.

Yan, N. D. (1979), Phytoplankton Community of an Acidified, Heavy Metal-contaminated Lake near Sudbury, Ontario: 1973-1977, Water, Air and Soil Pollution.

Yosumura, S., Vartsky, D., Ellis, K. J. and Cohn, S. H. (1980), Cadmium in Human Beings, Ecological Cycling.

APPENDIX -A

HEAVY METALS DIGESTION METHODS FOR SLUDGE

A.1 Extraction Methods for Heavy Metals (except Mercury)

A.1.1 Acid Digestion of Sediment, Sludge and Soils (USEPA Method 3050B)

- 2 gm of sample was taken in a conical flux.
- 10 ml 1:1 HNO_3 is added to make slurry of the sample. The sample was then covered with a watch glass.
- Sample was then heated to 80°C and was reflux for 10 to 15 minutes without boiling.
- Sample was then allowed to cool.
- 5mi of concentrated HNO_3 was added.
- Cover was replaced and the sample was reflux for 30 minutes.
- Above steps were repeated until brown flumes did not generate.
- Watch glass was removed and the sample was evaporated to 5 ml without boiling.
- After cooling, 2 ml DI water and 3 ml of 30% H_2O_2 was added.
- Sample was then returned on a hot plate covering with the watch glass.
- Sample was heated until effervescence subsided.
- After cooling the sample, addition of 30% H_2O_2 in 1 ml aliquots with warming continued until the effervescence is minimal or until the general sample appearance is unchanged (30% H_2O_2 not more than 10 ml in total).
- 5 ml of concentrated HCl and 10 ml of DI water was added and reflux on hot plate was done for additional 15 minutes.
- After cooling, the sample was diluted to 50 ml with DI water and then filter was done.
- Solids were washed with three aliquots of 10 ml DI water.
- Filtrated sample was then diluted by DI water to attain final volume of 100 ml.

A.1.2 Aqua-regia Method

- 1 gm of sample was taken in a conical flask.
- 2-3 ml of DI water was added to obtain slurry.
- 7.5 ml HCl (1:3) and 2.5 ml HNO_3 (1:3) was added.
- The sample was covered and kept overnight.
- Covered sample was then heated for about 2 hours under reflux condition.
- The sample was allowed to cool and the filtration was done.
- Residue was washed with warm HNO_3 (2M).
- DI water was added with through the filter to attain final volume of 100 ml.

A.2 Extraction Methods for Mercury (USEPA Method 7471A)

- Triplicate of 0.2 gm portions of each untreated samples were placed in the BOD bottles.
- Then 5 ml of reagent water and 5 ml of aqua-regia were added to each bottle and were kept in a water bath for 2 minutes at 95°C. Withdrawing from the water bath the samples were cooled.
- Afterwards, 50 ml of reagent water and 15 ml of 5% potassium permanganate solution were added to each sample bottle.
- The bottles were then thoroughly mixed and were placed in the water bath for 30 minutes at 95°C.
- Thereafter, the samples were cooled and 6 ml of sodium chloride–hydroxylamine chloride was added to each sample bottle to reduce the excess permanganate.
- Then adding 55 ml of reagent water and 5 ml of 10% stannous chloride the sample bottles were immediately attached to the aeration apparatus the maximum absorbance was measured using AAS.
- In this way, eventually all the samples were tested (one at a time) soon after the addition of stannous chloride solution.

APPENDIX -B

CONCENTRATION PLOTS OF HEAVY METALS IN LEACHATES

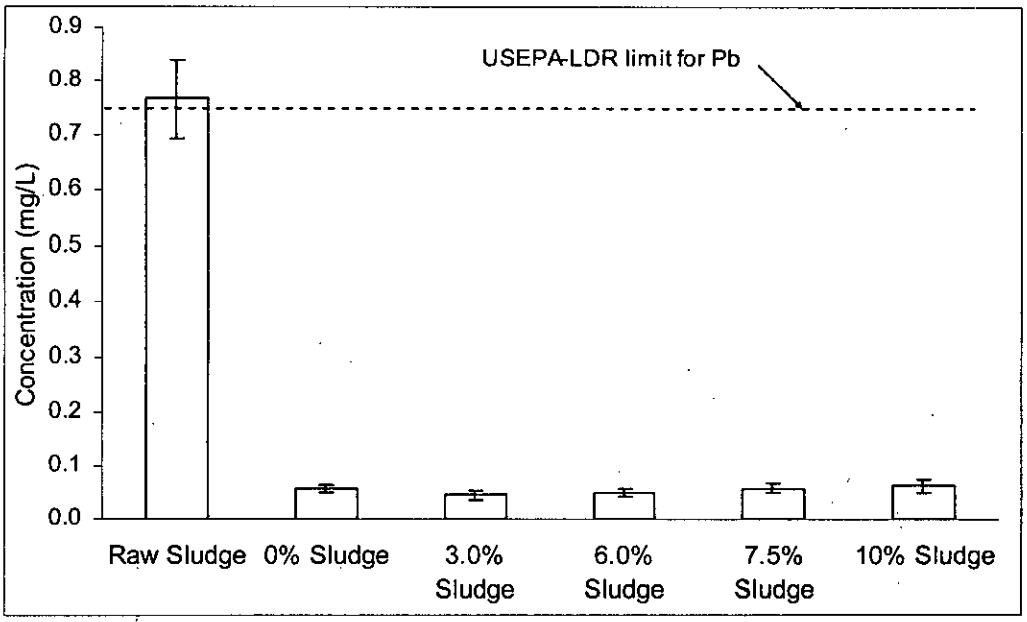

Figure B.1. Results of average concentration of Pb in standard TCLP leachates from raw sludge and crushed concrete sample for sludge S-A.

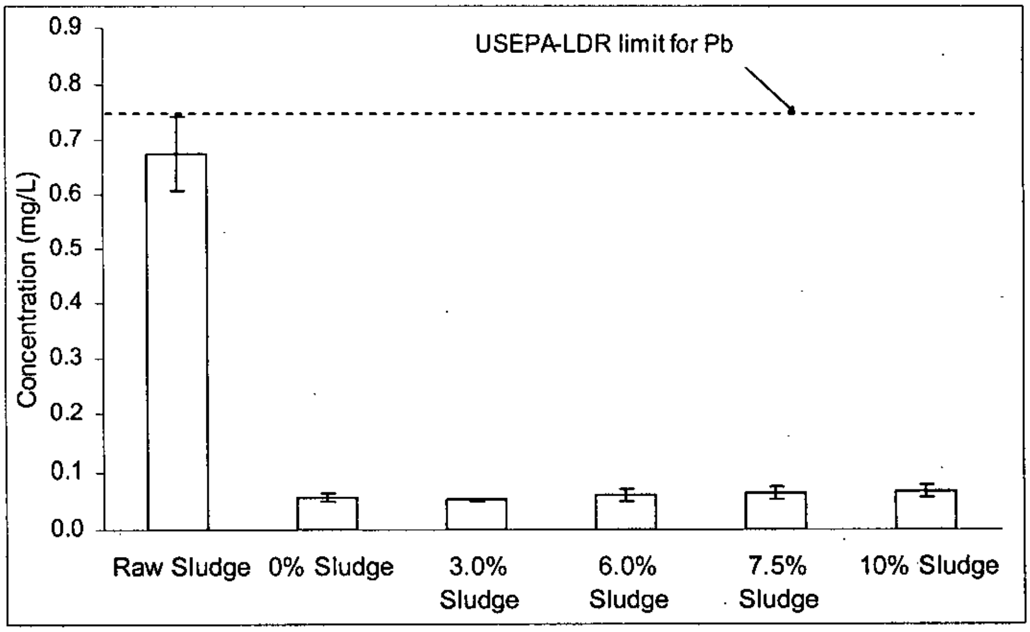

Figure B.2. Results of average concentration of Pb in standard TCLP leachates from raw sludge and crushed concrete sample for sludge S-B.

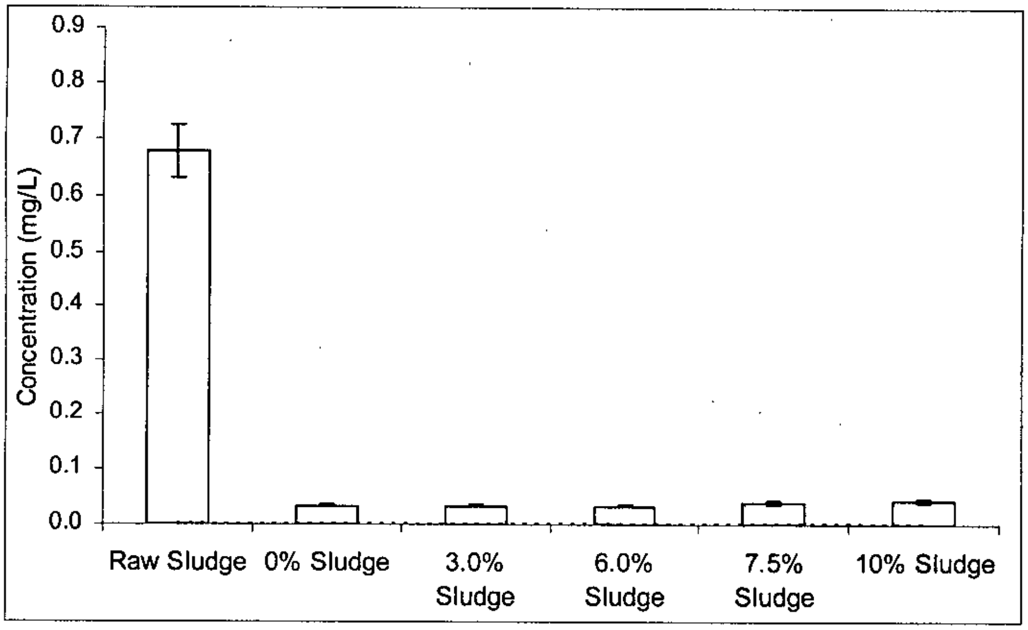

Figure B.3. Results of average concentration of Pb in modified leaching test leachates from raw sludge and crushed concrete sample for sludge S-A.

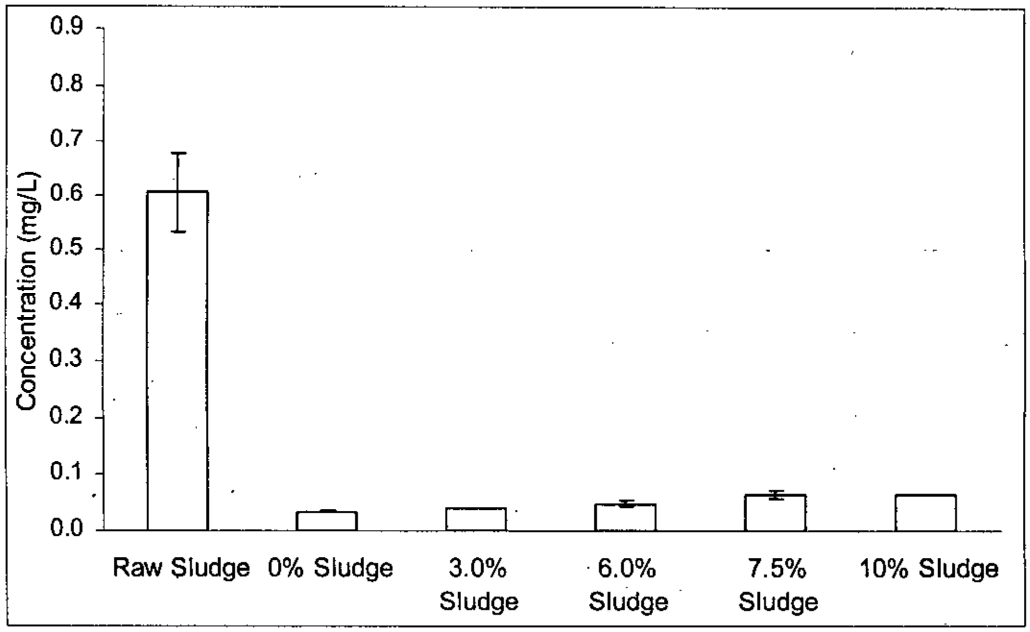

Figure B.4. Results of average concentration of Pb in modified leaching test leachates from raw sludge and crushed concrete sample for sludge S-B.

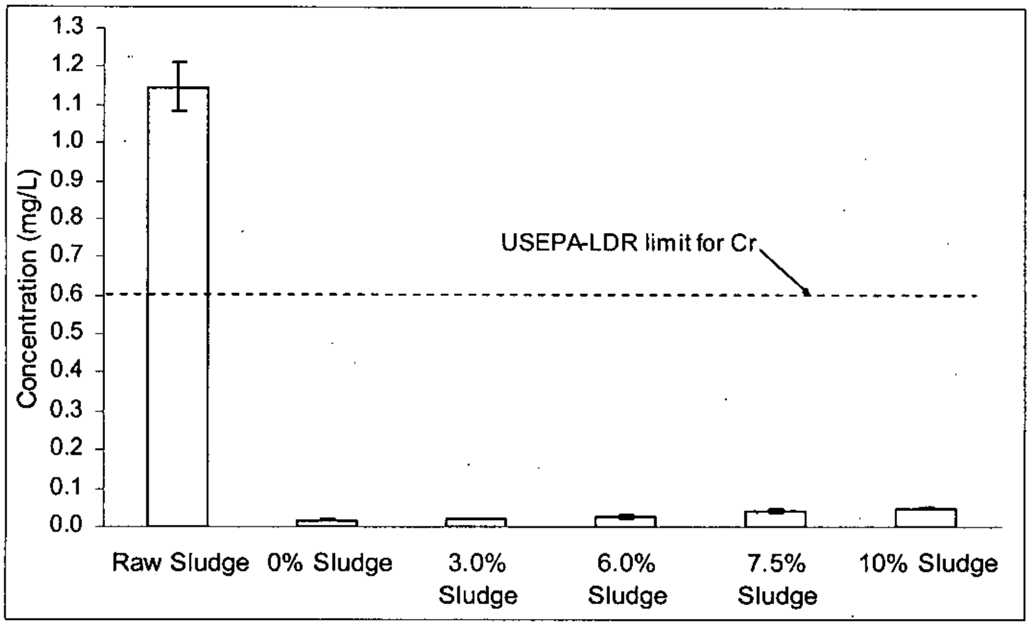

Figure B.5. Results of average concentration of Cr in standard TCLP leachates from raw sludge and crushed concrete sample for sludge S-A.

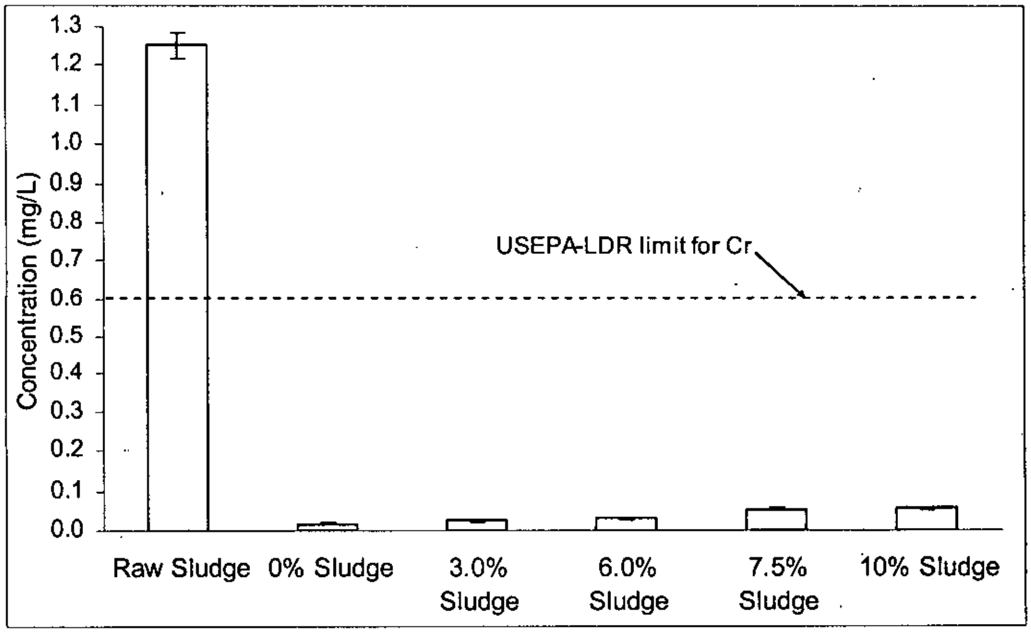

Figure B.6. Results of average concentration of Cr in standard TCLP leachates from raw sludge and crushed concrete sample for sludge S-B.

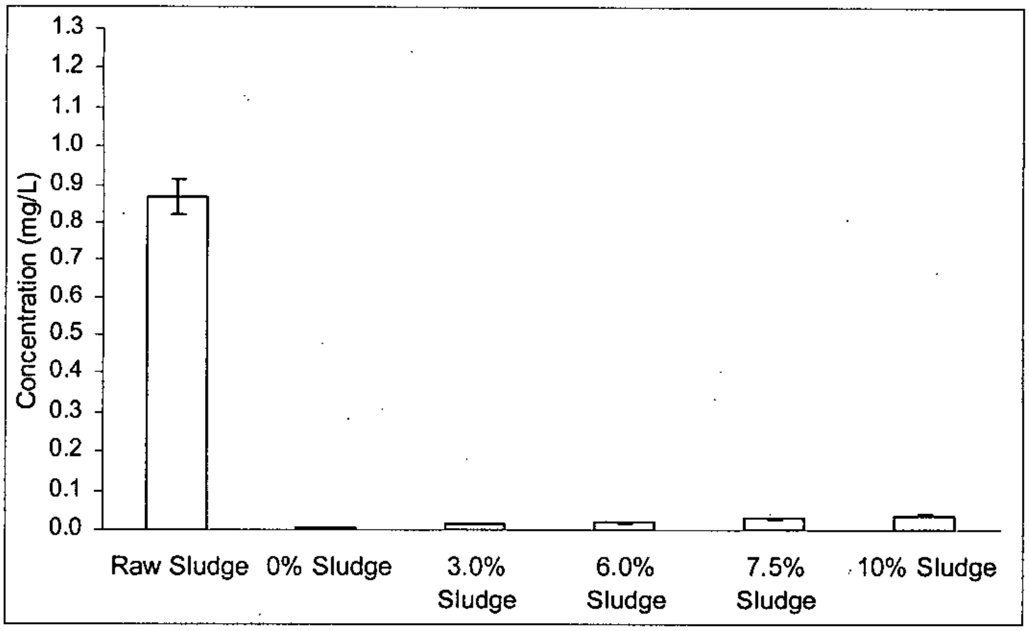

Figure B.7. Results of average concentration of Cr in modified leaching test leachates from raw sludge and crushed concrete sample for sludge S-A.

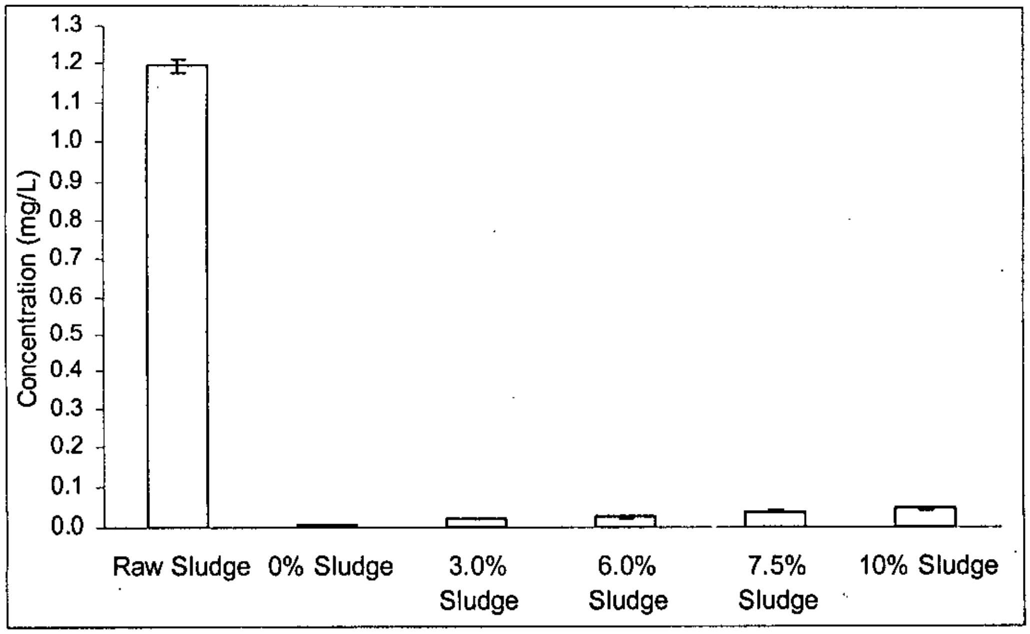

Figure B.8. Results of average concentration of Cr in modified leaching test leachates from raw sludge and crushed concrete sample for sludge S-B.