STABILIZATION OF TANNERY SLUDGE THROUGH BRICK PRODUCTION

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STABILIZATION OF TANNERY SLUDGE THROUGH BRICK PRODUCTION

A thesis

By

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It is hereby declared that this thesis has been performed by the author under the supervision of Dr. Tanvir Ahmed, Associate Professor of the Department of Civil Engineering, BUET. Neither this thesis nor any part of it has been submitted elsewhere for the award of any degree or diploma.

May, 2016

Md. Ariful Islam Juel

DEDICATED

TO

MY BELOVED FAMILY MEMBERS

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LIST OF ABBREVIATIONS
Glossary and Abbreviations

AAS	Atomic Absorption Spectrophotometer
AASHTO	American Association of Standard Highway and Traffic Organization
ASTM	American Standard of Testing and Materials
BDS	Bangladesh Standard
BOD	Biological Oxygen Demand
CETP	Central Effluent Treatment Plant
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
ETP	Effluent Treatment Plant
DOE	Department of Environment
GFAAS	Graphite furnace Atomic Absorption Spectrophotometer
LL	Liquid Limit
OMC	Optimum Moisture Content
PI	Plasticity Index
PL	Plastic Limit
TA	Tannery Sludge
TCLP	Toxicity Characteristics Leaching Procedure
TDS	Total Dissolved Solid
TKN	Total Kjeldahl Nitrogen
UNEP	United Nations Environment Program
UNIDO	United Nations Industrial Development Organizations
USEPA	United States Environmental Protection Agency
ZHE	Zero Headspace Extractor

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ABSTRACT

Chromium-rich Tannery Sludge (TS) has the potential to become a serious environmental burden for Bangladesh in future with very limited safe disposal options. One potential avenue for the disposal and stabilization of TS is by incorporating it in clay bricks and if deemed viable, such application can be practiced in a large scale in the country's huge brick-making industry. However, it must be ensured first that the essential engineering properties of bricks are not diminished and leaching of harmful materials do not occur as a result of incorporation of sludge as a brick constituent. In this study, laboratory experiments have been performed to assess the engineering properties of sludge-amended clay bricks as well as to determine the leaching potential of toxic heavy metals from such bricks. The goal was to explore the viability of chromium-rich TS as a brick constituent and determine the effectiveness of such bricks as a safe option for sludge management.

Clay bricks were prepared with different proportions of sludge (10%, 20%, 30% and 40% by weight) in both laboratory-controlled conditions and field conditions (i.e. in a brick kiln) and its suitability as a construction material was assessed based on its strength, water absorption, firing shrinkage, weight loss on ignition and bulk density. Results of the tests indicated that the sludge proportion and firing temperature are two key factors in determining the brick quality. Increasing the sludge content in bricks resulted in a decrease in compressive strength. On the other hand compressive strength increased with the increase of firing temperature. The compressive strength of TS bricks reduced considerably from 376 kg/cm^2 (36.83 MPa) to 165 kg/cm^2 (16 MPa) when TS content increased from 0% to 40% fired at 1000°C. On the other hand compressive strength increased with an increase of firing temperature for all brick samples. The addition of 40% sludge into the mixture reduces strength approximately 56% compared with the control bricks though all the TS bricks have been found to meet both the Bangladesh and ASTM requirements for building construction material.

Water absorption was increased with the increase of sludge addition but decreased with increasing firing temperature. 10% TS bricks burnt at 1000°C temperature absorbed the minimum amount of water and regarded as Grade S bricks according to BDS 208 (2009) standards. Moreover, it was estimated that an energy saving of 26%

can be achieved with 10% tannery sludge-amended bricks during firing due to calorific power of organic content present in the tannery sludge.

In case of TS bricks made in kiln, the quality was relatively inferior compared to bricks produced in the laboratory due to operating in a less-controlled environment with respect to maintaining adequate compaction and optimum moisture content.

Both the Netherland tank leaching test and TCLP test results indicated that the leaching behavior of several targeted heavy metals (Cr, As, Cu. Ni. Cd, Pb and Zn) have been found to be insignificant and far below the Dutch regulations and USEPA regulatory limits. The leaching concentration of Cr from 10% TS bricks fired at 1000°C was found to be reduced by 90% compared to the original raw sludge. Bricks firing at higher temperatures generally yielded improved engineering properties with lesser tendency of Chromium mobilization. Moreover, air quality may be an issue which was not analyzed in this study.

The recommended proportion of sludge in brick making can be 10% (by dry weight) with 20 to 22% moisture content and fired at 950°C to 1000°C for producing good quality bricks. Results from this study indicate that tannery sludge can be sustainably stabilized in clay bricks and large-scale application of this technique can be envisaged for Bangladesh where both the leather and brick industries continue to be important economic pillars of the country.

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Leather industry in Bangladesh is considered as one with considerable growth and investment potential, earned $1.29 billion from exports in the 2013-14 fiscal which accounts for 4.2 percent of the country's total exports (Hashem et al., 2015). In tanneries, raw skins/hides are transformed into leather by means of a series of chemical and mechanical operations that lead to discharge of hazardous chemicals into effluent treatment plants (ETP) (Tunay et al., 1995). Approximately 80 - 90% of the leather industry uses chromium in hide processing. Basic chromium sulfate is the most widely used tanning material for converting putrescible collagen fibers into non-putrescible leather matrix (Houshyar et al., 2012; Kiliç et al., 2011). Only 60% of the chromium salts react with the raw materials while rest of the chromium salts remain in the exhaust tanning bath and they are subsequently discharged into the wastewater (Cassano et al., 1997). The dissolved chromium and other different types of spent chemicals, namely sulfide, salt, proteins, polyphenolic compounds, surfactants,dyes,syntans etc., present in the wastewater are removed through the chemical precipitation technique using alum, lime or ferric chloride. The precipitated chromium along with the other organic compounds is discharged as sludge (Swarnalatha et al. 2006; Chang et al. 2001). Usually about 100-150 kg of sludge is generated per ton of hides/skins processed (UNIDO 1998) and this chromium rich sludge has the potential to contaminate soil, surface water and groundwater by generated leachate and pose a threat to the environment and natural resources if the sludge is not disposed properly (Thomson et al. 1999)

In conventional physico-chemical cum biological treatment system 70-80 per cent of the sludge is produced in the primary treatment and the remaining 20-30 percent is produced in the secondary biological treatment (UNIDO 1998a). The solids content in the tannery effluent will depend upon the raw material, type of process adopted, chemicals used in the process and other in-plant control measures. The United States of America environmental regulations consider chromium and chromium compounds as hazardous constituents in waste materials (US Environmental Protection Agency 1998). Moreover, the German environmental regulations consider all wastes from the leather and hide processing as hazardous (Basegio et al., 2009)

Tannery sludge (TS) contains elevated concentrations of heavy metals like Cr, As, Pb, Ni, Cu, Zn, and Cd due to use of basic chromium salt, different syntans, dyes, pigments, retanning agents etc. in the tanning process. These heavy metals are very harmful, because of their non-biodegradable nature, long biological half-lives and their potential to accumulate in biological systems (Manahan, 2005; Wilson and Pyatt, 2007; Singh et al., 2004). Metal-containing sludge application in agricultural land is risky, because these metals may be taken up by the crop roots and incorporated into the plant tissue. Ultimately, these toxic metals can get entrance into the human body and lead to bio-accumulation and bio-magnification. Excessive accumulation of heavy metals in agricultural soils through wastewater irrigation and sludge disposal may not only result in soil contamination, but also affect food quality and safety (Muchuweti et al., 2006).

Different techniques used for the disposal of tannery sludge are land-filling, hydrometallurgical methods to recover chromium, incineration and gasification (Basegio et al., 2002). The land-filling scenario is now under increased scrutiny, mainly because of highly-polluting emissions, the low recovery of energy and the limited capacity of available land-fill sites (Swarnalatha et al., 2006; Kirk et al., 2002). The hydrometallurgical method results in high cost and poor quality chromium due to the presence of organic lipolytic components, metals and other impurities (Cassano et al., 1997). Furthermore, this process is associated with the generation of additional effluent.The thermal treatment of sludge involves incineration, gasification, and pyrolysis as a means of disposal, whilst also recovering energy from waste. These are costly and may contribute to air pollution and the residuesof the process still have to be disposed of, but this ismore easily achieved than with untreated sludge (Basegio et al., 2002).

A technique to treat or stabilize hazardous waste is by solidification in construction materials such as brick or concrete which has been applied in several instances for the cases of sewage and textile sludge and arsenic-rich filter materials (Patel and Pandey, 2012; Cusidó and Cremades, 2012; Praveen et al., 2015; Chiang et al., 2009; Hassan et al., 2014). Stabilization refers to techniques that chemically reduce the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms, while solidification refers to techniques that encapsulate the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives. The solidified product may be disposed off to a secured landfill site or it can be recycled as construction materials if it meets the specific strength requirement and can be shown to leach toxic pollutants within acceptable limits (Rouf and Hossain, 2003; Rahmat, 2001)). Several studies have shown that tannery sludge can be effectively stabilized in construction materials such as concrete and ceramic tiles (Basegio et al., 2002; Montañés et al., 2014). Here in this study, experiments are demonstrated to show that tannery sludge can be stabilized in clay bricks, a dominant construction material in Bangladesh.

In Bangladesh, 85000 tons of wet salted hides and skins are processed annually (Paul et al., 2013) and it can be estimated that 19000 tons of partially dried sludge will be generated by the effluent treatment plants if the treatment plant of all tanneries become operational. On the other hand, 45,000 brick kilns in Bangladesh which together produce about 15 billion bricks per year (ESMAP, 2011) and the brick-making industry contributes to about 1 percent to the country's gross domestic product (GDP) (BUET, 2007). Due to unavailability of stone aggregate, brick has become the principal building material for the country's construction industry and will continue to be so in future. Therefore, exploring the brick manufacturing industry as a potential avenue for stabilization of the huge amount of tannery sludge in Bangladesh can be a viable option for commercial application.

The characteristics of sludge-incorporated clay bricks were evaluated with respect to its engineering properties as well as its environmental implications. Clay brick specimens were prepared with different proportions of sludge in both laboratory-controlled conditions and field conditions (i.e. in a brick kiln) and its suitability as an engineering material was assessed based on its strength, deformation, shrinkage, absorption and firing energy characteristics. Leaching test of sludge-incorporated bricks were also carried out to demonstrate the effectiveness of the solidification technique against the release of heavy metals in the environment.

1.2 OBJECTIVES OF THIS STUDY

Specific objectives of the thesis are:

- To assess the environmental viability of stabilization of heavy metals present in tannery sludge by solidification with clay mix in brick production.
- To assess the effect of using sludge (with the clay mix) on the strength and other physical properties of brick.
- To propose an optimum clay-sludge mix proportion that can be used for brick manufacturing paving way towards environment friendly recycling of toxic solid wastes.
- To compare and analyze the quality of sludge-incorporated bricks prepared in a commercial brick company in field condition with respect to those prepared under laboratory conditions.

1.3 OUTLINE OF METHODOLOGY

Raw materials (tannery sludge) was collected from a tannery effluent treatment plant. Upon collection, sludge sample was oven dried for 24 hours at 105°C. Basic physicochemical characteristics, including moisture content, pH, and organic compound was analyzed. Heavy metal content i.e. Chromium, Arsenic, Lead, Nickel, Copper, Cadmium and Zinc was determined by acid digestion with a HNO_3: HCl volume of ratio of 1:3 followed by analysis using FLAAS (Shimadzu AA 6800). The Toxicity Characteristics Leaching Procedure (TCLP) in accordance with USEPA Method 1311 (USEPA, 1992) was used to determine toxic characteristics of sludge.

Clay sample was collected from a typical brick manufacturing industry. Atterberg's limit tests was conducted according to ASTM D 4318 (2000) to obtain the plastic nature of the sludge-clay mixture and compaction test was conducted according to AASHTO T- 99 (1982) to establish the Optimum Moisture Content (OMC) in the brick making process.

Total 75 bricks samples (length 12 cm. width 6 cm and height 3.5 cm) of sludge-clay mixture in varying proportions (10%, 20%, 30% and 40%) at OMC was prepared in the laboratory. A clay-only mixture sample was prepared as a reference specimen. After 24 hours natural drying followed by another 24 hours at 105^{o}C oven-drying period, these samples was heated in an electric furnace (Nabertherm, LH 60/14, Germany) at the rate of 5°C/min up to design temperatures of 900°C, 950°C and 1000°C and held for 3 hours. The produced bricks then received a series of tests including firing shrinkage, weight loss on ignition, water absorption, soundness and compressive strength according to ASTM C67 to determine a suitable condition for producing qualified bricks that meets the BDS 208 (2009) standards. Calorific value of tannery sludge was determined using Bomb Calorimeter (Parr 6100). Energy saving due to the addition of tannery sludge was calculated during firing of bricks using calorific value of tannery sludge. Leaching test of all these burnt brick samples was carried out by TCLP in accordance with USEPA 1311 and Netherland tank leaching test (NEN 7345, 1993).

1.4 ORGANIZATION OF THE THESIS

This study shows the potential of tannery sludge to be incorporated in the clayey bricks in Bangladesh. Chapter 2 introduces a brief review of leather processing including a short description regarding the basic structure, behavior of chromium and some solidification and stabilization techniques of wastes. The latter part of Chapter 2 summarizes the previous work that was done regarding utilization of different types of sludge in the form of ceramic tiles, bricks and concrete. Chapter 3 describes the detail methodology that was adopted in this study. Chapter 4 deals with the results obtained in this study. Chapter 5 is on conclusion where overall findings, limitation and directions for future work have been discussed. At last, Appendix A contains the average results of different mechanical and physical properties of TS bricks. Appendix B contains calculation for energy saving and Optimum Moisture Content (OMC) and Appendix C contains BDS 208 (2009) standards for clay bricks.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter presents characterization of tannery wastewater, treatment technology of tannery wastewater, tannery sludge management and disposal practices, brick manufacturing technology and previous studies on stabilization of sludge through fired clay bricks.

2.2 CHARACTERISTICS OF TANNERY WASTEWATER

Usually tannery wastewater is characterized by strong color, high BOD, high COD, low pH and high dissolved salts. Disposal of these wastes into watercourses or onto land can cause irreversible damage to the environment in the vicinity (Rahman, 1988).

Soak liquor

Wastewater discharged from soaking operation is characterized with high BOD, COD, SS, DS value. The most important pollutants in soaking effluents are: salt, hide surface impurities, dirt and globular protein substances dissolved in water and salt solution. In conventional processing salt-preserved hides are commonly used. Calculated on the basis of wet salted weight, the amount of soaking effluent discharged varies from 7 m^3/t up to 9 m^3/t raw hide. When soaking dry hides, up to 20 m^3 water/t dried hide is required. The salinity of soak liquor is very high, varying from 15,000 to 20,000 mg/l (as cl). Soak liquors undergo putrefaction very rapidly since they contain a large amount of dissolved and suspended organic matters and a favorable pH for the growth of bacteria. The biochemical oxygen demand (BOD) of the soak liquor is usually between 1100 to 2500 mg/l.

Lime and Unhairing liquor

Liming is responsible for the most environmental pollution than other tannery operation. In this operation wastewater is characterized with high pH, COD, BOD, SS, DS, lime value. About 75 % of the BOD and COD load is produced in the beamhouse, with the main load coming from unhairing without hair saving (Rydin and Frendrup 1993)

A significant proportion of the COD (about 45 %) and BOD (about 50 %) load stems from liming/unhairing (UNEP 1991). Liming /unhairing is also the main generator of SS (about 60 %).Sulphides, lime, decomposed hair keratin, globular protein and other non-collagen protein, as well as saponified fractions of native fat constitute the load of liming effluents making them the most polluted wastewater streams. The amount of liming effluents, including washing, fluctuates between 9 and 15 m^3/t raw hide.

Deliming and Bate liquor

It has a high amount of organic matter and ammonical nitrogen due to the presence of soluble skin proteins and ammonium salts used in bating. BOD is usually low. Conventional deliming and bating methods are based on processing pelts in a bath containing salts derived from a strong acid and a weak alkali (mainly ammonium salts) together with proteolytic enzymes. BOD of this waste varies from 1,000 to 2,000 mg/l. The amount of deliming and bating effluents, including washing waters, fluctuates between 7 and 11 m^3/t raw hide. Calcium salts (mainly sulphates), sulphide residues, degraded proteins (collagen and hair) and residual proteolytic enzymatic agents and the like constitute the main pollution load of deliming and bating effluents

Spent pickle liquor

This waste contains a high amount of salt and also free acid. BOD of the waste ranges from 500 to 900 mg/l. However, in most cases spent pickle liquor is not separately discharged since the chrome tanning solution is prepared in the same pickling tank using the spent pickle liquor.

Vegetable tanning effluent

The spent vegetable tan liquor is probably the strongest fraction in a composite tannery effluent. Although its discharge is batch wise or intermittent and constitutes about 10% of the total volume of the effluent, its BOD ranges from 6,000 to 12,000 mg/l. It is acidic in nature and has a persistent color, which is difficult to remove by known chemical or biological method, and a characteristic offensive odor.

Chrome tanning effluent

The spent chrome tan liquor is greenish in color and highly acidic. The waste contains a high concentration of trivalent chromium ranging from 100 to 200 mg/l. Hexavalent chromium is not generally present in the waste chrome liquor because of the reducing agent used and one-bath process is utilized. BOD of the waste is usually about 1,000 mg/l.

Dyeing and fat-liquoring wastes

The effluents from the dyeing and fat-liquoring processes are generally small in volume and discharged intermittently. The principal components are the residuals of various dyes used in a tannery and oily emulsion.

Composite wastewater

The composite wastewater from a tannery is highly colored and foul smelling. It is also alkaline with a high amount of suspended and dissolved impurities. In spite of the highly acidic nature of some of the waste discharges, especially the spent chrome tan liquor including spent pickle liquor, the reason for the total mixed wastewater of a tannery, being in most cases alkaline, is that the amount of lime present in spent lime liquor is usually excessively high and as a result, maintenance the pH of the mixed wastewater in the alkaline range even after reacting with other acidic steams. BOD of the composite wastewater varies from 2000 to 3000 mg/l.

2.3 TREATMENT METHODS FOR TANNERY WASTEWATER

Tanning industry is one of the oldest industries of the world and the problem of treatment and disposal of these wastes is probably as old as the industry itself. Tanneries wastewater effluent is treated in many different ways. There are situations in which an individual tannery applies all the below-described wastewater treatment steps on site. In other situations an individual tannery may apply (on site) only pre-treatment or a part pre-treatment or no treatment at all, sending the effluent to a centralised effluent treatment plant. Nevertheless, a treatment is necessary due to the wide range of toxic effects on the environment caused by untreated tannery effluents and sludges.

The following treatment steps are necessary and will be described in more detail afterwards:

- Physical or mechanical treatment
- Chemical treatment
- Biological treatment
- Tertiary treatment
- sedimentation and sludge handling

2.3.1 Physical and Mechanical Treatment

Usually the first treatment of the raw effluent is the physical or mechanical treatment that includes screening to remove coarse material. Up to 30-40% of gross suspended solids in the raw waste stream can be removed by properly designed screens. Mechanical treatment may also include skimming of fats, grease, oils and gravity settling.

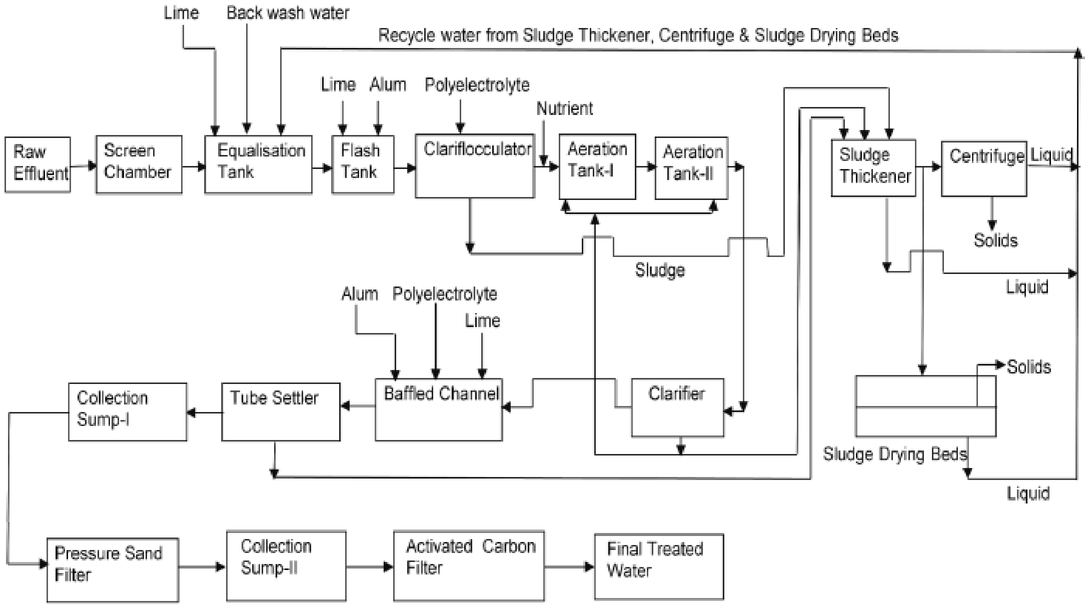

Figure 2.1. Flow diagram of effluent treatment plant of Apex Tannery Ltd. unit-2

2.3.2 Chemical Treatment

Chemical treatment involves the coagulation and flocculation process. Chemicals are added in order to improve and accelerate the settling of suspended solids, especially of fine and colloidal matter. In wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water. They are two distinct processes usually carried out in sequence as a combination of physical and chemical procedures. Finely dispersed solids (colloids) suspended in wastewater are stabilized by negative electric charges on their surfaces, causing them to repel each other. Since this prevents these charged particles from colliding to form larger masses, called flocs, they do not settle. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid. The common coagulating agents used in the treatment of tannery wastewater are alum, ferric chloride, lime and ferrous slufate.

Flocculation is the action of polymers to form bridges between flocs and bind particles into large agglomerates or clumps. In this process it is essential that the flocculating agent be added by slow and gentle mixing to allow for contact between the small flocs and to agglomerate them into larger particles. The newly formed agglomerated particles are quite fragile and can be broken apart by shear forces during mixing. Once suspended particles are flocculated into larger particles, they can usually be removed from

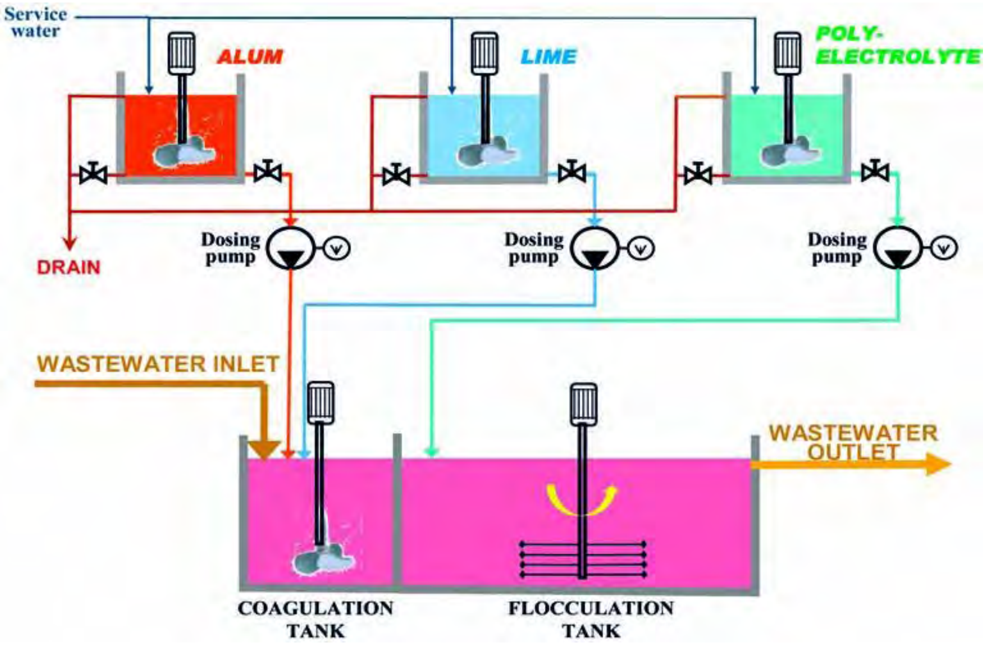

Figure 2.2. Schematic view of the coagulation and flocculation system (UNIDO, 2011)

the liquid by sedimentation, filtration, straining or floatation. The flocculation reaction not only increases the size of floc particles in order to settle them faster, but also affects the physical nature of flocs making them less gelatinous and thereby easier to dewater. The inorganic coagulants are compounds that break colloidal suspensions and help floc forming. The most frequently used coagulants in tannery effluent treatment are alum, lime, ferric chloride and ferric sulphate.

2.3.3 Biological Treatment

In most cases, biological treatment follows chemical treatment, its goal being the removal of biodegradable dissolved and colloidal organic matter. The main objective at this stage is to further reduce the amount of organic (expressed as BOD and COD) and other substances still present in the effluent after the primary treatment and thereby satisfy the standards/limits for discharge into surface waters (rivers, lakes). The biological treatment duplicates processes that take place in nature, but under controlled conditions and, especially, at a highly accelerated pace; however, the efficiency of this treatment largely depends on the biodegradability of the polluting substrate, i.e., its inherent capacity to decompose by biological processes. The remaining suspended and colloidal solids are removed by flocculation and adsorption. While biological treatment may be aerobic, facultative or anaerobic (or some combination thereof), in practice, almost only aerobic systems are used; exceptionally, in countries with a hot climate and where a lot of land is available, facultative (preferably aerated/facultative) lagoons are also used. Due to the inherent characteristics of tannery effluents, primarily their sulphide/sulphate content, in practice, anaerobic treatment is used only in sludge digestion. Among many variations of the aerobic process, the most widely used method is (complete-mix) activated sludge treatment with extended aeration; despite some very interesting features, membrane bioreactors (MBRs) have not made significant inroads in the tanning sector. The activated sludge process is an aerobic, biological process, which uses the metabolism of microorganisms to remove substances causing oxygen demand. The qualitative biochemical reaction taking place in the organic matter stabilization process can be summarized in the following manner:

Inert matter + organic matter + oxygen + nutrients + micro-organisms →

new micro-organisms + CO_2 + H_2O + additional inert matter

Figure 2.3. Aeration tank in operation

Bacteria metabolism has two component parts: Catabolism for energy and Anabolism for synthesis.

(1) Catabolism

$CxHyOzN + O_2$ $CO_2 + H_2O + NH_3$ + energy

(organic matter)

(2) Anabolism

$CxHyOzN$ + energy $C_5H_7NO_2$

(3) Autolysis

$C_5H_7NO_2 + 5O_2$ $5CO_2 + NH_3 + 2H_2O$ + energy

Micro-organisms are stimulated to convert (eat and digest) harmful, oxygen-demanding organic compounds into an environmentally more acceptable form (microorganisms) and low-energy, stable compounds like water and carbon dioxide. The microbial community that does that job comprises various species of bacteria, fungi, protozoa, sometimes rotifers (multicellular animals only found in very stable activated sludge with long retention times), even nematodes, the composition of the population depending on a plethora of factors

2.3.4 Advanced (tertiary) Treatment

Conventional tannery effluent treatment process if properly designed, conducted and operated succeed in reducing many of the pollutants present in the tannery effluent. Significant reduction of 90% or more can be seen in BOD_5, COD, chromium and suspended solids. Conventional processes however are not designed to treat TDS including chlorides. Also unless special arrangements are made, the nitrogen content of the effluent is not specifically addressed.

Under the Regional Programme for pollution control in the tanning industry in South-East Asia UNIDO has been actively looking for methods to improve conventional treatment processes which simultaneously reduce the nitrogen content and give the possibility of dealing with TDS/chlorides present in the effluent. The following technologies relating to the issues mentioned were implemented in pilot demonstration units:

- Mechanical/manual removal of excess salt from wet salted hides and skins
- Reverse osmosis (RO) of treated tannery effluent
- Improved solar evaporation
- Carbon dioxide (CO_2) deliming in a small scale tannery to reduce ammonical nitrogen

A preliminary study had been conducted on the suitability of ultrafiltration for treatment of tannery effluent and as replacement for secondary clarifier in the treatment process. The system uses membrane technology for separation of treated effluent from activated sludge instead of conventionally used settling tanks or dissolved air flotation system. Thus the ultrafiltration system has been integrated in the effluent treatment plant. This process has been patented under the name ZenoGem ®. Separation of the activated sludge from the treated effluent is carried out either by pressure ultrafiltration or through under pressure (vacuum) micro filtration (UNIDO, 1998b)

2.4 DEFINITION OF SLUDGE

Sludge is a semi-solid slurry and can be produced as tannery sludge from tannery wastewater treatment processes. Sewage sludge can be produced from wastewater treatment processes or as a settled suspension obtained from conventional drinking water treatment and numerous other industrial processes. The term is also sometimes used as a generic term for solids separated from suspension in a liquid; this 'soupy' material usually contains significant quantities of 'interstitial' water (between the solid particles).Industrial wastewater solids are also referred to as sludge, whether generated from biological or physical-chemical processes. Surface water plants also generate sludge made up of solids removed from the raw water.

Tannery sludge is a high chromium rich solid waste which can disposed off by landfilling, incineration or can be reused as soil coordinator if chromium content can be reduced.

2.4.1 Sedimentation and Sludge handling

Sedimentation and sludge handling are the last step in wastewater treatment. With sedimentation the sludge in the wastewater treatment plant is separated from the water phase by gravity settlement. After dewatering this sludge by means of filter presses, a sludge cake with up to 40% dry solids can be achieved, whereas belt presses produce a sludge cake with up to 20-25% dry solids. Centrifuges achieve up to 25-45% dry solids and thermal treatment up to 90% dry solids. Energy is an important factor in these processes.

In comparison with sanitary sludges, tannery sludge has greater inorganic matter content, greater heavy metal content, especially chromium and greater sulfur compound content. However, the main stumbling block is the chromium content, with legislation and practice varying a lot from country to country.

2.5 GENERAL CHEMISTRY OF CHROMIUM

2.5.1 Introduction

Many tanning industries had commonly dumped their Cr-containing solid and liquid wastes to neighboring land and water bodies. Although Cr(III) is the predominant species discharged in tannery solid and liquid wastes, the presence of Cr(VI) in groundwater near old tanning industries raised critical questions about the thermodynamic stability of Cr(III). However, in natural systems, manganese oxides can oxidize Cr(III) to Cr(VI). A number of highly contaminated tannery waste disposal sites exist in countries throughout the world. The development of analytical techniques to speciate aqueous Cr, and reports of groundwater contamination of Cr(VI) in the vicinity of old tannery industries, have increased the attention of scientists toward historical sites where tannery waste has been disposed.

2.5.2 Stable Oxidation States of Cr

Chromium exists in a number of oxidation states of variable stability. It is clear from the reduction potential diagram constructed by Neiboer and Jusys (1988) in Figure 2.5 that in solution Cr(III) is the most thermodynamically stable species, because in solution considerable energy would be required to convert it to either lower or higher oxidation states. Although CrO^{2-} is also relatively stable, its high positive reduction potential means that it is also a strong oxidizing agent and therefore unstable in acid solutions in the presence of electron donors such as Fe^{2+}, H_3AsO_3, and $HSO^{3\,-}$ or organic molecules with oxidizable groups (alkanes, alkenes, alcohols, aldehydes, ketones, carboxylic acids, mercaptans, etc.) (Avudainayagam et al., 2003). As Cr(III) and Cr(VI) are the most stable species of Cr in the environment, the chemistry of these species is discussed in greater detail in the following sections.

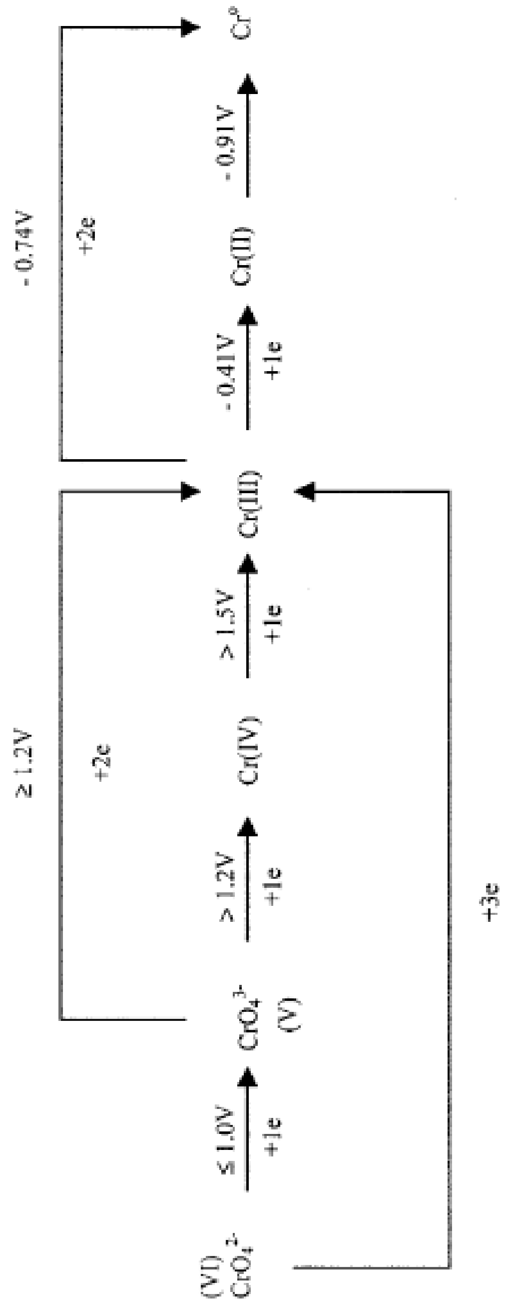

Figure 2.4. Reduction potential diagram for chromium (Nieboer and Jusys, 1988)

2.5.3 Chemistry of Cr (VI)

Hexavalent Cr is a strong oxidizer and consequently Cr (VI) exists only as pH dependent soluble oxygenated species governed by the following equilibria (Nieboer and Jusys, 1988):

$$H_2CrO_4 \Leftrightarrow H^+ + HCrO_4^{\,-} \qquad \log(K_{a1}) = 0.6$$

$$HCrO_4^{\,-} \Leftrightarrow H^+ + CrO_4^{\,2-} \qquad \log(K_{a2}) = -5.9$$

Because in environmental matrices the pH varies only between 3 and 10, $HCrO_4^-$ and CrO_4^{2-} are the dominant species present in natural systems. In addition, at concentrations of Cr(VI) greater than 0.01 M, dimerization of the chromate ion occurs yielding the dichromate ion (Avudainayagam et al., 2003)

$$Cr_2O_7^{\,2-} + H_2O \Leftrightarrow 2HCrO_4^{\,-} \qquad \log(K) = -2.2$$

In biological systems, where the chromate concentrations are below 0.01 M the existence of dichromate is not expected to be significant, especially at physiological pH values of 7 to 8.

2.5.4 Chemical Reactivity of the Chromate Ion

Chromic acid has been used extensively as an oxidizing agent in both organic and inorganic chemistry. Discussing the oxidizing power of chromate, Nieboer and Jusys (1988) concluded that chromate is chemically unstable at physiological pH values, but does not decompose as easily as expected on the basis that it has a highly positive standard reduction potential and a biological half-life in hours. The chromate ion is kinetically nonlabile because it is difficult to displace the oxygen atoms from the chromate ion (CrO_4^{2-}). In contrast, the hydroxyl group of the monoprotonated form of chromate ($HCrO_4^-$) is more readily replaced.

2.5.5 Chemistry of Cr(III)

Trivalent Cr species are generally considered to be nonlabile because ligand displacement is slow (hours to days at room temperature) compared to most other metal ions (10^{-9}–10^{-3} sec at room temperature). Due to this kinetic inertness, many Cr(III) complex species can be isolated that are stable in solution. As other trivalent metal ions, namely, Fe(III) and Al(III), the hydrated Cr(III) ion, $Cr(OH_2)_6^{\,3+}$, has a tendency to hydrolyze and this step is often accompanied by polymerization. Hydrolysis involves the conversion of a bound water molecule to the hydroxide ion and results in the release of a proton. Equilibrium measurements have identified the existence of the following species: $Cr(OH)^{2+}$, $Cr(OH)^{2\ +}$, $Cr(OH)_3(S)$, $Cr_2(OH)_2{}^{4+}$, $Cr_3(OH)_4{}^{5+}$, and $Cr_4(OH)_6{}^{6+}$ in solution (Avudainayagam et al., 2003)

2.5.6 Toxicity to Plants and Microorganisms

Plant growth studies in solution cultures with low levels of Cr have indicated that although Cr is essential for human and animal nutrition it might not be an essential component of plant nutrition (Avudainayagam et al., 2003). Although $CrO_4{}^{2-}$ exhibited toxicity effects in plants at concentrations between 18 and 34 mg/kg dry wt it was observed that barley crops could tolerate a Cr-spiked nutrient solution up to 5.0 mg/L (Skeffington et al. 1976), although at 5.0 mg/L a yield reduction of 75% was observed. Generally Cr accumulates in the roots of plants more than in the shoots. Mishra et al. (1997) also observed this tendency of Cr accumulation in roots of a paddy crop grown under flooded conditions. Glasshouse plant growth studies using tannery sludge-treated soils have shown toxicity of Cr when sludge was applied at a rate exceeding 3 gm/kg, and a significant yield reduction was also observed (Avudainayagam et al., 2003). In this study the toxicity was attributed to the presence of Cr(VI) in the amended sludge. Cr (VI) has adverse effect on microorganism. About 10–12 mg Cr(VI)/L was inhibitory to most of the soil bacteria in a liquid media, whereas at this level Cr(III) had no effect. Studies using the Microtox test (Beckman Instruments, Carlsbad, CA) have shown that Cr(VI) is approximately twice as toxic as Cr(III) in the Photobacterium phosphoreum-based test at the optimum pH of 6.5. Two Cr(VI)-resistant bacteria were isolated from the tannery waste-contaminated site at Adelaide and studied for Cr(VI) toxicity. The growth of Arthrobacter sp. was not affected by Cr(VI) up to 50 mg/L whereas 10 mg/L was toxic to Bacillus sp. (Megharaj et al., 1999).

2.5.7 Toxicity to Animals and Humans

Systemic toxicity may occur in both the oxidation states, mainly because of increased absorption of Cr through broken skin that results in renal chromate. toxicosis, liver failure, and eventually death. Acute exposure of rats to Cr(VI) by various routes of administration affected mainly the liver and kidneys (USEPA 1980). Soluble salts of chromates are also highly toxic when administered parenterally (intravenously), with an LD_{50} of 10–50 mg/kg, compared to LD_{50} values of 200–350 and 1500 mg/kg obtained from dermal or oral exposure, respectively (Carson et al., 1986). Conversely, oral administration of Cr(III) compounds is relatively nontoxic. Studies using rats and mice indicated oral LD_{50} values of 1.87 and 3.25 gm/kg for $CrCl_3$ and $Cr(NO_3)_3$, respectively. The oral LD_{50} of $Na_2Cr_2O_7$ in humans is 50 mg/kg. Other effects of Cr(VI) poisoning include gastric distress, olfactory impairment, nosebleeds, liver damage, and yellowing of the tongue and teeth (Avudainayagam et al., 2003).

2.5.8 Chemistry of Soil Cr

The concentration of Cr in soil is determined by the amount present in the parent material from which the soil was formed, plus the amounts added through wind, water, and human activities, minus the amounts removed through leaching, surface runoff, volatilization, and phyto-uptake. The literature contains numerous reviews on the chemistry of Cr in soil and water. These reviews describe factors that influence the transformations between the two stable Cr species of Cr(VI) and Cr(III) in soils (Avudainayagam et al., 2003). The most important of these reactions of Cr in the soil and water environment are summarized in the Cr cycle (Figure 2.6).

2.5.9 Chromium Cycle in Soil and Water

In soil the predominant species is Cr(III). However, Cr(VI) is also found at significant levels. Because Cr(VI) is a toxic species and reduction reactions are more favored in most soil environments, the starting point for the Cr cycle is Cr(VI). The speciation of chromate in soil solution is pH dependent and dominated by $HCrO_4^{-}$ or CrO_4^{2-}. Chromium can be temporally removed from soil by adsorption/precipitation reactions, uptake by plants,

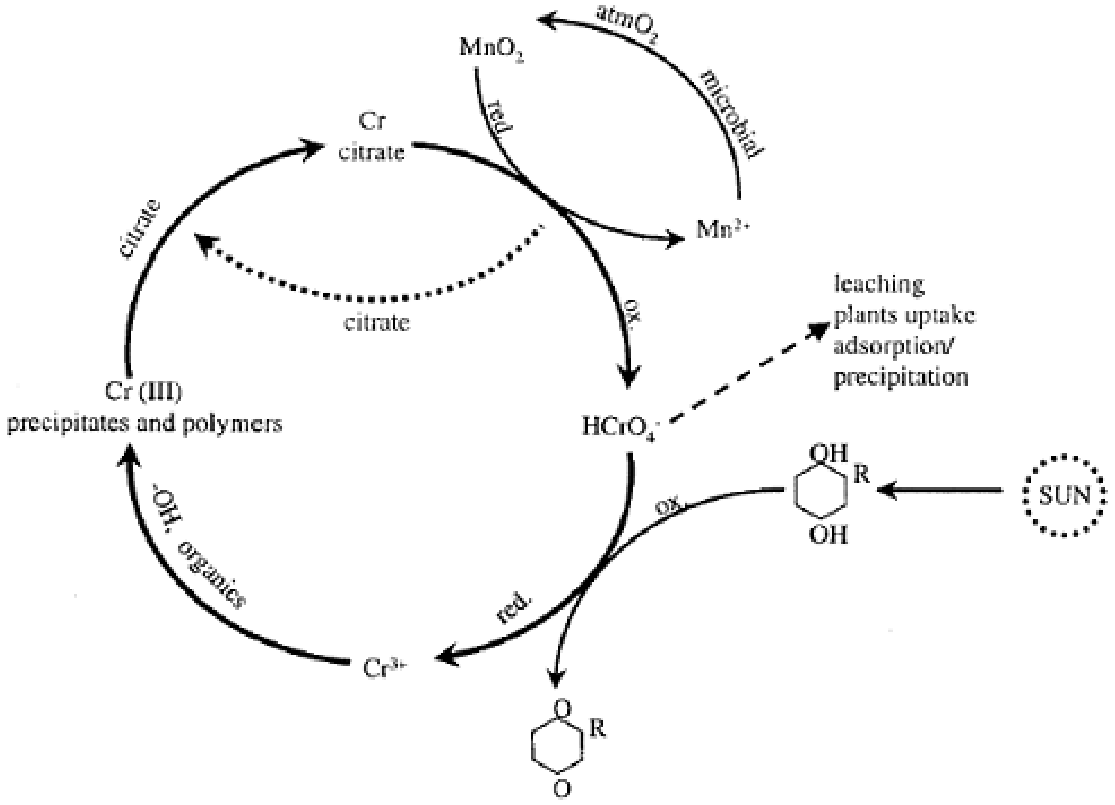

Figure 2.5. Chromium cycle in soil and water.(Bartlett, 1991)

or leaching from the subsurface layers if soil pH and moisture conditions are favorable. Some of the Cr(VI) even undergoes reduction to Cr(III) by carbon during photosynthesis. In addition, species such as Fe^{2+} or S^{2-} or products of microbial decomposition of soil organic matter can serve as the direct electron donors. Bartlett (1991) referred to this step as “dechromification,” and it is the most important part of the Cr cycle. In terms of decontamination, this step is also important because during this step the toxic form of Cr [Cr(VI)] is reduced to the nontoxic form [Cr(III)]. Reduced Cr(III) is typically bound by a variety of ligands in soil solution that render it insoluble, immobile, and unreactive. However, ligands such as citrate can mobilize Cr(III) and deliver it to MnO_2 surfaces where both the organic ligand and Cr become oxidized. MnO_2 surfaces are formed by the oxidation of Mn by either atmospheric O_2 or soil microbes. Sometimes the organic ligand is recycled because Mn(III) formed by reverse dismutation accepts electrons from the Cr(III) in preference to those from the organic ligand and therefore only Cr is oxidized. When organic ligands are in excessive concentrations they tend to induce reverse dismutation of MnO_2 by binding the Mn(III), and this Mn(III)–organic complex may prevent the formation of Cr(VI) or reduce Cr(VI) as fast as it forms, short-circuiting the cycle or speeding up cycling (Bartlett, 1991). For the present review, most attention was directed toward the first step of the Cr cycle, i.e., partitioning of Cr in soil fractions, soil solution factors influencing adsorption and desorption of Cr(VI), and reduction of Cr(VI) to Cr(III) in soils. In the following sections, the first reactions of the Cr cycle involving both the Cr species are reviewed and the implications for tannery waste-contaminated soil are discussed.

2.5.10 Adsorption and Desorption of Cr(III)

Cr(III) sorption and desoprtion kinetics are important determinants of the availability of soluble forms of Cr for further oxidation to toxic Cr(VI) in soils. Cr(III) has been shown to be sorbed strongly on to soil minerals, to be bound to soil organic matter, and to form mineral precipitates (Bartlett, 1991). Sorption of Cr(III) decreases when other inorganic cations or dissolved organic ligands are present in solution. The mechanism of Cr(III) sorption on silica forming a monodentate surface complex on silica. the geochemical parameters of soils such as organic content, type of clay mineral, presence of complexing ions, and redox potential are very important for controlling metal uptake. Montmorillonite (in bentonite and smectite) shows the highest retention of Cd, Cr(III), and Pb among all minerals and soil materials, whereas illite and kaolinite show lower retention than the soils. The clay mineral montmorillonite shows highest retention because due to its highest surface activity. The difficulty in displacing Cr from smectite indicates that the Cr is bonded specifically because if Cr was held through outer sphere complexes, the smallest hydroxy polymers would be readily displaced by Ca, While the montmorillonite was still wet, the adsorbed Cr could be easily exchanged with other cations but, upon drying, Cr becomes virtually nonexchangeable (Avudainayagam et al., 2003). The interlayer region collapsed due to loss of water, Cr came into close contact with the siloxane surface, allowing inner sphere complexes to form. Cr(III) is held strongly, likely through covalent bonds, and its displacement is extremely difficult through simple exchange reactions. However, the potential for Cr(III) to be oxidized to the more toxic Cr(VI) form is of some concern because of the instability of bonding under strong oxidizing conditions. Both adsorption and precipitation reactions and both specific and nonspecific reactions are possible for the retention of Cr(III) in soils. However, organically complexed Cr(III) could be available in soil solution even at high soil pH for oxidation to toxic Cr(VI) in soils.

2.5.11 Oxidation of Cr(III) to Cr(VI)

Oxidation of Cr(III) to Cr(VI) represents a significant environmental hazard because a relatively nontoxic species is transformed into a more toxic one. Manganese oxides are the only naturally occurring oxidant of Cr(III) and oxidation of Cr(III), in the presence of MnO_2, was first observed by Bartlett and James (1979). They noted that Cr(VI) was present in the effluents of most soils reacted with Cr(III). Even the manganese oxide with the highest zero point charge and the most crystalline structure, pyrolusite, is an effective oxidant of Cr(III).

Adsorption of Cr(III) by Mn oxides is possibly the first step in its oxidation by Mn. In soils, manganese oxides typically accumulate on the surface of clay and iron oxides at relatively high redox potentials. McKenzie, (1977) noted that Mn minerals tend to have large surface areas and high negative charge at all but extremely acidic pH. These properties are associated with high adsorptive capacities, particularly for heavy metals. Cr(III) can be oxidized to Cr(VI) in the presence of Mn^{4+} where Mn^{4+} acts as the oxidizing agent and is reduced to Mn^{2+}, as shown by the equation:

$$2Cr^{3+} + 3MnO_2 + 2H_2O \Leftrightarrow 2CrO_4^{2-} + 3Mn^{2+} + 4H^+$$

Effect of pH

Bartlett and James, (1979) studied the influence of pH from 3 to 10 on Cr(III) oxidation in a soil having 1200 mg/kg of 1 M HCl extractable manganese. In this study, the soil solution was shaken for 0.5 min of every 2 min for 18 hr. They observed that at pH 3.2 all the Cr(III) was oxidized to Cr(VI) and that about one-quarter of the Cr(VI) formed was adsorbed by soil. The oxidation and adsorption decreased with increasing pH. The percentage of Cr(III) oxidation to Cr(VI) decreased from 100% to 30% at pH 6 and stayed constant at 30% up to pH 9. They used a large solution/soil ratio (2000 : 1) to control the change of pH caused by addition of $CrCl_3$ to the soil.

Solubility of Cr(III) and Oxidation

As previously discussed, solubility and availability of Cr(III) in soil solution are critical for the oxidation of Cr(III) to Cr(VI) in soils, although at soil pH > 5.5 the solubility of Cr decreases due to its precipitation as $Cr(OH)_3$. Complexation of Cr(III) with some of the low molecular weight organic acids such as citrate and gallic acid increases its solubility and mobility even at higher pH, thereby facilitating its oxidation. Milacic and Stupar (1995) studied the oxidation of Cr(III) in tannery waste amended to three soil types. Their fractionation study showed that after 5 min 1.1% of the total Cr added was oxidized in clay, 0.45% in sand, and only 0.03% in peat soil. The degree of Cr(III) oxidation was found to be proportional to the concentration of manganese (IV) oxides and water-soluble Cr(III) in the soils. They also observed a decrease in the concentration of water-soluble Cr and Cr(VI) on continuance of the experiment because Cr was redistributed to more sparingly soluble fractions.

2.6 TANNERY SLUDGE MANAGEMENT AND DISPOSAL PRACTICES

There is certainly no universal solution for sludge utilization/application. Each ETP produces sludge of specific characteristics and different regions and countries have quite different regulations regarding sludge utilization. Therefore, prior to any ETP construction, a detailed assessment of options should be prepared and the most suitable application proposed (UNIDO, 2011). A number of solutions for utilization and/or safe disposal of tannery sludge have been proposed, practiced, tested, and applied at pilot and industrial scale. These are landfill, composting, anaerobic digestion, thermal treatment, pyrolisys, solidification and stabilization process (UNIDO, 2011).

2.6.1 Landfilling

Utilization or safe disposal of sludge generated by tannery effluent treatment plants poses a challenge worldwide; landfill disposal should be considered only in case when no other viable option is possible. Unfortunately, in some areas and/or developing countries properly designed and constructed landfills are not available either (UNIDO, 2001).

The main drawback of landfilling of sludge is that a new landfill area must be used. In many countries it will not be allowed to use landfills for deposition of sludge with an organic content above 5 %. In general, sludge disposal on landfill gets less and less acceptance. Odour problems seem mostly to depend on disposal of sludge that is not sufficiently stabilized (Ahamed and Kashif, 2014).

With the technical assistance of UNIDO, CETP-Ranitec in Ranipet, Tamil Nadu, India, established a pilot scale landfill in October 1997. The capacity of the landfill, constructed in four rectangular cells, is 3300 m^3. The landfill had been constructed as a shallow basin in cement concrete due to the high ground water table at site. The bottom of the landfill consisted of one layer of 50 mm of sieved sand, a 0.6 mm LDPE sheet on top of it and another layer of 50 mm sieved sand, covered by mass concrete of 50 mm thickness. The sides were also sealed with 50 mm pre cast cement concrete slabs, pointed with cement mortar. For leachate collection, channels on four sides of the cell, covered by pre-cast concrete slabs, had been made. The floor as well as the channels sloped towards one corner of the cell where a leachate collection sump was provided. Dumping of the sludge was done manually using trolleys. The sludge dumped remained partly below ground but mostly above the landfill embankment. Three cells of the landfill have been filled up and covered, using three different materials – one with clay, the second with LDPE sheet and soil and the third with a mixture of sludge and clay. The results were satisfactory (UNIDO, 2001).

2.6.2 Composting

Composting is a controlled biological process that uses natural aerobic processes to increase the rate of biological decomposition of organic materials. It is carried out by successive microbial populations that break down organic materials into carbon dioxide, water, minerals and stabilized organic matter. Carbon dioxide and water are released into the atmosphere, while minerals and organic matter are converted into a potentially reusable soil-like material called compost. The loss of water and carbon dioxide typically reduces the volume of remaining material by 25–60%. Compost can be used as a soil amendment in a variety of agricultural, horticultural or landscaping applications, as long as appropriate measures are taken to eliminate contaminants and impurities from the finished product. The release of organic acids may decrease the pH and production of ammonia from nitrogenous compounds may raise the pH. At higher pH levels, more ammonia gas is generated and may be lost to the atmosphere. A pH value between 6.5 and 8.5 is optimal for compost microorganisms. As bacteria and fungi digest organic matter, they release organic acids (Renkow and Rubin, 1998). The standard physicochemical parameters required for composting is give in Table 2.1.

Table 2.1. Standard Values of Physicochemical Parameters for Composting (Gautam et al., 2010)

S.No	Physicochemical parameters	Standard values suitable for composting
1	pH	5.5-8.0
2	Moisture (%dry basis)	<50
3	Organic matter (%dry basis)	>20
4	Nitrogen (%dry basis)	>0.6
5	Carbon (%dry basis)	30-40
6	C:N ratio (total dry basis)	25-50:1

The important physical parameters requiring consideration include size of constituents, density and moisture content. Smaller size of the constituents aids in faster decomposition of the waste. Wastes of high density reflect a high proportion of biodegradable organic matter and moisture. Low density wastes, on the other hand, indicate a high proportion of paper, plastics and other combustibles. Moisture content indicates water contents of the waste, which is the percentage of the wet weight material to dry material. Microorganisms can only use organic molecules if they are dissolved in water, so the compost pile should have a moisture content of 60-80% of water holding capacity. If the moisture content falls below 40% of water holding capacity the microbial activity will slow down or become dormant. If the moisture content exceeds 80% of water holding capacity, aeration is hindered, nutrients are leached out, decomposition slows, and the odor from anaerobic decomposition is emitted (Gautam et al., 2010).

Ahmed et al. (2007) studied about composting of tannery sludge and focused on the heavy metal characterization and the influence of changing the physico-chemical properties of the medium throughout the composting on the concentrations, bioavailability or chemical forms of Cr, Cu, Zn, Pb and Cd in tannery sludge. The physical and chemical properties of the composted sludge during treatment showed the stability and maturity of end product. Total metal content in the final compost were much lower than the limit values of composts to be used as good soil fertilizer. Furthermore, it was observed in using a sequential extraction method in sludge compost at different phases of treatment, that a large proportion of the heavy metals were associated to the residual fraction (70– 80%) and more resistant fractions to extraction X–NaOH, X–EDTA, X–HNO3 (12–29%). Less than 2% of metals bound to bioavailable fractions X–(KNO3 + H2O). Bioavailable fractions of all elements tend to decrease. Mobile fractions of metals are poorly predictable from the total content.

Santos et al. (2011) investigated the effect of tannery sludge compost (TSC) amendment rates on microbial biomass and activity in Brazilian soils. The soils (sandy and clayey soils) were amended with TSC at rates of 0 (control), 7.5, 15, 30 and 60 Mg ha $^{-1}$ (equivalent to 0, 0.3, 0.6, 1.2 and 2.4 g per 100 g of soil, respectively), incubated at 28 °C for 60 days. Soil Microbial biomass, soil respiration and enzyme activities were evaluated at 15, 30 and 60 days after incubation. The application of 7.5 Mg ha $^{-1}$ TSC significantly increased the microbial biomass and activity. There were no negative or positive effects by the application of 7.5 Mg ha $^{-1}$ on soil enzymes. The results of this study suggested that TSC increased soil microbial biomass and activity when it was amended at a low rate. On the other hand, the amendment with the TSC, in all rates, did not negatively affect the soil microorganisms and their activities.

2.6.3 Incineration

Incineration is the process of direct burning of wastes in the presence of excess air (oxygen) at temperatures of about 800°C and above, liberating heat energy, inert gases and ash. It is a waste treatment process that involves the combustion of organic substances contained in waste materials. The ash is mostly formed by the inorganic constituents of the waste, and may take the form of solid lumps or particulates carried by the flue gas. The flue gases must be cleaned of gaseous and particulate pollutants before they are dispersed into the atmosphere. Net energy yield depends upon the density and composition of the waste; relative percentage of moisture and inert materials, which add to the heat loss, ignition temperature, size and shape of the constituents, design of the combustion system (fixed bed/ fluidised bed), etc.

In practice, about 65% to 80% of the energy content of the organic matter can be recovered as heat energy, which can be utilised either for direct thermal applications or for producing power via steam turbine generators (with typical conversion efficiency of about 30%) (Abajihad, 2012). The combustion temperatures of conventional incinerators fuelled only by wastes are about 760^{0}C in the furnace and in excess of 870^{0}C in the secondary combustion chamber. These temperatures are needed to avoid odour from incomplete combustion but are insufficient to burn or even melt glass. To avoid the deficiencies of conventional incinerators, some modern incinerators utilise higher temperatures of up to 1650^{0}C using supplementary fuel. These reduce waste volume by 97% and convert metal and glass to ash (Abajihad, 2012).

Ash is the weight of residue after combustion in an open crucible. By resource recovery facilities, several solid residuals are produced including bottom ash and fly ash. Bottom ash is the unburned and non-burnable portion. It can contain considerable amounts of metals and glass as well as unburned organics. Fly ash is composed of the micron and submicron particulates that have been collected by the air pollution control system, it must be handled very carefully to avoid fugitive dust emissions, which may be harmful to workers and the surrounding environment. Wastes burned solely for volume reduction may not need any auxiliary fuel except for start- up. When the objective is steam production, supplementary fuel may have to be used with the pulverized refuse, because of the variable energy content of the waste or in the event that the quantity of waste available is insufficient. While incineration is extensively used as an important method of waste disposal, it is associated with some polluting discharges which are of environmental concern, although in varying degrees of severity. These can fortunately be effectively controlled by installing suitable pollution control devices and by suitable furnace construction and control of the combustion process.

The lower calorific value must on average be at least 7000KJ/kg, and must never fall below 6000KJ/kg in any season. Higher calorific value indicates the combustion of waste with a lesser amount of auxiliary fuel support. The amount of energy generated at a waste to energy facility depends primarily on the calorific value of the waste. To facilitate self combustion of waste, the calorific value of the waste should be at least 5000kJ/kg and approximately 6000KJ/kg for power generation

Use of incineration produces relative small volumes of ashes and the constructed landfill may at present sludge production last more than 50 years before it is filled-up. This solution may therefore be seen as a long-range solution especially if methods can be developed to recover chromium from the ashes. If incineration is used it is recommended to use only small additions of inorganic material as these will significantly increase the volumes of ashes and to avoid oxidation of chromium(III) to chromium(VI) that occurs at high redox potentials and at high pH-values. Two other problems in use of incineration is the poor dewatering properties of the sludge that makes incineration energy consuming and the relative small size of the plant to make incineration cost-effective (Ahamed and Kashif, 2014).

One of the most attractive features of the incineration process is that it can be used to reduce the original volume of combustibles by 80 to 95 %. The community is willing to absorb the increased treatment cost. Air pollution control remains a major problem in the implementation of incineration of tannery sludge.

2.6.4 Pyrolysis/ Gasification

Gasification and pyrolysis are similar processes; both decompose organic waste by exposing it to high temperatures. Both processes limit the amount of oxygen present during decomposition; gasification allows a small amount of oxygen, pyrolysis allows none. In other words, gasification and pyrolysis limit or prevent oxidation. The gasification process means treating a carbon-based material with a limited oxygen or steam to produce a gaseous fuel. The gas can either be cleaned and burned in a gas engine, or transformed chemically into methanol that can be used as a synthesis compound. Nowadays, this technology is not used for mass waste but for somewhat homogeneous waste (BREDL, 2009).

Pyrolysis is the application of heat in an atmosphere of zero or limited oxygen to a substance in order to induce chemical decomposition and avoid combustion. Organic material is processed within an enclosed chamber where heating releases valuable gas, leaving residual solids and coke, and in some cases, oil. The gas is afterwards combusted to obtain energy. The residual solids can be land filled or vitrified. Like gasification, pyrolysis is a technology sufficiently developed only for homogeneous waste.

Kantarli and Yanik (2009) investigated the conversion of waste sludge from the tannery industry to useful products by pyrolysis and activation methods. This study showed that sludge from the tannery industry could be effectively used as a raw material for the preparation of activated carbon by both physical and chemical activations. Pyrolysis studies revealed that the temperature was effective on the pyrolysis product distribution. The gaseous product yield increased from 17.5 to 21.9 wt %, while the liquid product and char yield slightly decreased (from 26.8 to 24.3 wt % and 55.7 to 53.8 wt %, respectively) with the increase in the pyrolysis temperature from 450 to 600 °C. The result of pyrolysis gas analysis showed that this gas has a considerable gross calorific value. Therefore, it was suggested that pyrolytic gas from tannery sludge can provide some part of the energy requirements of the pyrolysis process. For the activated carbons derived in this study, the methylene blue, phenol, and Cr(VI) adsorption capacities were investigated and found to be higher than those of most of the commercial and lignocellulosic material-derived activated carbons found in the literature.

2.6.5 Anaerobic Digestion (Bio-Methanation)

In anaerobic digestion (AD) process the organic fraction of waste is segregated and fed to a closed container (biogas digester) where, under anaerobic conditions, the organic wastes undergo bio-degradation producing methane-rich biogas and effluent/sludge. The biogas production ranges from 50 - 150 m^3 /tonne of wastes, depending upon the composition of waste. The biogas can be utilised either for cooking/heating applications, or through dual fuel or gas engines or gas/steam turbines for generating motive power or electricity. The sludge from anaerobic digestion, after stabilisation, can be used as a soil conditioner, or even sold as manure depending upon its composition, which is determined mainly by the composition of the input waste (World Bank, 1999). Fundamentally, the anaerobic digestion process can be divided into three stages with three distinct physiological groups of micro-organisms:

Stage I: It involves the fermentative bacteria, which include anaerobic and facultative micro- organisms. Complex organic materials, carbohydrates, proteins and lipids are hydrolyzed and fermented into fatty acids, alcohol, carbon dioxide, hydrogen, ammonia and sulphides.

Stage II: In this stage the acetogenic bacteria consume these primary products and produce hydrogen, carbon dioxide and acetic acid.

Stage III: It utilizes two distinct types of methanogenic bacteria. The first reduces carbon dioxide to methane and the second decarboxylates acetic acid to methane and carbon dioxide. Factors, which influence the anaerobic digestion process, are temperature, pH (Hydrogen Ion Concentration), nutrient concentration, loading rate, toxic compounds and mixing. For start- up a good inoculums such as digested sludge is required. A temperature of about 35-38^{0}C is generally considered optimal in mesophilic zone (20-45^{0}C) and higher gas production can be 24 obtained under thermophillic temperature in the range of 45-60^{0}C.

The important chemical parameters to be considered for determining the energy recovery potential and the suitability of waste treatment through bio-chemical or thermo-chemical conversion technologies include volatile solids, fixed carbon content, inerts, calorific value, C/N ratio (Carbon/Nitrogen ratio) and toxicity. The desirable range of important waste parameters for technical viability of energy recovery through different treatment routes is given in the Table 2.2.

The parameter values indicated therein only denote the desirable requirements for adoption of particular waste treatment method and do not necessarily pertain to wastes generated/collected and delivered at the waste treatment facility. In most cases the waste may need to be suitably segregated/processed/ mixed with suitable additives at site before actual treatment to make it more compatible with the specific treatment method. This has to be assessed and ensured beforehand. For example, in case of anaerobic digestion, if the C/N ratio is less, high carbon content wastes (straw, paper etc.) may be added; if it is high, high nitrogen content wastes (sewage sludge, slaughter house waste etc.) may be added, to bring the C/N ratio within the desirable range (Abajihad, 2012).

Table 2.2. Desirable Range of Important Waste Parameters for Technical Viability of Energy Recovery (Abajihad, 2012)

Waste Treatment Method	Basic Principle	Important Waste parameters	Desirable Range
Thermo-chemical conversion	Decomposition of organic matter by action of heat	Moisture content	<45%
		Organic/volatile matter	>40%
Incineration		Fixed carbon	<15%
Pyrolysis		Total inert	<35%
Gasification		Calorific value	>5040KJ/kg
Bio-chemical Conversion	Decomposition of organic matter by microbial action	Moisture content	>50%
Anaerobic Digestion/ Bio-Methanation		Organic/volatile matter	>40%
		C/N ratio	25-30

Zupančič and Jemec (2010) investigated the anaerobic digestion potential of different tannery wastes, including fleshings, skin trimmings and tannery wastewater sludge. Conventional semi-continuous and Anaerobic Sequencing Batch Reactor (ASBR) experiments was shown that Organic Loading Rate (OLR) of 4.0 kg m^{3} d $^{-1}$ of VSS (corresponding to 8.5 kg m^{3} d $^{-1}$ of TCOD) represents the limits of successful and economic operation. In the ASBR process with OLR of 3.96 kg m^{3} d $^{-1}$, a SMP of 0.596 m^{3} kg $^{-1}$, and a VSS removal of 71.4% were found. The anaerobic digestion of selected substrates was possible at 268 mg L $^{-1}$ of chromium (VI) and 2650 mg L $^{-1}$ of sodium. The specific methane production potential at 55 °C was estimated to be 0.617 m^{3} kg $^{-1}$ of volatile suspended solids for tannery waste sludge, 0.377 m^{3} kg $^{-1}$ for tannery waste trimmings and 0.649 m^{3} kg $^{-1}$ for tannery waste fleshing. Chromium content and salinity showed no adverse effects; however a reactor temperature reduction of 4.4 °C led to a drop in biogas production of 25%, indicating a requirement to keep the temperature constant at 55 °C.

2.6.6 Solidification and Stabilization (S/S)

The main objective of immobilization technology is to convert the hazardous and toxic wastes into an inert, physically stable mass, with very low leachability and sufficient strength to allow for land filling or land reclamation. Immobilization (or chemical stabilization) is a process in which the waste is converted to a more chemically stable or more insoluble or immobile form.

Solidification or cementation is a process in which the waste is converted to an insoluble rock like material by mixing with suitable material to form a solid product. Encapsulation is the coating or enclosure of waste with an inert durable material. Micro-encapsulation is applied to the individual particles of a waste, while macro encapsulation is applied to the individual practices of a waste, while macro encapsulation is the encapsulation of a mass of waste in a container (UNIDO, 1998a).

The most common material used are cementing agents such as cement, lime, fly ash and gypsum mixtures. However, although highly successful in reducing the morbidity of the waste, these methods often lead to a considerable increase in volumes, thus considerably increase the cost of both transportation and disposal. However, new products based on heat treated natural clays have recently become available. These are capable of absorbing liquid wastes and sludge, either organic or inorganic, to produce products that easily pass normal leachability test. Also used are bitumen, polymers such as polythene, and glass materials which are used in the process called vitrification (but this has largely been applied to radioactive wastes).

These processes which greatly reduce the mobility of wastes in a landfill plays an important role in the disposal of wastes to landfill. Wastes with relatively high concentration of hazardous materials could be immobilized and therefore disposed as a wastes with much lower pollution potential.

The use of solidification and stabilization (S/S) process can greatly reduce the effective concentration of waste disposed at a site and thus could be used to limit the amount of macro-encapsulation in specially designed cells of both inorganic (such as arsenic) and organic wastes (such as pesticides) that are contained in sealed drums. The cell is constructed with in an appropriate containment landfill and is designed to minimize the potential leakage of waste from the cell and is of such a size that damage due to earth movements and earthquakes is likely to be minimal. Macro-encapsulation of inorganics always has an important role to play but it is preferable to incinerate organics rather than encapsulate them.

Solidification and stabilization of sludge uses additives to reduce the mobility of pollutants. It has gained popularity in recent years following strict regulations on land disposal of waste classified as hazardous. S/S is essentially a cost-effective disposal option as compared to landfill disposal for hazardous wastes. S/S typically involves easily available and inexpensive raw materials and simple technologies.

Solidification / stabilization of tannery sludge is a promising emerging treatment / disposal technology. It has not received the same attention as secure land filling. Furthermore it has to be ascertained that S/S does not provide a solution to every disposal problem.

At present S/S can be grouped into seven classes of processes.

- Cement based
- Lime / Pozzolanic
- Thermoplastic
- Organic Polymer
- Encapsulation
- Self-Cementing
- Vitrification

Cement based

Ordinary Portland cement (OPC) and sludge with certain other additive including fly ash or other aggregates are used to form a monolithic, rock like mass. This process improves the physical characteristics and decreases the leaching losses from the resulting solidified waste. Hazardous waste is mixed in a slurry with water and anhydrous cement powder. The mechanism of stabilisation is the formation of hydration products from silicate compounds and water to form a gel. This gel then swells and forms the cement matrix composed of interlocking silicates fibrils and hydration products.

A number of compounds can interfere with the solidification process. Metal salts of tin, manganese, copper, lead and zinc increase setting times and greatly decrease physical strength. Sodium salts as arsenate, borate, phosphate and sulphide act as retarders in cement mixtures. A high pH of the cement mixture tends to keep the metals in the form of insoluble hydroxide or carbonate salts. Certain inorganic or organic compounds present in sludge are often deleterious to the setting and curing of the cement waste mixture. Impurities such as organic materials, silt, clay, coal or lignite may delay the setting and curing of OPC for several days. If some of the inorganic constituents (NaCl, borate, sulphates, hydrates) or the organic constituents (volatile compounds, insecticides, pesticides and fungicides) in the waste are present in large amounts then the only alternative adopted should be S/S.

Additives like clay and vermiculite (sodium silicate bind contaminants in cement fixation) are found to be successful absorbents that can be incorporated into cement waste structures. The setting agent i.e. OPC, reinforces the gelling action of clay and forms a physically stable material which has the ability to entrap and bind the contained wastes. Thus, the waste material is converted into a chemically and physically stable solid stimulating, soil which is claimed to be substantially insoluble in water but is spongy so as to reabsorb water without leaching out to any appreciable extent.

Patel and Pandey (2012) investigated the physical stability and leachability of Portland Pozzolona Cement (PPC) solidified chemical sludge generated from textile wastewater treatment plants. The result showed that the unconfined compressive strength of the sludge–PPC blocks ranged between 2.78–17.42 MPa after 14 days of water curing and 3.62–33.37 MPa after 28 days of curing. The compressive strength was increasing as the blocks were cured for more number of days. The heavy metal concentrations in the leachate was less than the stipulated USEPA TCLP limits showing that leaching of heavy metals from stabilized/solidified materials was not significant. The merits of cement based process are given below:

- Additives are available at a reasonable price
- Process of cement mixing and handling is well developed
- The necessary processing equipment is readily available
- The process is reasonably tolerant of chemical variation of sludge

- The strength and permeability of the final product can be varied by controlling the amount of cement added in the process

The demerits of cement based process are as follows-

- Cement and other additives considerably increase the weight and bulk of the sludge.
- Low strength cement waste mixtures are often vulnerable to acidic leaching solutions. Extreme conditions may result in the decomposition of the contaminants.
- Pre-treatment, more expensive cement types or costly additives may be necessary for stabilisation of waste containing impurities that effect setting and curing of cement.

Lime / Pozzolanic based process

Lime based processes behave similar manner to cement based ones. Pure lime $Ca(OH)_2$ does not form a solid matrix when mixed with water. However, if the lime remains in contact with air, it will slowly absorb CO_2 forming lime stone (calcium carbonate). The same can happen if the lime slurry remains in contact with water containing dissolved CO_2 or sulphur oxides. These reactions require migration of CO_2 from the air or aqueous phase into a solid, which is taking place over years. This is one of the principal reasons why waste treated by lime based S/S processes continue to gain strength for very long period of time.

Lime process based products usually depend on the reaction of lime with a fine-grained silicious (pozzolanic) material and water to produce a concrete like solid. The cementious matrices, chemically and physically, entraps the waste. Pozzolanics, though not cementious in itself, contain constituents which will combine with lime at ordinary temperature in the presence of water to form durable insoluble compounds having such properties. The most common pozzolanic material used in waste treatment is fly-ash., ground blast furnace slag and cement kiln dust.

Swarnalatha et al. (2006) studied the stabilization tannery sludge through this type of stabilization method. In this investigation, the sludge was subjected to starved-air combustion at 800 °C, which prevented the conversion of Cr3+ to Cr6+. The calcined sludge was solidified/stabilized using fly ash, clay, lime and Portland cement as mixture constituents. The solidified specimens were tested for compressive strength and heavy metal fixation. The compressive strength and metal fixation of the calcined sludge (Cs)–fly ash (F)–cement (C) mortar at a ratio of 41.66% Cs, 41.66% F, 16.66% C were 185 kgcm−2 and 93.84%, respectively. The stabilization of chromium (III) in the cement gel matrix was confirmed with scanning electron microscopy.

Lime based techniques suffer from the same type of problems with regard to setting and curing as the cement based techniques. The techniques are generally better suited for stabilising inorganic wastes rather than organic wastes. The decomposition of organic material in the sludge mass after curing can result in increased permeability along with some decrease in the strength of the material. The strength with a greater lime of the final solid is increased with a greater lime concentration. An excess of water is undesirable as in cement based process (UNIDO, 1998a). The merits and demerits of lime based process are given below:

- The additives are inexpensive and widely available
- The equipment required for processing is simple to operate
- The chemistry of pozzolanic reaction is relatively well known

The demerits of cement based process are given below:

- Lime and other additional generally add to the weight and bulk of the waste sludge.
- Stabilised sludge is vulnerable to acidic solutions and setting problems associated with inorganic contaminants in the waste sludge.

Thermoplastic process

This process was initially developed for use in radioactive disposal but later adopted for ultimate disposal of industrial hazardous wastes. Thermoplastic materials include asphalt, bitumen, polyethylene, polypropylene and nylon or other organic plastics capable of reversible softening and hardening upon heating and cooling.

In this process the waste is dried and then mixed with the polymer (usually bitumen) at an elevated temperature (usually 100 °C). The mixture solidifies as it cools and then it is buried in a secondary contaminant system, such as a steel drum.

This process requires a special equipment for heating extremely high volume waste. The bitumen is usually added in a ratio of 1:1 or 1:2 (bitumen : waste). Bitumen process limits the types of waste sludge that can be fixed. Organic chemicals that act as solvents towards bitumen cannot be stabilized. High concentration of strong oxidising salts, e.g. nitrates chlorates of perchlorates, react with bitumen and cause slow deterioration. Variation in the system can be made using organic material such as paraffin or polyethylene.

Leach or extraction testing on anhydrous salts embedded in bitumen as a matrix indicates that rehydration of the embedded compound can occur when the sample is soaked in water and thus can cause the asphalt or bitumen to swell and split apart increasing the surface area and rate of waste loss.

Organic polymer process

This process was developed to solidify waste for transportation. The most extensively tested organic polymer solidification process is the urea formaldehyde (UF) system. In this process monomer is added to the waste and mixed thoroughly. Then a catalyst is added to the mixture and mixing is continued until the catalyst is dispersed. The mixtures is then allowed to cool and harden. The polymerised material does not generally combine chemically with the waste but it forms a spongy mass that traps the solid particles. Any liquid associated with the waste will remain after polymerisation. The polymer mass must often be dried before disposal but is often without drying in containers. This method is used successfully for solidification / stabilisation of phenolic waste.

Encapsulation process

Encapsulation process involves the complete coating or enclosure of waste with a new substance e.g. the S/S additive or binder. In surface encapsulation the waste has been pressed or bonded together is enclosed in a coating or jacket of inert material. A number of systems for coating solidified sludge have been investigated, and the most commonly used process involved the use of a polybutadiene binder for sludge, followed by application of a thin polyethylene jacket around the sludge mass. The encapsulated block is then disposed off.

In most cases, coated material suffers from lack of adhesion between coating and bound waste and lack of long term integrity in the coating materials. The encapsulates have good mechanical strength and are presently undergoing field leaching tests. There are two types of encapsulation viz. Micro encapsulation and Macro-encapsulation.

Micro encapsulation is the encapsulation of individual particles. The process involves in-site polymerisation forming an impervious coating surrounding the waste particles. Organic monomers are thoroughly mixed with the waste and a promoter / catalyst is added to initiate

polymerisation. Macro-encapsulation is the encapsulation of an agglomeration of waste particles or micro-encapsulated materials. The process consists of setting the waste materially in treated or untreated form with an impervious and inert covering. It involves the use of a generally applicable S/S process (e.g. pozzolana, lime, fly ash, cement) to micro encapsulate the contaminant to compensate for potential incomplete contaminant isolation. This is followed by macro encapsulation of the matrix containing the contaminant. Several alternatives exist for macro encapsulation. Improvements have been made with plastic liners and new closures devices. Plastic containers with heat sealed and friction sealed lids have been introduced.

Self cementing process

Self cementing can be applied to waste containing large amounts of calcium sulphate or calcium sulphite (e.g. flue gas cleaning or desulfurization sludge). This process has been developed to treat such wastes so that they become self cementing. Generally about 8-10 % by weight of dewatered waste sulphate / sulphite sludge is calcined under carefully controlled conditions to produce a partially dehydrated cementitious calcium sulphate or sulphite. This calcined waste is then reintroduced into bulk of waste sludge with other proprietary additives. Fly ash is added to absorb excess moisture. The end product is a hard, plaster like material with good handling characteristics and low permeability.

Vitrification process

This process is applied for extremely dangerous chemical wastes and radioactive wastes. The wastes are used / mixed with silica and heated to a very high temperature, and allowed to cool into a glass like solid or a synthetic silicate material. Glass / crystalline silicates are very slowly leached by naturally occurring water. Therefore, these waste products are generally considered safe material for disposal without secondary containment.

Basegio et al. (2009) investigated the immobilization of chromium ion present in the ash from the incineration of chromium-tanned leather shavings (ACS) by means of vitrified ceramic bodies. The immobilization samples were initially produced adding soda-lime glass to ACS. After that, new formulations were produced with the addition of pure oxides, TiO_2 and MgO, to the soda lime glass and ACS sample. These samples were conformed by pressing and fired in an electrical furnace, at temperatures of 750, 800, 950 and 1000 °C. The results confirmed the immobilization of the chromium ion within the allowed limits of Brazilian Regulations, NBR 10004 (5 mg/L), with the use of glass and vitrification/densification agents such as titanium and magnesium oxides.

2.7 MANUFACTURING OF BRICKS

The fundamentals of brick manufacturing have not changed over time. However, technological advancements have made contemporary brick plants substantially more efficient and have improved the overall quality of the products. A more complete knowledge of raw materials and their properties, better control of firing, improved kiln designs and more advanced mechanization have all contributed to advancing the brick industry.

2.7.1 Raw materials

Clay is one of the most abundant natural mineral materials on earth. For brick manufacturing, clay must possess some specific properties and characteristics. Such clays must have plasticity, which permits them to be shaped or molded when mixed with water; they must have sufficient wet and air-dried strength to maintain their shape after forming. Also, when subjected to appropriate temperatures, the clay particles must fuse together.

Clays occur in three principal forms, all of which have similar chemical compositions but different physical characteristics.

- *Surface Clays:* Surface clays may be the upthrusts of older deposits or of more recent sedimentary formations. As the name implies, they are found near the surface of the earth.
- *Shales:* Shales are clays that have been subjected to high pressures until they have nearly hardened into slate.
- *Fire Clays:* Fire clays are usually mined at deeper levels than other clays and have refractory qualities.

Surface and fire clays have a different physical structure from shales but are similar in chemical composition. All three types of clay are composed of silica and alumina with varying amounts of metallic oxides. Metallic oxides act as fluxes promoting fusion of the particles at lower temperatures. Metallic oxides (particularly those of iron, magnesium and calcium) influence the color of the fired brick. The manufacturer minimizes variations in chemical composition and physical properties by mixing clays from different sources and different locations in the pit. Chemical composition varies within the pit, and the differences are compensated for by varying manufacturing processes. As a result, brick from the same manufacturer will have slightly different properties in subsequent production runs. Further, brick from different manufacturers that have the same appearance may differ in other properties.

2.7.2 Method of Manufacturing

The manufacturing process has six general phases: 1) mining and storage of raw materials, 2) preparing raw materials, 3) forming the brick, 4) drying, 5) firing and cooling and 6) de-hacking and storing finished products.

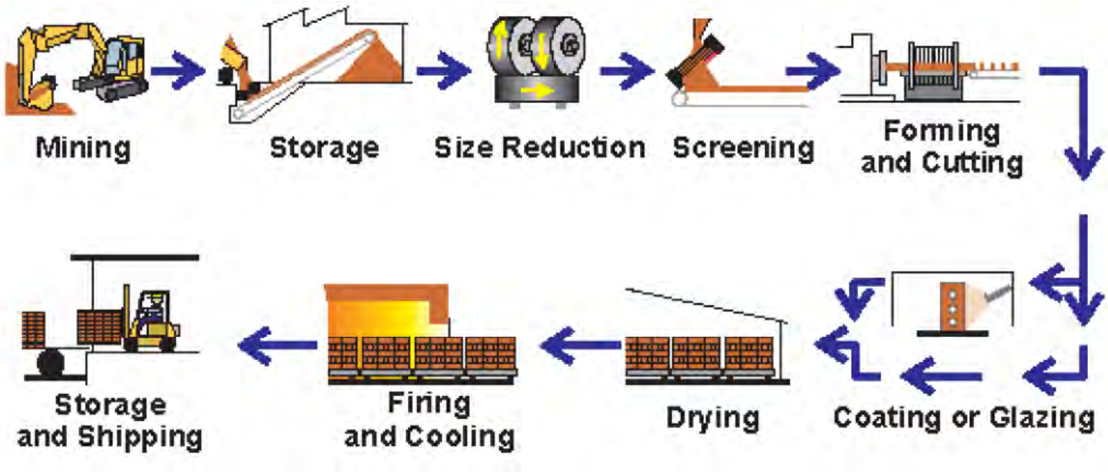

Figure 2.6. Diagrammatic representation brick manufacturing process. Source: (Brick Industry Association 2006)

2.7.2.1 Mining and Storage

Surface clays, shales and some fire clays are mined in open pits with power equipment. Then the clay or shale mixtures are transported to plant storage areas (see Photo 1). Continuous brick production regardless of weather conditions is ensured by storing sufficient quantities of raw materials required for many days of plant operation. Normally, several storage areas (one for each source) are used to facilitate blending of the clays. Blending produces more uniform raw materials, helps control color and allows raw material control for manufacturing a certain brick body.

2.7.2.2 Preparation.

To break up large clay lumps and stones, the material is processed through size-reduction machines before mixing the raw material. Usually the material is processed through inclined vibrating screens to control particle size.

Figure 2.7. Clay is thoroughly mixed with water in pug mill extrusion. Source: (Brick Industry Association 2006)

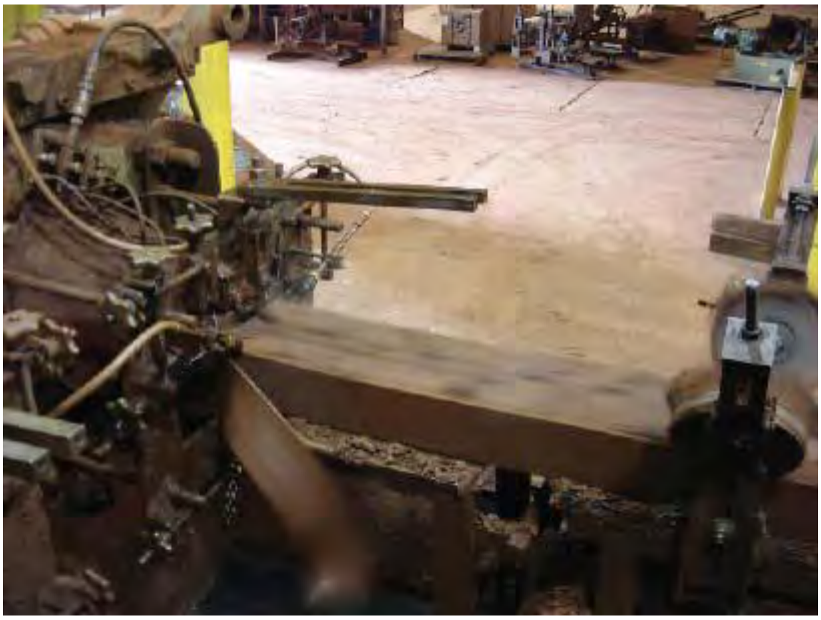

Figure 2.8. Clay is extruded through a die and trimmed to specified dimension before firing. Source: (Brick Industry Association 2006)

2.7.2.3 Forming.

Tempering, the first step in the forming process, produces a homogeneous, plastic clay mass. Usually, this is achieved by adding water to the clay in a pug mill (Figure

2.7) a mixing chamber with one or more revolving shafts with blade extensions. After pugging, the plastic clay mass is ready for forming. There are three principal processes for forming brick: stiff-mud, soft-mud and dry-press.

Stiff-Mud Process

In the stiff-mud or extrusion process (Figure 2.8), water in the range of 10 to 15 percent is mixed into the clay to produce plasticity. After pugging, the tempered clay goes through a de-airing chamber that maintains a vacuum of 15 to 29 in. (375 to 725 mm) of mercury. De-airing removes air holes and bubbles, giving the clay increased workability and plasticity, resulting in greater strength. Next, the clay is extruded through a die to produce a column of clay. As the clay column leaves the die, textures or surface coatings may be applied. An automatic cutter then slices through the clay column to create the individual brick. Cutter spacings and die sizes must be carefully calculated to compensate for normal shrinkage that occurs during drying and firing. About 90 percent of brick in the United States are produced by the extrusion process.

Soft-Mud Process

The soft-mud or molded process is particularly suitable for clays containing too much water to be extruded by the stiff-mud process. Clays are mixed to contain 20 to 30 percent water and then formed into brick in molds. To prevent clay from sticking, the molds are lubricated with either sand or water to produce “sand-struck” or “water-struck” brick. Brick may be produced in this manner by machine or by hand. This process is followed in Bangladesh

Dry-Press Process

This process is particularly suited to clays of very low plasticity. Clay is mixed with a minimal amount of water (up to 10 percent), then pressed into steel molds under pressures from 500 to 1500 psi (3.4 to 10.3 MPa) by hydraulic or compressed air rams.

2.7.2.4 Drying

Wet brick from molding or cutting machines contain 7 to 30 percent moisture, depending upon the forming method. Before the firing process begins, most of this water is evaporated in dryer chambers at temperatures ranging from about 100 ºF to

400 ºF (38 ºC to 204 ºC). The extent of drying time, which varies with different clays, usually is between 24 to 48 hours. Although heat may be generated specifically for dryer chambers, it usually is supplied from the exhaust heat of kilns to maximize thermal efficiency. In all cases, heat and humidity must be carefully regulated to avoid cracking in the brick.

2.7.2.5 Firing

Brick are fired between 10 and 40 hours, depending upon kiln type and other variables. There are several types of kilns used by manufacturers. The most common type is a tunnel kiln, followed by periodic kilns. Fuel may be natural gas, coal, sawdust, methane gas from landfills or a combination of these fuels. In a tunnel kiln brick are loaded onto kiln cars, which pass through various temperature zones as they travel through the tunnel. The heat conditions in each zone are carefully controlled, and the kiln is continuously operated. A periodic kiln is one that is loaded, fired, allowed to cool and unloaded, after which the same steps are repeated. Dried brick are set in periodic kilns according to a prescribed pattern that permits circulation of hot kiln gases. Firing may be divided into five general stages:

1) Final drying (evaporating free water); 2) dehydration; 3) oxidation; 4) vitrification; and 5) flashing or reduction firing. All except flashing are associated with rising temperatures in the kiln. Although the actual temperatures will differ with clay or shale, final drying takes place at temperatures up to about 400 ºF (204 ºC), dehydration from about 300 ºF to 1800 ºF (149 ºC to 982 ºC), oxidation from 1000 ºF to 1800 ºF (538 ºC to 982 ºC) and vitrification from 1600 ºF to 2400 ºF (871 ºC to 1316 ºC).

Clay, unlike metal, softens slowly and melts or vitrifies gradually when subjected to rising temperatures. Vitrification allows clay to become a hard, solid mass with relatively low absorption. Melting takes place in three stages:

1) Incipient fusion, when the clay particles become sufficiently soft to stick together in a mass when cooled;

2) Vitrification, when extensive fluxing occurs and the mass becomes tight, solid and nonabsorbent; and

3) Viscous fusion, when the clay mass breaks down and becomes molten, leading to a deformed shape. The key to the firing process is to control the temperature in the kiln so that incipient fusion and partial vitrification occur but viscous fusion is avoided.

The rate of temperature change must be carefully controlled and is dependent on the raw materials, as well as the size and coring of the brick being produced. Kilns are normally equipped with temperature sensors to control firing temperatures in the various stages. Near the end, the brick may be “flashed” to produce color variations (Brick Industry Association 2006)

2.7.2.6 Cooling

After the temperature has peaked and is maintained for a prescribed time, the cooling process begins. Cooling time rarely exceeds 10 hours for tunnel kilns and from 5 to 24 hours in periodic kilns. Cooling is an important stage in brick manufacturing because the rate of cooling has a direct effect on color.

2.8 PREVIOUS STUDIES ON STABILIZATION OF SLUDGE THROUGH FIRED CLAY BRICKS

Brick is one of the most common masonry units as a building material due to its properties. Many attempts have been made to incorporate wastes into the production of bricks. Recycling wastes such as rubber, limestone dust, wood sawdust, processed waste tea, fly ash, polystyrene and sludge by incorporating them into building materials is a practical solution for pollution problem (Kadir and Sarani, 2012). Baskar et al. (2006) studied the feasibility of incorporation of textile sludge into bricks. 3 to 30% sludge were added to clay bricks and fired at 200°C to 800°C and the different properties of fired bricks were investigated. This study claimed that all brick sample satisfied the weight loss and shrinkage criteria but only 9% sludge mix met the compressive strength criterion. Another paper represented the effect of incorporation of textile sludge, fly ash, cement and quary dust to clay brick (Praveen et al. 2015). The study showed that with increase in sludge content, there was a decrease in compressive strength of bricks. Pulverized and sieved bricks showed better compressive strength when compared pulverized form and grinded form. There was increase in compressive strength with increase in sand, fly ash, cement and quarry dust proportion.

Rouf and Hossain (2003) used 5%, 15%, 25% and 50% of iron and arsenic sludge in clay bricks with firing temperatures of 950°C, 1000°C and 1050°C. In this study, they claimed that 15% to 25% by weight with 15% to 18% optimum moisture content is the appropriate percentage of sludge mixture to be incorporated. The compressive strength test indicated that the strength of the brick depends significantly on the amount of sludge in the brick and the firing temperature. The results showed that 15% by weight is the optimum amount of sludge with a 1000°C firing temperature. However, the strength of the brick can be as high as normal clay bricks with up to 25% sludge at a firing temperature of 1050°C.

Hassan et al. (2014) also studied the effect of using arsenic – iron sludge waste in brick making. This study was involved with the addition of sludge at the ratios of 3%, 6%, 9% and 12% of the total weight of sludge–clay mixture. It was recommended that 6% (by weight) sludge could be incorporated safely to produce good bonding of clay–sludge bricks.

Many researcher studied the feasibility of the application of sewage sludge to clay bricks and got successful results (Weng et al. 2003, Liew et al. 2004, Cusidó and Cremades 2012). These papers reported that though compressive strength decreased with the addition of sewage sludge but strong enough to be used as construction material. Heavy metal concentration from leachate was also within the regulation limit.

Basegio et al. (2002) discussed the utilization of tannery sludge as a raw material for ceramic tiles in Brazil. Tannery sludge and clay were mixed together with different proportions (9%, 10%, 20% and 30%) as the raw materials in this study. The ceramic tiles was fired at 1000°C, 1100°C and 1180°C and was shaped in the mould using the hydraulic pressing method. The study showed that water absorption increased with the increase in percentage of sludge. With an increased firing temperature the water absorption and porosity decreased considerably. A higher firing temperature and a lower amount of sludge showed the greatest dry density of all. This study recommended that a material containing 10% tannery sludge can be used safely considering the environmental aspects. These papers reported the results based on laboratory based studies but not on field condition.

There are about 45,000 brick kilns in Bangladesh which together produce about 15 billion bricks per year (ESMAP 2011) and the brick-making industry contributes to about 1 percent to the country's gross domestic product (GDP) (BUET 2007). Due to unavailability of stone aggregate, brick has become the principal building material for the country's construction industry and will continue to be so in future. Therefore, exploring the brick manufacturing industry as a potential avenue for stabilization of the huge amount of tannery sludge in Bangladesh can be a viable option for commercial application.

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This chapter narrates the working procedure which was followed in this study. The methodology for collection of samples (soil and sludge), analytical procedures to determine characteristics of sludge and sludge – clay mix, preparation and tests for bricks using sludge-clay mixtures and leaching test of bricks are discussed in a sequential manner.

3.2 COLLECTION OF SLUDGE SAMPLES

Sludge samples were collected from Apex Tannery Ltd, unit-2, Gazipur, (Figure 3.1) during January to April 2015. Apex Tannery Ltd. unit-2, a sister concern of Apex Footwear Ltd, is a renowned leather tanning factory in Bangladesh which produces about one million sft. finished leather per year. A bio-chemical Effluent Treatment Plant (ETP) with capacity of 30 m^3/h is employed to treat the wastewater coming from the tannery. Ferrous sulfate ($FeSO_4.18\ H_2O$), Lime ($Ca(OH)_2$) are used as coagulants and polymer is used as flocculent. Sludge generated from chemical and biological treatment is transferred to sludge thickener then to sludge drying beds for drying. Raw sludge was collected from sludge drying beds and six-month and twelve-month aged sludge were collected from stabilized bed (dump site) shown in Figure 3.2 to assess the temporal variation of sludge constituents. The samples were stored and conveyed using polythene bags.

3.3 COLLECTION OF CLAY SAMPLES

Soil samples are collected from Taha Brick Company situated at Atti Bazar, Keraniganj, Dhaka. There are cluster of brick field in this area and meet the partial demand of clay bricks of Dhaka city. Soil sample was collected from different collection site at varying depth. Sample was collected in plastic sandbags. Soil sample was transported up to BUET laboratory without much shock and vibration on the soil sample.

Figure 3.1. Location of Apex Tannery unit – 2 (From Google map)

Figure 3.2. Raw sludge pond and stabilized bed (dump site)

3.4 CHARACTERISTICS OF SLUDGE AND SOIL

The flow chart of this study has been presented in Figure 3.3. The summary of analytical methods adopted in this study of samples has been shown in Table 3.1. Physical characteristics like moisture content, presence of organic compound were tested. Wet method was followed in determining moisture content of sludge samples. Both soil and Sludge samples of 2.5 gm., respectively were taken at ambient temperature. Thereafter samples were oven dried at 105°C for about 24 hours. After oven drying the samples were placed in a desiccator for half an hour. After half an hour, weight of the samples were taken again. Now the reduced weight was divided with wet weight and moisture content was found in terms of percentage. pH was measured by conventional pH paper.

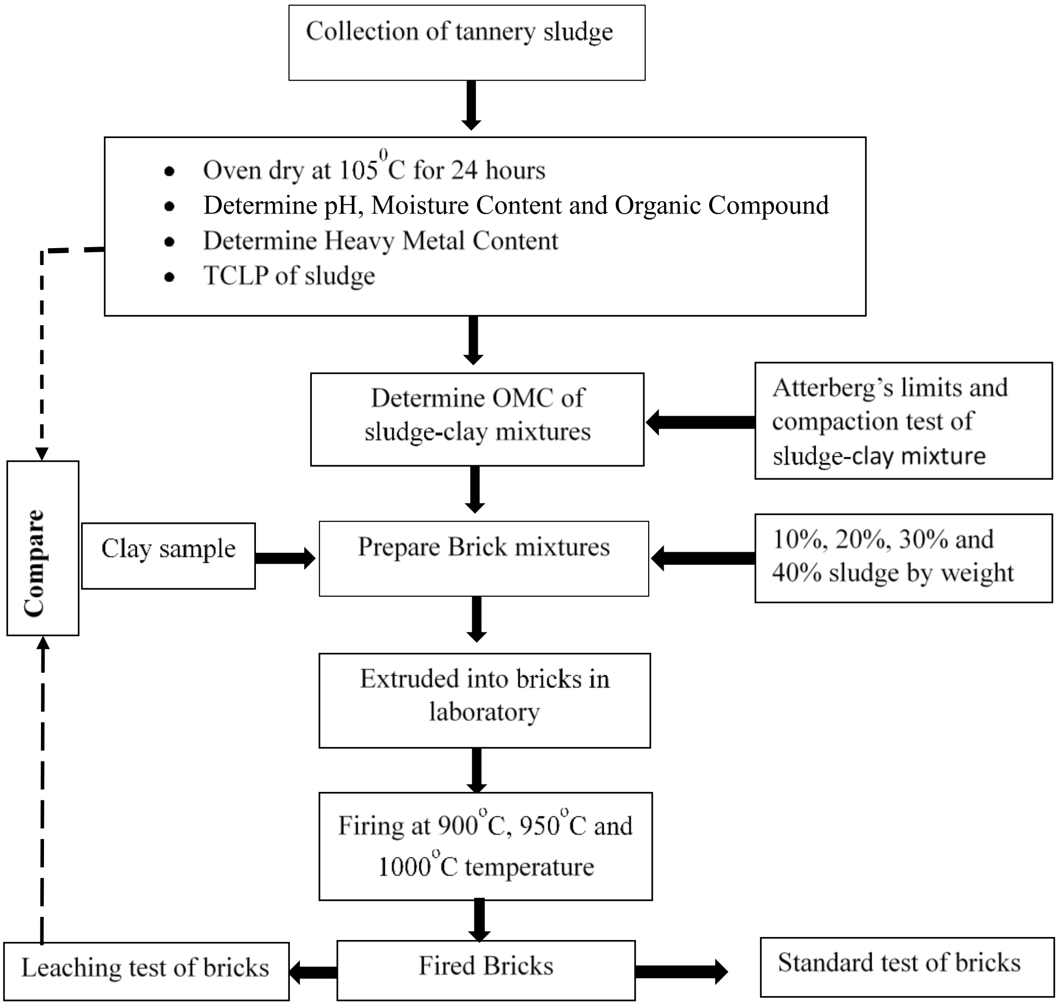

Figure 3.3. Flow chart of the experiment

Table 3.1. Analytical methods for characterization of clay, sludge and bricks.

Parameters	Test method
pH	BS 1377 (1990): Part 2
Moisture content	BS 1377 (1990): Part 2
Organic content	BS 1377 (1990): Part 2
Atterberg limit tests	
Plastic limit	ASTM D 4318
Liquid limit	ASTM D 4318
Plasticity Index	ASTM D 4318
Compaction test	AASHTHO T-99 (1982)
Chemical composition	X-Ray Fluorescence (XRF)
Compressive strength	ASTM C 67
Water absorption	ASTM C 67
Weight loss on ignition	Thermal method
Firing shrinkage	ASTM C 210-95
Total Heavy metal	EPA 3050B & AAS
TCLP	USEPA 1311
Tank leaching test	NEN 7345
Calorific value	Bomb calorimeter (Parr 6100)
Chloride content	BS 1377 (1990): Part 3
Sulphate content	BS 1377 (1990): Part 3
Conductivity	Conductivity meter

Test for organic compound was carried following same procedure for obtaining moisture content with few exceptions. Wet weights of samples were taken at 105°C oven dry condition and dry weight was taken after 550°C oven dry for 6 hours in

Carboilite muffle furnace. Following the same computation formula of moisture content organic content of sludge samples were determined. X-Ray Fluorescence (XRF-1800, Shimadzu) was used to determine the chemical composition of tannery sludge and soil.

3.5 HEAVY METAL DETERMINATION

After collection of sludge, some portion of sludge samples were dried in a vacuum oven at 105°C until constant weight, lightly ground for homogenization and to pass 2-mm sieve. For heavy metal analysis, sample preparation was carried out according to EPA 3050B with a slight variation. 5 gm. of dried sample was digested with acid (HNO_3: HCl =1:3 volume ratio) for 24 hour. After adding 350-400ml distilled water, sample was boiled for 2.5 hour and prepared a 500ml solution. Then, solution was filtered through 0.45 μm pore size filter paper and filtrate was collected to determine the concentration of seven heavy metals (As, Pb, Cd, Cr, Ni, Cu, and Zn) by using Atomic Absorption Spectrophotometer (AAS) (Shimadzu AA 6800) in the environmental engineering laboratory, BUET.

3.6 CHARACTERISTICS OF CLAY – SLUDGE MIXTURE

This heading includes Atterberg limit test and compaction test of sludge – clay mixture.

3.6.1 Atterberg tests

Both air-dry sludge and clay samples were grind into finer particles and passed through 40 number sieve. Clay-sludge mixtures were made with 0%, 10%, 20%, 30% and 40% sludge (by dry weight). Atterberg limit test of these samples were carried out following ASTM D 4318 (2000) for determining liquid limit, and plastic limit. The amount of water which must be added to change a soil from its plastic limit to its liquid limit is an indication of the plasticity of the soil. The plasticity is measured by the “plasticity index” which is equal to the liquid limit minus the plastic limit.

3.6.2 Compaction test

In order to determine the optimum moisture content (OMC), which is an important factor affecting the properties of brick, a standard AASHTO T- 99 (1982) compaction test was used in this study. Air dry samples were grind to pass through sieve number 4. Sample amounting 2.5 kg for each type of mix proportion was taken to determine individual parameters of optimum moisture content (OMC) and dry density corresponding to OMC. 11.68 cm × 10.16 cm diameter mold and 2.49 kg (5.5 lb) hammer was used. Three compaction layer with 25 equal blows per layer was applied.

3.7 PREPARATION OF BRICKS

Sludge and clay samples were lightly ground with porcelain mortar for homogenization. The appropriate amounts of water were determined from the compaction test described in AASHTO T 99 (1982) to obtain the Optimum Moisture Contents (OMC), which gave the maximum dry density of five mix ratios of clay-sludge mixtures. In addition to the corresponding OMC values, additional water of about 2-3% was added (based on the dry mass of each brick) to all the mix ratios while mixing. Total 75 bricks sample (length 12cm, width 6cm and height 3.5cm) of sludge-clay mixture in varying proportion (10%, 20%, 30% and 40%) were prepared in the laboratory as shown in Figure 3.5. Three 100% clay samples were prepared as a reference specimen. The sludge-amended clay bricks were hand-molded by compaction using a rammer. Forma for the preparation of brick samples as shown in Figure 3.4. were prepared with corrugated steel plate. Prepared brick samples were then kept for 24 h for natural drying and followed by another 24 h oven drying at 105°C. All these samples were heated in Carbolite heavy-duty electric furnace (Nabertherm, LH 60/14, Germany) at the rate of 5°C/min up to the design temperatures of 900°C, 950°C and 1000°C, respectively for 3 hours which was shown in Figure 3.6.

A separate set of sludge-incorporated bricks was prepared in a commercial brick kiln (‘field condition’) as per their usual procedure (Figure 3.7). There are two types of brick molding process mostly used in Bangladesh, by hand molding and by automatic pressed molding. In this study hand molding method was used for brick production. The percentage of sludge-clay mix was 10% (by dry weight). After the bricks were manufactured in the kiln, they were subjected to the same tests as were done for those produced under 'laboratory condition'.

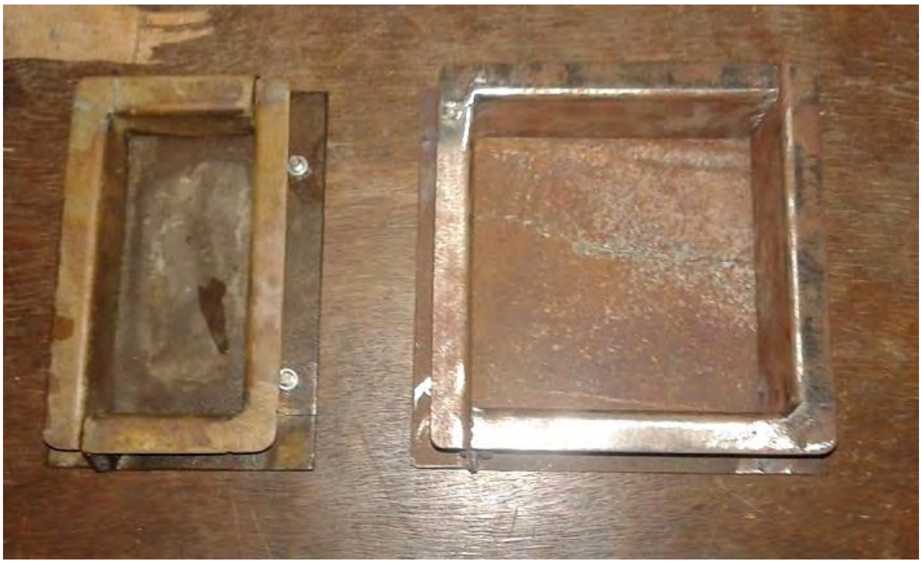

Figure 3.4. Brick forma (replica & half size)

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Figure 3.5. Prepared raw bricks in the laboratory

Figure 3.6. Bricks after firing at muffle furnace (N.B: In Figure 3.6; 0, 1, 2, 3, 4 indicates 0%, 10%, 30% and 40% sludge amended bricks and M & N indicates firing temperature of 1000°C and 950°C, respectively.)

Figure 3.7. Brick prepared in the kiln (Field condition)

3.8 STANDARD TEST OF BRICKS

There are some tests which indicate the quality of bricks by which it can be decided whether these bricks would be suitable to be used as construction materials or not. These test include compressive strength, water absorption, weight loss on ignition, firing shrinkage and bulk density. All these test method are described as follows.

3.8.1 Compressive strength of bricks

The compressive strength test was conducted according to ASTM C 67 method. There are two method viz. Sulfur-Filler Capping and Gypsum capping method. Here Sulfur-Filler Capping method was followed.

Figure 3.8. Compressive strength test machine (Macklow-Smith Ltd. Camberly, London)

The load is applied up to one half of the expected maximum load, at any convenient rate, after which, the controls of the machine were adjusted so that the remaining load is applied at a uniform rate in not less than 1 or more than 2 min. The compressive strength is computed using equation (3.1).

$$C = \frac{W}{A} \tag{3.1}$$

Where,

C = compressive strength of the specimen, kg/cm^2.

W = maximum load, kgf.

A = average of the gross areas of the upper and lower bearing surfaces of the specimen, cm^2.

3.8.2 Water absorption of bricks

Water absorption test of bricks was carried out according to ASTM C 67 method. According to this method brick samples were oven dried at 105°C for 24 h. After drying, the specimens were cooled at room temperature. The dry, cooled specimen were submerged, without preliminary partial immersion, in distilled water at 26 - 30°C for 24 h. Then the specimen were wiped off the surface water with a damp cloth and taken the weight the specimen within 5 min after removing the specimen from the bath. Then, water absorption of the sample is calculated using equation (3.2)

$$\text{Water Absorption, \%} = \frac{100(W_s - W_d)}{W_d} \tag{3.2}$$

Where,

W_d = dry weight of the specimen, and

W_S = saturated weight of the specimen after submersion in cold water.

Figure 3. 9. An arrangement of conducting water absorption test.

3.8.3 Weight loss on ignition

The raw brick samples were oven dried at 105°C until constant mass. The weight of samples were measured after cooling of the samples. Then these samples were fired at defined temperature (900°C, 950°C and 1000°C). Loss of Ignition (LOI) was determined by measuring the weight loss of the sample between the drying and firing stage.

$$LOI(\%) = \frac{100(W_d - W_f)}{Wd} \tag{3.3}$$

Where,

W_d = Mass of oven dried specimens (g)

W_f = Mass of fired specimens (g)

3.8.4 Firing shrinkage of bricks

Total volumetric shrinkage values were obtained by measuring the volume of the samples with a caliper before and after the firing stage using equation (3.4).

$$\text{Firing shrinkage, } (\%) = \frac{100(V_p - V_f)}{V_p} \tag{3.4}$$

Where,

Vp = volume of bricks before firing (cm^3).

V_f = volume of bricks after firing (cm^3).

3.8.5 Bulk density

The weight of fired brick samples and volume of the samples was also measured. Volume was accounted from multiplying the average length, width and height of the sample. Bulk density was measured by the following equation.

$$\text{Bulk density (g/cm}^3\text{)} = \frac{M}{V} \tag{3.5}$$

Where,

M = dry mass of fired brick (g)

V = volume of fired brick (cm^3)

3.8.6 Soluble salt content and Electrical conductivity of bricks

Soluble chloride content and sulphate content was determined according to BS 1377 (1990). 100 gm. sample passing through 2 mm sieve was wetted with 200 ml distilled water in a 500 ml container. Sample was then shaked for 18 hours. After shaking, sample was filtered with 0.45 µm filter paper. Collected filtrate was titrated with silver nitrate for the determination of chloride content whereas sulphate content was determined using DR 4000 Spectrophotometer (HACH, USA).

For the determination of Electrical Conductivity (EC), 50 gm. crushed sample was taken in a beaker containing 150 ml distilled water. Sample was initially stirred and kept for 24 hours, then EC was measured by immersing prove of conductivity meter.

3.9 FIRING ENERGY SAVING

Brick production industries is considered to be one of the highest energy consuming sectors and have a large negative impact on the environment relating to energy use (Koroneos and Dompros, 2007). So savings in energy consumption by incorporating tannery sludge may lead to a sustainable brick production. The firing energy saved due to incorporating sludge can be calculated using equation (3.6) derived by Mohajerani et al.(2016)

$$\text{Energy saved, } \Delta E = \frac{q.m_1 - (q.m_2 - CV.m_3)}{q.m_1} \times 100\% \tag{3.6}$$

Where, q = Specific energy for brick firing, MJ kg $^{-1}$, m_1= mass of clay in control brick (kg), m_2= mass of TS brick (kg), m_3= mass of sludge in TS brick (kg), CV = calorific value of tannery sludge MJ kg $^{-1}$.

The specific firing energy is measured by dividing the firing energy (MJ) with the mass of brick (kg) (Mason, 2007). Whittemore (1994) reported that the specific firing energy varies from 2 - 10 MJ kg $^{-1}$depending on the type of brick and kiln used. A survey report on ASEAN countries conducted in 1993–1994 showed that the specific firing energy consumption was between 2 and 3 MJ/kg (Prasetsan, 1995). In this study, the specific firing energy was assumed to be 2.5 MJ kg$^{-1.}$ The calorific value of tannery sludge is measured using Bomb calorimeter (Parr 6100).

3.10 LEACHING TEST OF BRICKS

The toxicity and leachability tests were carried out to ensure the environmental compatibility of these fired bricks to be used as building materials. In this study, Netherlands Tank Leaching Test according to NEN 7345 (1993) and Toxicity Characteristics Leaching Procedure (TCLP) test according to USEPA 1311 (1992) was followed. The toxicity characteristic leaching procedure (TCLP) test of the sludge samples was carried out according to USEPA 1311 method (USEPA, 1992). In TCLP test, dried samples are ground and passed through 9.5 mm standard sieve. An acetic acid solution (0.57% v/v) was added to samples at a constant ratio of liquid: solid (20:1). The pH of the extraction fluid was 2.88 ± 0.05. After 18 h rotating with rotary mixture at 30±2 rpm, the leachate was filtered with 0.45 µm pore size filter paper and analyzed for Cr, Cu, As, Ni, Cd, Pb and Zn using FLAAS (Shimadzu AA 6800).

Figure 3.10. An arrangement for carrying TCLP test according to USEPA 1311

The NEN 7345 method is generally suited to building materials and mostly followed in Netherlands and EU (Cusidó and Cremades, 2012). To carry out the tests, volume, surface area and mass of brick samples were measured. Each piece of samples was introduced into a polyethylene container and filled with acidified water (with HNO_3 at pH = 4). Volume of extractant fluid in each recipients was approximately 5 times the volume of sample, and the sample was completely submerged with the fluid level not less than 5 cm high from the top of the sample. For each sample, eight extraction were done. The leachate is removed and replaced with fresh extractant fluid 8 times after 0.25, 1, 2.25, 4, 9, 16, 36 and 64 days as per NEN 7345. Leachate obtained from each extraction was filtered through a 0.45 m filter, its pH corrected to 2 with nitric acid and analyzed using FLAAS (Shimadzu AA 6800) for the specified heavy metals. Equation (3.7) was used to compute leachability of heavy metals at the i-th extraction.

$$E_i = \frac{(C_i - C_o)V}{1000A} \tag{3.7}$$

Where, E_i = Leaching of a pollutant at the i-th extraction (mgm^{-2}); C_i = pollutant concentration at the i-th extraction (mg/L); C_o = pollutant concentration in the blank (mg/L); V = volume of extractant agent (L); A = surface area of the entire sample (m^2).

After eight extractions, equation (3.8) was used to compute the leachability, *E*, for the targeted heavy metals.

$$E = \sum_{i=1}^{8} E_i \tag{3.8}$$

Figure 3.11. An arrangement of the leaching test (according to NEN 7345) being carried out in the laboratory with sludge-amended bricks.

CHAPTER 4

RESULT AND DISCUSSION

4.1 INTRODUCTION

This chapter deals with the results obtaining from this study. This chapter presents laboratory experiments to determine the characteristics of sludge and sludge – clay mixtures, engineering properties of sludge-amended bricks and leaching test results of both sludge and sludge incorporated fired bricks.

4.2 CHARACTERISTICS OF SLUDGE

The characteristics of different aged sludge samples were shown in Table 4.1. The pH of sludge samples was found to be 7.56±0.2 and therefore, the sludge can be regarded as neutral. The moisture content of the sludge samples ranged between 60% - 76%. The organic contents of one month, six month and twelve month aged sludge were 33.53%, 27.11% and 24.75%, respectively. This indicated that with the increasing age of sludge the organic content reduced gradually due to degradation of organic substances.

Table 4.1. Characteristics of different aged tannery sludge.

Sludge age (month)	pH	Moisture Content (%)	Organic content (%)
1	7.4	76	33.53
6	7.5	68	27.11
12	7.8	60	24.75
Average	7.56	68	28.46
Standard Deviation	0.2	8	4.5

4.3 HEAVY METAL CONTENT IN SLUDGE

The selected heavy metal concentrations for each sample found in the sludge in this study are shown in Table 4.2, where sample 1, sample 2 and sample 3 represent one-month, six-month and twelve-month aged sludge, respectively. Metal contents ranged over the following intervals: As: 1.52-2.07 mg/kg; Pb: 57.5-67 mg/kg; Cd: < 0.001 mg/kg; Cr: 15,339-26,501 mg/kg; Cu: 261.3- 579.5 mg/kg; Zn: 210.2-329.1 mg/kg and Ni: 137.5-141.3 mg/kg (dry weight basis). Mean concentration of the metals were: As: 1.769 mg/kg; Pb: 63.77 mg/kg; Cd: BDL; Cr: 19,229 mg/kg; Cu: 385.73 mg/kg; Zn: 250.6 mg/kg; Ni: 139.5mg/kg, allowing to arrange the metals from higher to lower mean content in this sludge as: Cr > Cu > Zn> Ni > Pb > As > Cd. The total heavy metals content found in the sludge were compared to several international regulatory limits of heavy metal content for sludge utilization.

Table 4.2. Concentration of heavy metals in tannery sludge and different legislations for sludge utilization.

Parameter	**Heavy metals in the sample (mg/kg)**						
	As	**Cr**	**Pb**	**Cd**	**Ni**	**Cu**	**Zn**
Sample 1	1.7	15339	57.3	<0.001	139.7	579.5	210.2
Sample 2	2.1	26501	67.0	<0.001	137.5	261.3	212.5
Sample 3	1.5	15847	67.0	<0.001	141.3	316.4	329.1
Average	1.8	19229	63.8	-	139.5	385.7	250.6
Standard Deviation	0.3	6303	5.6	-	1.91	170.1	68.0
Permissible limit in India[a]	-	-	250-500	3-6	-	135-270	300-600
SEPAC limit in China [b]	-	250	350	0.6	26600	100	300
USEPA limit[1]	75	3000	840	85	420	4300	7500

NA: Not Available, [a] Source: Bhatnagar & Awasthi (2000), [b] Source: SEPA (1995)

The present study found that the average concentration of Arsenic, Cadmium, Lead, Nickel and Zinc were well below the India, China and USA Land Disposal Restriction

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[1] USEPA, *Land Application of Sewage Sludge*. Available at http://www3.epa.gov/npdes/pubs/sludge.pdf

Limits. But the mean concentration of Cr exceeded the all the mentioned standard (Table 4.2) and Cu exceeded the India and China regulation limit.

When compared with recommended limits, Cr showed more than 75 times higher than SEPAC (State Environmental Protection Administration of China) limit and about 7 times higher than USEPA limit (Table 4.2). Usually tannery sludge contains high levels of chromium as most of hides and skins are tanned with basic chromium salt and more than 60% of the chromium is wasted and ultimately transferred to sludge through wastewater treatment processes (Kolomaznik et al., 2008). Due to high chromium content, the sludge will not be suitable for soil amendment applications in agricultural land or home vegetation. The average concentration of copper in the sample was 385.73 mg/kg which exceeded the India (270 mg/kg) and China (100 mg/kg) land disposal restriction limit but was below the USEPA (4300 mg/kg) limit.

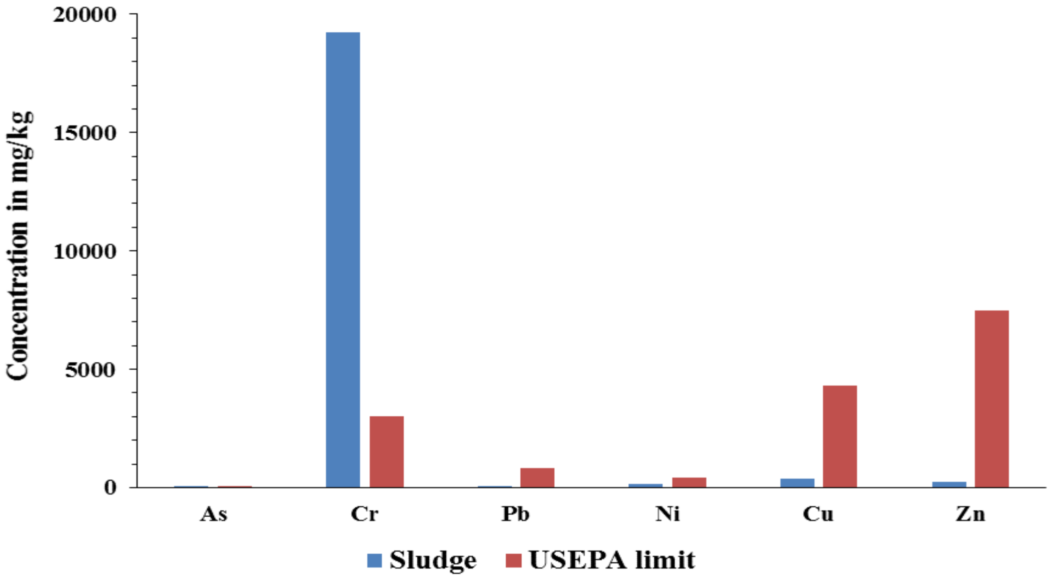


Figure 4.1. Heavy metal concentration in the sludge and their USEPA restriction limit

The chemical composition of tannery sludge and soil was determined using X-Ray Fluorescence (XRF-1800, Shimadzu) in Glass and Ceramic Engineering department, BUET. The chemical composition found as percentage of major oxides was shown in Table 4.3. This showed that the main components of tannery sludge were Fe_2O_3 (34.32%), SO_3 (28.71%), CaO (26.26%), SiO_2 (3.55%), Cr_2O_3 (3.36%).

Table 4.3. Chemical composition (dry weight, %) of sludge and soil.

Analytes	Sludge (%)	Soil (%)
SiO_2	3.55	63.47
CaO	26.26	2.19
Al_2O_3	0.48	13.08
Fe_2O_3	34.32	8.94
SO_3	28.71	0.56
MgO	1.69	3.9
Cr_2O_3	3.36	0.04
TiO_2	0.41	1.25
MnO	0.2	0.11
ZnO	0.08	0.02

Clay that was used for brick manufacturing consist of similar components present in the tannery sludge but in different quantities. So clay can be partially replaced by tannery sludge as raw material for brick production

Toxicity Characteristics Leaching Procedure (TCLP) test result of sludge were given in Table 4.4. The mean concentration of Cr leaching from the sludge sample is 2.75 mg/l which is below the USEPA regulatory limit of 5 mg/l. Though the leaching value is below from hazardous limit, it can have long term effect on ground water pollution and cannot be disposed directly. The concentration of As, Pb, Cu, Zn and Ni were very small and far below the USEPA limit.

Table 4.4. Leaching of heavy metals from original sludge samples.

Metals	n	Leached as mg/l
Cr	3	2.75 ± 0.35
As	3	0.13 ± 0.01
Pb	3	0.18 ± 0.05
Ni	3	0.32 ± 0.05
Cu	3	0.70 ± 0.02
Zn	3	0.04 ± 0.01

n = number of replication of tests

4.4 CHARACTERISTICS OF SLUDGE – CLAY MIX

4.4.1 Atterberg Limit

The behavior of soil is related to the amount of water in the system. The Liquid Limit is the boundary between the liquid and plastic states whereas the Plastic Limit is the boundary between the plastic and semi-solid states. The effect of moisture on the plastic behaviour of the pulverized materials is evaluated by the Atterberg Limit test. Panjaitan (2014) showed that plasticity index states the properties of soil. Sand has a Plasticity Index of 0 whereas clay has greater than 17 (Table 4.5). A small Plasticity Index such as 5, shows that a small change in moisture content will change the soil from semi-solid to liquid.

Table 4.5. Plasticity Index and properties of soil (Panjaitan, 2014)

PI range	Plastic nature	Soil properties
0	Non plastic	Sand
< 7	Low plastic	Silt
7 – 17	Medium plastic	Silt clay
> 17	High plastic	Clay

The Plasticity Index also gives a good indication of compressibility. The greater the PI, the greater the soil compressibility. The results of Atterberg tests of sludge-clay mixture shown in Figure 4.2 indicate that the value of Plasticity Index decreases when sludge content increases in the mixture. Plastic Limit values have revealed that with the addition of sludge, the plastic nature of the mixture is lowered and the bonding ability of the mixture is also decreased. When the mixture contains high amounts of sludge, the adhesiveness of the mixture will decrease.

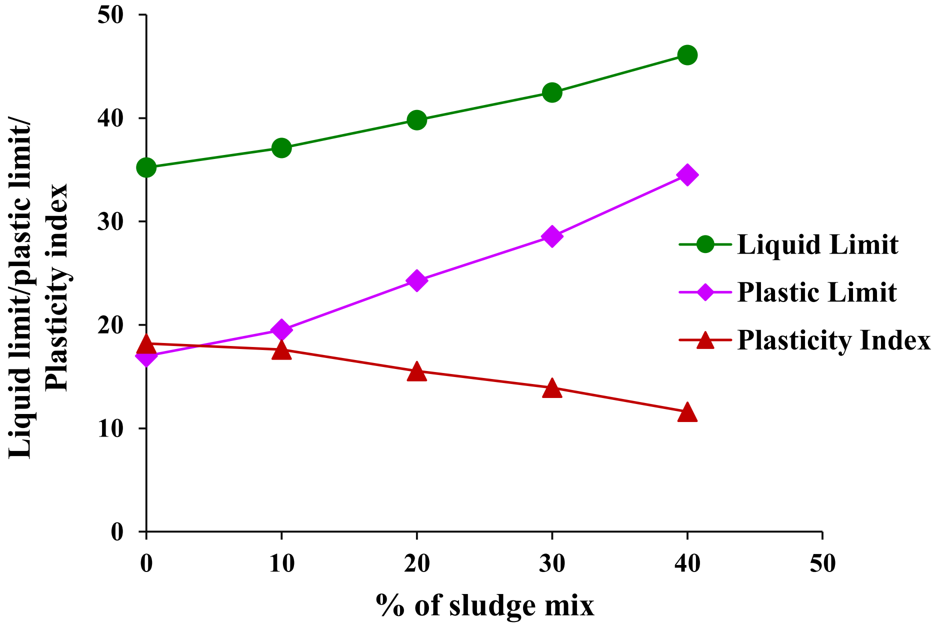


Figure 4.2. Relation between Plastic Limit, Liquid Limit and Plasticity Index with sludge content.

A PI value of soil that is used in brick manufacturing process is 18.2 (Table 4.6) that can be classified as high plastic material. The Plasticity Index of sludge – clay mixture ranged from 17.6, 15.54, 13.92 and 11.6 for the addition of 10%, 20%, 30% and 40% TS into mixture, respectively. According to the soil properties stated in Table 4.5, 10% of sludge can be applied to brick making without losing the significance plastic behavior.

Table 4.6. Effect of moisture content on OMC, Dry density, Liquid Limit, Plastic Limit, and Plasticity Index of sludge-clay mixtures

Sludge proportion (% by dry weight)	**0**	**10**	**20**	**30**	**40**
Optimum Moisture Content (%)	18.3	20	26	31	37
Dry density (gm/cm ^{3})	1.73	1.64	1.62	1.59	1.55
Liquid Limit (%)	35.2	37.1	39.8	42.47	46.1
Plastic Limit (%)	17	19.5	24.26	28.55	34.5
Plasticity Index (%)	18.2	17.6	15.54	13.92	11.6

4.4.2 Compaction test

Moisture content has the potential to affect the properties of bricks. Up to a certain point additional water replaces air from the soil voids, but, after a relatively high degree of saturation is reached, the water occupies space which would otherwise be occupied with soil particles (Lambe, 1993). Therefore, an optimum amount of mixing water in brick manufacturing process is usually sought which would give the maximum level of compaction for a given amount of soil sample. This will result in increased bulk density, lower tendency of water absorption and eventually the highest compressive strength. The results of the compaction test from Figure 4.3 shows that OMC increases with the increase of sludge incorporation into the mixture. On the other hand dry density of sludge – clay mixture decreased with the increase of sludge content to the mixture.

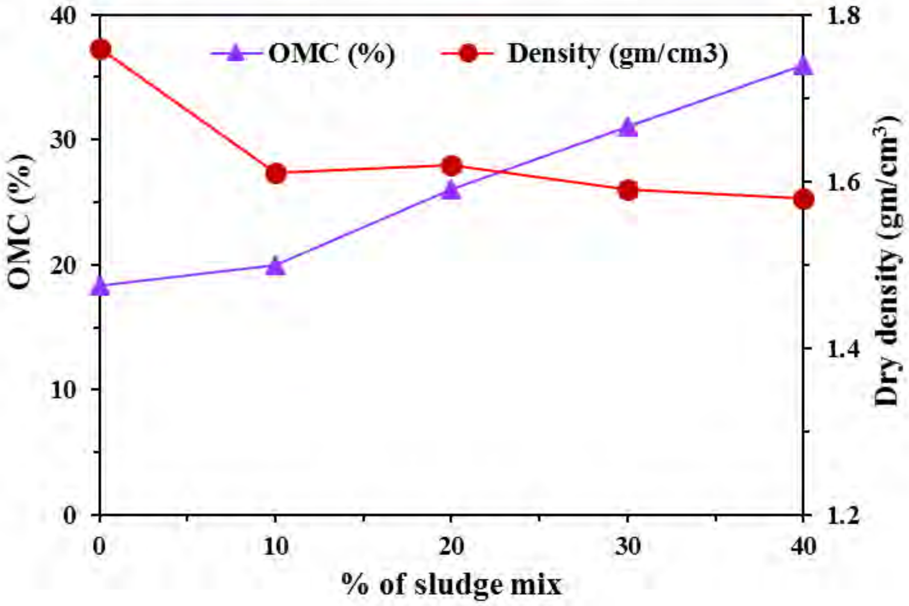


Figure 4.3. Effect of sludge addition on optimum moisture content and bulk density of mixtures.

4.5 PROPERTIES OF FIRED BRICKS PREPARED AT LABORATORY

After firing at different temperature the produced bricks were received a series of tests including firing shrinkage, weight loss on ignition, water absorption and compressive strength following standard methods.

4.5.1 Compressive strength of bricks

The compressive strength test is the key test for ensuring the engineering quality of a building material. The strength of a material, in general terms, is its ability to resist forces at failure. The results of the compressive strength test of the bricks were shown in Figure 4.4. The compressive strength of TS incorporated bricks ranged from 112 kg/cm^2 (10.98 MPa) to 302 kg/cm^2 (29.61 MPa). It appears that the content of sludge and firing temperature have a profound effect on the compressive strength of bricks.

Compressive strength has been found to be inversely proportional to the sludge content and directly proportional to the firing temperature. This proportional trend may be due to decrease in porosity and increase in bulk density resulting from increased firing temperature (Bhatnagar and Goel, 2002).

The comparison of the properties of TS bricks found in this study with those found in other studies using different types of sludges were shown in Table 4.9. It shows Similar pattern of compressive strength reduction with sludge content in other studies using different types of sludges (Ukwatta et al. 2016, Monteiro et al., 2008, Rouf and Hossain 2003, Basegio et al. 2002).

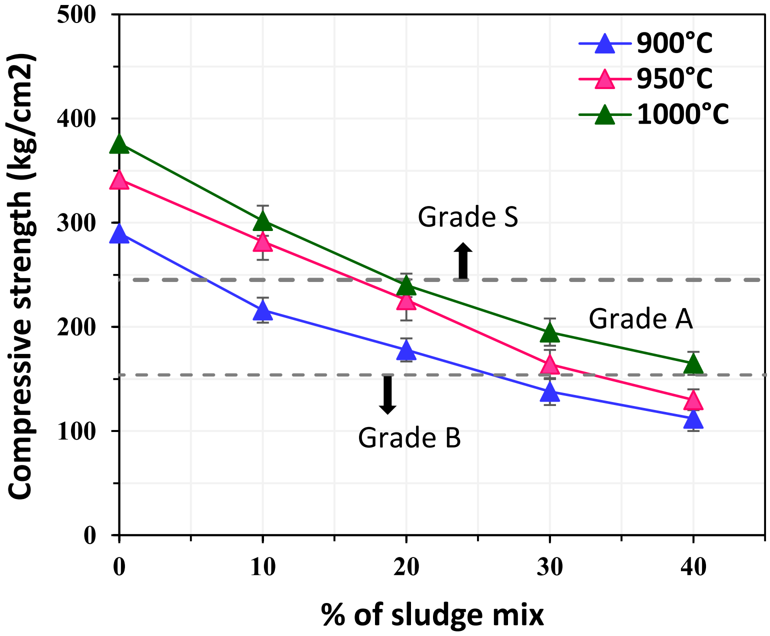


Figure 4.4. Compressive strength of bricks at different firing temperature.

Table 4.7. Criteria of bricks in Bangladesh (BDS 208, 2009)

Name of Parameters	Grade S	Grade A	Grade B
Compressive strength (kg/cm^2)	≥ 245	≥ 154	≥ 105
Water absorption (%)	≤ 10	15	≤ 20
Weight loss on ignition (%)	≤ 15	≤ 15	≤ 15
Firing shrinkage (%)	≤ 8	≤ 8	≤ 8

Note: Grade S: This type of bricks may be used for breaking into aggregate for plain and reinforced concrete and for making base course of pavement. **Grade A**: This type of bricks may be used in construction of buildings of long duration. **Grade B**: This type of bricks may be used for one storied building, temporary shed, where intended durability is not very long.

Table 4.8 shows that the addition of 40% sludge into the mixture reduces strength approximately by 56%, 62% and 61% for firing temperature of 1000^{0}C, 950^{0}C and 900^{0}C, respectively compared with the control bricks (i.e. 0% sludge). The addition of 10%, 20%, 30% and 40% sludge into the mixture reduces strength approximately by 19%, 31%, 48% and 56%, respectively compared with the control bricks (i.e. 0% sludge) for firing at 1000°C.

Table 4.8. Compressive strength of bricks fired at 900°C, 950°C and 1000°C temperature (n = 3).

Sludge content (%)	Firing at 900°C	Strength loss w.r.t control (%)	Firing at 950°C	Strength loss w.r.t control (%)	Firing at 1000°C	Strength loss w.r.t control (%)
0	290	0	341.5	0	376	0
10	216 ± 12.6	25.52	282 ± 17	17.42	302 ± 14	19.68
20	178 ± 11.3	38.62	226 ± 19	33.82	240 ± 11	36.17
30	138 ± 13	52.41	164 ± 14	51.98	195 ± 13	48.14
40	112 ± 12.4	61.38	130 ± 10	61.93	165 ± 11	56.12

According to BDS 208 (2009) Standards (Table 4.7) 10% TS bricks burnt at both 950°C and 1000°C can be considered as Grade S category and 20% to 40% TS bricks fired at 1000°C, 20% to 30% TS bricks fired at 950°C as well as 10% to 20% TS bricks fired at 900°C fall within Grade A category bricks. However all the brick samples have met the both ASTM (ASTM C 62) and Bangladesh BDS 208 (2009) standards which set out that the value of compressive strength should be greater than 87.69 kg/cm^2 (8.6 Mpa) and 105 kg/cm^2, respectively.

4.5.2 Water absorption of bricks

The degrees of firmness and compaction of bricks, as measured by their water absorption characteristics, vary considerably depending on factors such as the type of clay and methods of production used (BS 1377, 1990). Water absorption is a key factor affecting the durability of brick. The less water infiltrates into brick, the more durability of the brick and resistance to the natural environment are expected (Weng et al. 2003). Thus, the internal structure of the brick must be intensive enough to avoid the intrusion of water.

Figure 4.5 shows the results of the water absorption test as function of sludge content and firing temperature. It has been found that the water absorption of the bricks increased with increased sludge addition thereby potentially increasing its susceptibility to weathering action. On the other hand, water absorption was found to decrease when firing temperature was increased. This can be due to the formation of the amorphous phase at high firing temperature (Cultrone et al., 2004). Generally sludge contains high amount of organic content which generates pore spaces within the brick during firing and these pore spaces favor water absorption. The tannery sludge used in these experiments contained high amount of organic content (28.75%, see Table 4.1) and it was found that the quantity of absorbed water increased with the increase of TS proportion. In case of bricks containing 10% (by wt.) sludge firing at 900°C, water absorption was 14.14% which was reduced to 9.1% when firing temperature increased to 1000°C. On the other hand water absorption increased from 9.1% to 20.91% when TS proportion was increased from 0% to 40% (Fig. 4.5). Similar trends in water absorption with sludge fraction in bricks and other construction materials have been observed in other studies (Chiang et al. 2009, Liew et al. 2004, Weng et al. 2003).

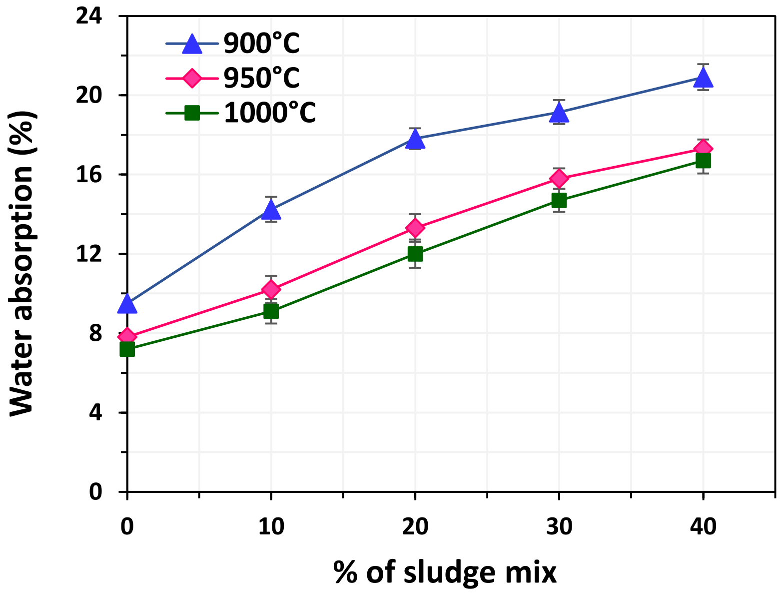


Figure 4.5. Water absorption of bricks as function of sludge content and firing temperature.

According to the criterion of water absorption of bricks stated in BDS 208 (2009) Standards (Table 4.8), bricks made with 10% sludge burnt at 1000°C can be regarded as Grade S category and bricks with 20% to 30% sludge fired at 1000°C and 10% to 20% sludge fired at 950°C as well as 10% TS bricks fired at 900°C fall within Grade A category bricks.

4.5.3 Weight loss on ignition

The brick weight loss on ignition is not only attributed to the organic matter content in the clay, but it also depends on the inorganic substance in both clay and sludge being burnt off during the firing process (Karaman et al., 2006). The effect of sludge content and firing temperature on weight loss of bricks are shown in Figure 4.6. It was found that the weight loss of bricks increased as percent of sludge increased. The weight loss of bricks was also depended on the firing temperature. With the increase of firing temperature weight loss also increased. The control bricks fired at 900°C showed the lowest weight loss of 5.52%, while the 40% sludge incorporated bricks fired at 1000°C showed the highest weight loss of 16.5%. This weight loss could be due to the combustion and decomposition of the organic and inorganic matter present in both the tannery sludge and clay during the firing process (Weng et al.2003, Liew et al., 2004). Similar kind of weight loss result in case of sewage sludge, textile sludge and arsenic rich sludge incorporated bricks were found in other studies (Ukwatta et al., 2016, Weng et al., 2003, Rouf and Hossain, 2003) which was shown in Table 4.9.

Normally, the weight loss criterion for a clay brick is 15% (AASHTO T- 99, 1982). In this regard, bricks incorporating up to 20% sludge fired at all three different temperatures have met weight loss criteria. Beside this bricks made with 30% sludge fired at 900°C and 950°C as well as bricks made of 40% sludge fired at 900°C also met this criteria.

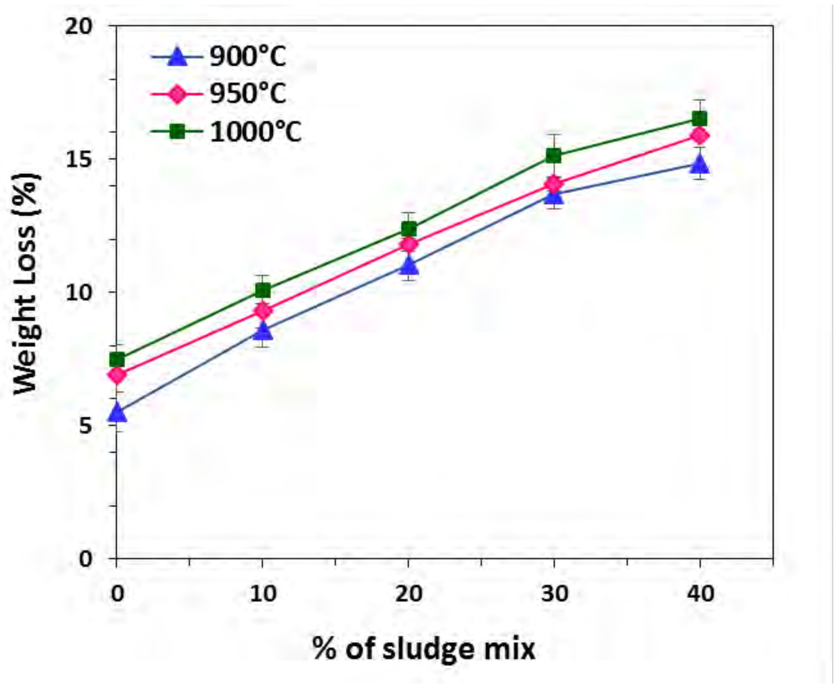


Figure 4.6. Weight loss of bricks as function of sludge content and firing temperature.

4.5.4 Brick firing shrinkage

Firing shrinkage is also an important parameter for ensuring the quality of bricks. Shrinkage in bricks occurs as chemically and mechanically bound water is lost during firing (Karaman et al., 2006). It is very similar to the weight loss in ignition parameter, the only difference is that firing shrinkage measures the volumetric deformation of bricks during firing or drying stages of production while the other is a measure of weight loss though the reasons for shrinkage can also cause weight loss of bricks. High shrinkage is an undesirable property in any engineering material. Figure 4.7 shows the volumetric shrinkage of bricks due to firing as a function of firing temperature and sludge content. It can be seen that that shrinkage of bricks is largely dependent on firing temperature as with the increase in firing temperature the shrinkage of bricks was found to increase.

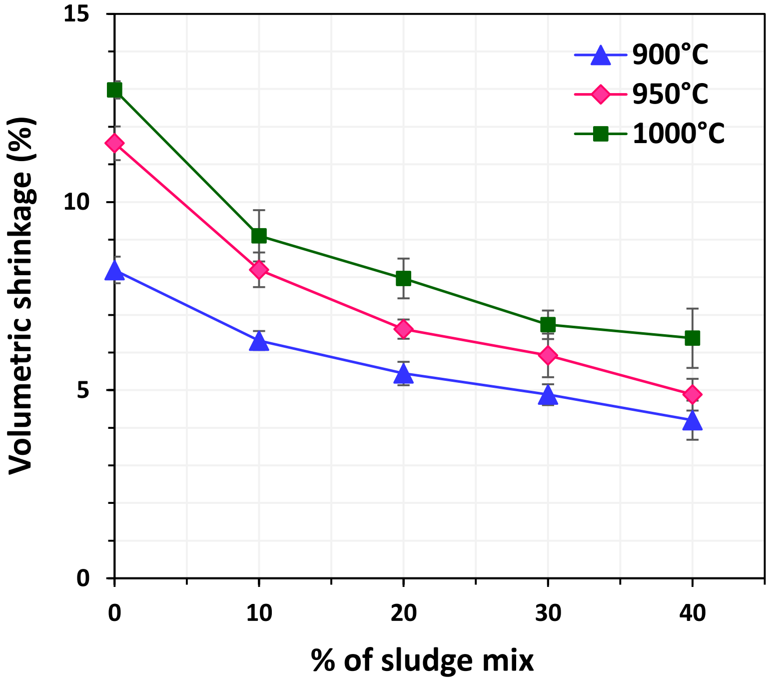


Figure 4.7. Shrinkage of bricks as function of firing temperature and sludge content.

In case of 10% sludge incorporated bricks shrinkage increased from 6.32% to 9.1% as firing temperature increased from 900°C to 1000°C. Firing shrinkage in this study did not increase with the increase of sludge addition as was previously reported by Basegio et al. (2002) but decreased with higher sludge content. For 40% sludge amended bricks fired at 1000°C, the volumetric shrinkage reduced by up to 50.8% compared to the control bricks. There are two hypothesis as to why this happened. Firstly, the decreasing trend obtained here may be due to nonplastic nature of dried sludge. Rhodes and Hopper (2000) reported that low plastic soil shrinks less than high plastic soil. The plasticity index of tannery sludge - clay mixtures were decreased for increased sludge content (Table 4.5) rendering the mixture to become more and more non-plastic. Secondly, the decreasing trend obtained here may be due to expansion in the bricks during the firing stage. Bricks incorporated with sludge could release more gases compared to control bricks due to burning of organic matter, generating voids which caused a net expansion within the sludge-clay matrix and eventually resulting in a lower net shrinkage (Ukwatta et al., 2016).

4.5.5 Bulk density

The bulk density for different percentage of TS-amended bricks fired at three defined temperatures are shown in Figure 4.8. It has been found that an inverse relationship exists between the bulk density of the TS-amended bricks and the amount of sludge added in the mixture. In this study, bulk density decreased from 1.87 to 1.5 gm/cm^3 (reduction of 19.5%) as the TS content increased from 0% to 40% at 1000°C firing temperature. This finding is closely related to the quantity of water absorbed as shown in Figure 4.5. More water absorption indicates larger pore size than the one with less water absorption, which, in turn, causes smaller bulk density. The firing temperature can also have an effect on the bulk density of the bricks. The results show that increasing the temperature results in a slightly higher bulk density. Light weight bricks can be more favorable in construction for their lower dead load, ease in handling, and savings in cost in transportation. Bricks with low bulk density also have good thermal insulation property.

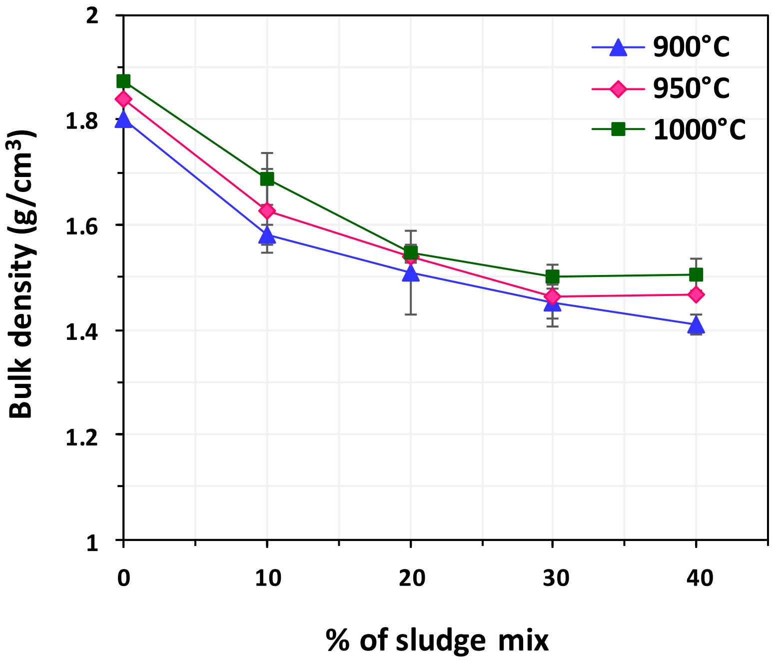


Figure 4.8. Bulk density of the bricks as function of sludge content and firing temperature.

Table 4.9. Comparison of results found in present study with the results from other studies for 10% sludge incorporated bricks fired at 1000°C.

Parameters	**Results of present study (10% TS bricks)**	**Other studies**		
		[a] Tannery sludge (Ceramic tiles)	**Sewage sludge (Bricks)**	**[d]Arsenic - Iron sludge (Bricks)**
Compressive strength	20% decrease	33% decrease	[b]15% decrease; [c]30% decrease	29% decrease
Water absorption	21% increase	50% increase	[b]12% increase; [c]21% increase	15% increase
Firing shrinkage	30% decrease	No change	[b]27% decrease; [c]8.1% decrease	45% increase
Weight loss on ignition	26% decrease	-	[b]13% decrease	12% decrease
Bulk density	10% decrease	24% decrease	[b]2.5% decrease	5% increase
Firing energy saving	26% saving	-	[b]25% saving	-

[a] (Basegio et al., 2002); [b] (Ukwatta et al., 2016); [c] (Monteiro et al., 2008); [d] (Rouf and Hossain, 2003). Percentage of increase or decrease was based on control (100% clay) bricks.

4.5.6 Soluble salt content and Electrical Conductivity of bricks

Salt content is an important for durability of construction material. The most common salts in masonry are sulphates, chlorides and nitrates. The presence of soluble salt in capillary pores of brick masonry can, under changing climate conditions, cause deterioration of wall structures due to the change between dissolved ions in solution and nucleated salt. Ions move in brick masonry depending on the water content, and salts may then be precipitated (Ottosen et al., 2007). Different type of damages may occur due to this concentrating phenomenon including, decomposition of bricks and mortar from salt-induced decay, damage of adhesion of paint or plaster by precipitating salts on the surface. Table 4.10 shows the soluble chloride content, sluphate content and electrical conductivity of sludge and TS bricks. Soluble chloride content of 10% TS brick (kiln fired) and 10% TS brick (laboratory) was found to be 0.002% and 0.003%, respectively which were lower than European limit of 0.03%.

Table 4.7. Soluble salt content and electrical conductivity of sludge and TS bricks

Parameters	**Raw Sludge**	**Control brick (kiln fired)**	**10% TS brick (kiln fired)**	**10% TS brick (laboratory)**	**European limit (BS EN772-1)**
Chloride content	0.2%	0.003%	0.002%	0.003%	0.03%
Sulphate content	1.15%	0.08%	0.23%	0.31%	0.50%
Electrical Conductivity (µs/cm)	8250	614	960	1535	-

Soluble sulphate content of 10% TS bricks made in kiln and laboratory was 0.23% and 0.31%, respectively which was below from European limit of 0.50%. However, sulphate content was higher in percentage compared to chloride content for both raw sludge and 10% TS bricks. This may be due to use of basic chromium sulphate in the tanning process of leather. These soluble salt restriction limits are not applicable for bricks which are under complete protection from water penetration (BS EN 772-1, 2003). Electrical conductivity of raw sludge was found to be 8250 µs/cm but it was reduced to 960 µs/cm and 1535 µs/cm for 10% TS bricks (kiln fired) and 10% TS bricks (laboratory). This result indicated that raw sludge contains higher amount of free electrolytes which increases its electrical conductivity.

4.6 ENERGY SAVING DURING FIRING

The incorporation of tannery sludge in bricks has the potential to reduce the energy required during firing. Currently, energy efficiency and environmental concerns have become as great an issue as quality and cost in brick manufacturing, due to increased awareness of the effects on the environment (Mohajerani et al. 2016)

Calorific value of TS used in this study has been found to be 5.85±0.76 MJ/kg which was measured by Bomb Calorimeter (Parr 6100). The estimated amount of energy saved during firing of TS bricks was calculated using equation (3.6) which has been interpreted in Table 4.11. The result showed that an estimated of 26% energy would be saved for 10% TS bricks and 50% energy saving for 20% TS bricks during firing compared to control bricks. Similar kind of energy saving result was reported in Ukwatta et al. (2016) for ETP biosolid incorporated bricks and at Mohajerani et al. (2016) for cigarettes butt incorporated bricks. Tannery sludge used in this study contained about 28.75% organic content which could facilitate heat input to furnace and reduced the amount of energy required for firing.

Table 4.8. Calculation for energy saved per unit brick during firing of 10% and 20% TS bricks

Sludge content (%)	Mass of control brick, m_1 (kg)	Mass of TS brick, m_2 (kg)	Mass of TSs in TS brick, m_3 (kg)	Energy used for control brick, Q_1(MJ)	Energy used for TS brick, Q_2 (MJ)	Energy saved (Q_1 - Q_2), MJ	% of energy saved / brick
10	0.505	0.489	0.049	1.2625	0.9355	0.327	25.90
20	0.505	0.473	0.094	1.2625	0.6326	0.633	49.89

4.7 COMPARISON OF PROPERTIES WITH KILN FIRED BRICKS

As 10% TS bricks made in the laboratory have shown the properties of Grade S bricks according to the BDS 208 (2009), this specific percentage of TS was used for preparing bricks in the field condition. Table 4.12 showed the properties of kiln fired TS-amended brick (10% by dry wt.) along with control bricks prepared in the field condition. Tests were carried out for compressive strength, water absorption, weight loss on ignition and firing shrinkage for these bricks as were done for those prepared in the laboratory condition and the results are shown in Table 4.12. All the parameters in the kiln fired TS-amended brick showed similar trend values (compared to the control bricks) as were found for bricks in laboratory condition. However, the exact values of the parameters were somewhat different when compared to the 10% TS-amended brick prepared in laboratory conditions. The compressive strength of kiln fired 10% TS brick ("field condition") was found to be 166 kg/cm^2 (16.27 MPa) which 41% lower in strength when compared to 10% TS brick made in laboratory condition. Despite the reduction in compressive strength, these bricks still satisfied the ASTM standard (Minimum 8.6 MPa compressive strength) and BDS 208 (2009) requirement for building construction (Table 4.8). Kiln fired TS bricks absorb about 46% more water than those prepared in laboratory condition.

Table 4.9. Comparison of properties of sludge incorporated bricks made in kiln and laboratory.

Parameters	**Test replication (n)**	**Field condition (Kiln fired)**		**Laboratory condition**	**% Increase or decrease w.r.t laboratory condition**
		10% TS bricks	**Control bricks**	**10% TS bricks fired at 950°C**	
Compressive strength	16	166± 30	171±25	282±19.69	– 41
water absorption	3	19±1.1	16±0.6	10.2±0.68	+46
weight loss on ignition	3	10.8±1.2	8.5±0.8	9.3±0.64	+13
Firing shrinkage	3	10.5±1.3	11.2±1.4	8.2±0.46	+21
Bulk density	3	1.50±0.5	1.52±0.2	1.62±0.08	– 0.07

Quality of kiln fired TS bricks (field condition) in terms of firing shrinkage, weight loss on ignition and bulk density was also slightly degraded compared to TS bricks made in laboratory. This difference in quality between the bricks manufactured in two different conditions is expected as there is a variation in molding process and OMC. During brick molding at laboratory, OMC was accurately maintained and compaction by hand was applied very carefully for individual bricks under controlled conditions which may have contributed to improved compaction of clay and sludge mixture resulting in increased compressive strength, lower water absorption, lower shrinkage and higher bulk density. Under field conditions in the kiln, the OMC was not maintained and practically no compaction was applied to the clay mixture during molding. Quality of TS-amended bricks can be improved infield condition if automatic molding machines are used which applies pressure during molding.

4.8 ENVIRONMENTAL ASPECTS OF SLUDGE AMENDED BRICKS

Heavy metal leaching

Leaching of heavy metal is the prime concern as heavy metal contaminated sludge is introduced to the finished products. It should be ensured that leaching of heavy metal from bricks does not exceed the maximum permissible limit even under extreme condition. Two types of leaching test was carried out in this study. The Netherland tank leaching test (NEN 7345) is specially dedicated to building materials and largely applied in Netherlands and EU, in general (Cusidó and Cremades, 2012). Following the procedure mentioned in section 3.10, The NEN 7345 leaching test was carried out for the sludge-amended bricks and Equation (3) was used to compute the cumulative leachability of six heavy metals (Cr, Zn, Cu, Zn, As and Ni) after eight extractions. Here experiments were done only for the set of bricks which were fired at 1000°C. The cumulative leachability values of six heavy metals from the sludge incorporated and control bricks fired at 1000°C are summarized in Table 4.13 and these values were compared with the Dutch Standards of leaching restriction limits for construction materials.

According to the Dutch regulations, if cumulative results from the NEN 7345 leaching test do not exceed U1 values, sludge incorporated bricks can be used in construction without any restrictions. If cumulative results exceed U2 values, they cannot be used as construction materials and if the results are between U1 and U2 they can be used as construction materials but they need to be treated once their life cycle is ended (NEN 7345, 1993). The cumulative leachability values for all heavy metals analyzed in this study from all samples are insignificant as they were found to be far below U1 (Table 4.13). Even, Zn, Cu, Pb, Ni, and As have been found to have leached in lower concentration from sludge amended bricks compared to control brick (100% clay).

Table 4.10. Result of the tank leaching tests in bricks samples after 8 extractions (64 days) according to NEN 7345.

Sludge content	Cr (mg/m^2)	Zn (mg/m^2)	Cu (mg/m^2)	Pb (mg/m^2)	Ni (mg/m^2)	As (mg/m^2)
0%	0.008	0.006	0.021	0.086	0.008	0.007
10%	0.161	0.004	n.d	0.027	0.002	0.002
20%	0.345	0.005	0.003	0.020	n.d	n.d
30%	0.290	0.001	0.003	0.055	n.d	n.d
40%	0.499	n.d	0.003	0.062	n.d	n.d
Leaching limits set by the Netherlands Tank Leaching Test (NEN 7345)						
U1	150	200	50	100	50	40
U2	950	1500	350	800	350	300

"n.d" = not detected. Detection limit for Cu, Ni and As is > 0.001 mg/l

The Toxicity Characteristics Leaching Procedure (TCLP) test is designed to identify wastes that are likely to leach hazardous concentrations of particular toxic constituents into the groundwater. During the TCLP test, constituents are extracted from the waste to simulate leaching actions that actually occur in landfills. If the concentration of the toxic constituents exceeds the regulatory limit, the waste is classified as hazardous.

The leachate analysis according to USEPA 1311 from sludge amended bricks fired at 1000°C, 950°C and 900°C temperature is given in Table 4.14. Ni and Cd did not leach from the sludge amended bricks as their concentrations were far below detectable levels. Other metals like Cr, Pb, Cu, Zn and As leached from sludge amended bricks, although the concentration are far below the US-EPA regulatory limits that are 5 mg/l, 5mg/l, 100 mg/l, 500 mg/l and 5 mg/l for Cr, Pb, Cu, Zn and As, respectively. From Table 4.14 it is revealed that the leaching concentration of Cr, Pb and Cu are reduced by 90%, 48% and 70%, respectively, for the 10% sludge amended bricks fired at 1000°C compared to original sludge. These metals are believed to be locked inside the fired bricks as metal oxide (Liew et al., 2004). On the other hand the leaching of Zn from sludge amended brick is slightly higher than that from raw sludge, although the concentration is far below the USEPA regulatory limit of 500 mg/l. This might be attributed to the fact that Zn is a naturally occurring heavy metal and it is possible that the clay samples used in these experiments contained Zn which was released along with the Zn in sludge in the course of the TCLP tests. Firing temperature is a very important factor affecting leachability of heavy metal.

Table 4.11. TCLP test result of TS amended bricks fired at 1000°C, 950°C and 900°C temperature (n = 3)

Metals	Dry sludge	Firing temp.	Cont. brick	10% TS brick	20% TS brick	30% TS brick	40% TS brick	US EPA limit [a]
Cr (mg/l)	2.75 ±0.35	1000°C	0.033	0.28±0.12	0.91±0.2	1.07±0.23	1.08±0.26	5
		950°C	n.d	0.66±0.15	1.04±0.31	1.25±0.02	1.17±0.03	
		900°C	0.02	0.74±0.05	1.18±0.4	1.67±0.03	2.18±0.03	
Pb (mg/l)	0.18 ±0.02	1000°C	0.17	0.09±0.03	0.13±0.06	0.12±0.02	0.11±0.04	5
		950°C	0.063	0.09±0.08	0.12±0.05	0.12±0.05	0.13±0.04	
		900°C	0.07	0.13±0.02	0.14±0.02	0.09±0.01	0.10±0.02	
Ni (mg/l)	0.32 ±0.05	1000°C	n.d	n.d	n.d	n.d	n.d	11
		950°C	n.d	n.d	n.d	n.d	n.d	
		900°C	n.d	n.d	n.d	n.d	n.d	
Cu (mg/l)	0.70 ±0.02	1000°C	0.214	0.21±0.02	0.12±0.1	0.234±0.1	0.24±0.07	100
		950°C	0.085	0.18±0.07	0.18±0.01	0.19±0.06	0.12±0.09	
		900°C	0.216	0.27±0.02	0.12±0.05	0.16±0.01	0.31±0.03	
Zn (mg/l)	0.04 ±0.01	1000°C	0.181	0.31±0.2	0.30±0.3	0.587±0.3	0.76±0.4	500
		950°C	1.625	0.73±0.1	0.24±0.05	0.35±0.03	0.24±0.08	
		900°C	1.48	0.5±0.1	1.1±0.03	1.26±0.1	1.15±0.07	
As (mg/l)	0.13 ±0.01	1000°C	0.017	0.12±0.16	0.13±0.16	0.03±0.12	0.08±0.08	5
		950°C	0.047	0.12±0.02	0.11±0.03	0.12±0.05	0.11±0.02	
		900°C	0.067	0.12±0.16	0.12±0.16	0.03±0.12	0.08±0.08	
Cd (mg/l)	n.d	1000°C	n.d	n.d	n.d	n.d	n.d	1
		950°C	n.d	n.d	n.d	n.d	n.d	
		900°C	n.d	n.d	n.d	n.d	n.d	

"n.d" = not detected; Detection limit for Ni and Cd is > 0.001 mg/l; [a] United States Environmental Protection Agency (USEPA) (1996).

The leaching of Cr have reduced from 0.745 mg/l to 0.28 mg/l when firing temperature increased from 900°C to 1000°C.This result is in congruence with the previous observations by Magalhaes et al. (2005) who reported that high firing temperature could immobilize Cr from Cr-rich sludge in a ceramic matrix. With the increase of sludge content in the brick the leaching of Cr increases, whereas the leaching of other metals appear not be dependent on the sludge content in the bricks. This might be because other than Cr, the concentration of the rest of the heavy metals tested was quite low in the original sludge and therefore the immobilization of heavy metals from sludge through incorporation in bricks was also more pronounced for Chromium (Table 4.2).

From leaching test, it can be concluded that sludge amended bricks can be used for construction material without any environmental restriction and even after the end of life cycle of these bricks, leaching of heavy metals will also be insignificant.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 INTRODUCTION

In developing country like Bangladesh, bricks are used in a large extent for the building construction. To meet the demands of millions and millions of bricks, a large number of brick fields have been established and their number is increasing day by day. For this reason a tremendous pressure is being exerted on soil for raw materials of bricks resulting the reduction of agricultural fields. So the tannery sludge can be useful substitute of soil to some extent for the brick production which will also reduce the environmental burden of sludge disposal.

5.2 CONCLUSION

This study has investigated the effect of incorporating sludge generated from ETP of tannery in fired-clay bricks on their physical and mechanical properties as well as on their environmental aspects. The bricks were manufactured incorporating 0%, 10%, 20%, 30%, and 40% (by dry weight) of tannery sludge and fired at 900°C, 950°C and 1000°C with clay for 3 hours and several relevant engineering properties of the fired-clay bricks were assessed.

The major findings of this study are as follows:

- Atterberg limit test indicates that Plasticity Index of clay – sludge mixture reduces with increasing sludge addition and up to 10% of sludge can be applied to brick making without losing the plastic behaviour.
- Water absorption increases with the increase of sludge addition but decreases with increasing firing temperature. 10% TS bricks burnt at 1000°C can be regarded as Grade S category and bricks with 20% to 30% sludge fired at 1000°C and 10% to 20% sludge fired at 950°C as well as 10% TS bricks fired at 900°C fall within Grade A category bricks according to BDS – 208 (2009).
- The compressive strength of TS bricks reduced considerably from 376 kg/cm^2 (36.83 MPa) to 165 kg/cm^2 (16 MPa) when TS content increased from 0% to

40% fired at 1000°C. On the other hand compressive strength increased with an increase of firing temperature for all brick samples. The addition of 40% sludge into the mixture reduces strength approximately for 56% compared with the control bricks though all the TS bricks have been found to meet the both ASTM (ASTM C 62) and Bangladesh (BDS-208: 1980) standards for construction.

- Firing shrinkage increases with increasing firing temperature but decreases with increasing sludge content.
- It was estimated that the firing energy of bricks can be saved up to 26% and 50% by incorporating 10% and 20% TS content, respectively which may be due to the contribution of calorific power of organic content present in the tannery sludge.
- Sludge addition and higher firing temperature caused higher weight loss in manufactured bricks, which was due to the combustion of organic matter. The incorporation of TS also reduced bulk density and shrinkage in bricks which which can impart favorable properties in bricks such as thermal insulation and dead weight reduction.
- The 10% TS bricks produced in the kiln, though exhibiting inferior mechanical properties compared to the 10% TS bricks produced in laboratory, satisfied the minimum strength requirement for building construction (8.6 MPa). Both the Netherland tank leaching test (NEN 7345) and TCLP test (USEPA 1311) showed that the leaching concentration of targeted heavy metals analyzed in this study for all samples have been found to be insignificant and far below the Dutch regulations and USEPA regulatory limits. The results from TCLP tests showed that an increase in firing temperature causes further immobilization of heavy metals such as chromium.

Based on the results obtained from laboratory and field condition, bricks with TS content of 10% by dry weight and fired between 950°C to 1000°C can produce good quality bricks which can satisfy all the desirable mechanical and physical properties as per ASTM and BDS standards. Also, there will be minimal cause for concern for leaching of toxic metals in the environment. Incorporating tannery sludge in clay bricks therefore can be a promising venture for successfully recycling waste materials into building materials.

5.3 LIMITATION OF THE STUDY

- Only a handful of tanneries in Bangladesh have ETPs. Therefore, the scope for sludge collection was very limited. Sludge from different tanneries can have a wide range of constituents (including toxic metals); but the investigation in this thesis was limited to only a specific tannery.
- A raw hide or skin have to go through the three main operations; Wetblue, Retanning and Finishing to produce final leather. For this study, sludge was collected from a tannery which did not have wetblue section. So, the tannery sludge collected for this study is not likely to contain the most comprehensive range of harmful constituents that are typical for a tannery sludge that is generated from a full tannery operation. Therefore, leaching behavior of the pollutants (heavy metals) found in this study can be considered conservative.
- Temperature is an important factor affecting the quality of bricks. Due to the lack of capacity of furnace the brick samples were not fired at more than 1000°C. So effect of higher temperature (>1000°C) on brick quality could not be analyzed.
- Optimum Moisture Content is also an important factor which was probably not accurately maintained through hand molding. If mechanical extruder was used then all bricks would have been prepared evenly.
- Toxic gas may be emitted during firing of TS bricks due to oxidation or reduction of sulfur, ammonia, Cr and other heavy metals which was not investigated in this thesis.

5.4 RECOMMENDATION FOR FUTURE WORK

- Bangladesh Govt. are relocating the tanneries at Savar, Dhaka where a Central Effluent Treatment Plant (CETP) have already been constructed. So, similar studies can be carried out with sludge generated from CETP after commencement of the plant in a full swing. This will provide sludge with a wide range of properties.
- Different researchers showed that sludges generated from sewage, textile can be successfully utilized through ceramics tiles, pavement blocks and concrete. So, similar studies can be carried out for tannery sludge.

- As mechanical properties and leaching behavior was developed with the rise of firing temperature, high capacity of furnace can be used to investigate the effect of firing at a higher temperature on brick quality and leaching behavior of heavy metals.
- Gas emitted from furnace during burning of TS bricks should be analyzed.
- Mass balance analysis can be carried out for chromium and other heavy metals in TCLP extracts.

REFERENCES

AASHTO T- 99, (1982). Standard test methods for moisture-density relations of soils and soil-aggregate mixtures using 5.5 lb rammer and 12 in drop. Standard Specifications for Highway Materials and Methods of Sampling and Testing, Part II. American Association of State Highway and Transportation Officials, Washington, DC.

Abajihad, Z., (2012). Assessment of tannery solid waste management and characterization. M.Sc. thesis report, department of chemical engineering, Addis Ababa University, Ethiopia

Ahamed, M.I.N., Kashif, P.M., (2014). Safety Disposal of Tannery Effluent Sludge : Challenges To Researchers- a review 5, 733–736.

Ahmed, M., Idris, A., Omar, S.R.S., (2007). Physicochemical characterization of compost of the industrial tannery sludge, J. Eng. Sci. Technol. 2, 81–94.

ASTM C 62, (2012). Standard Specification for Building Brick (Solid Masonry Units Made From Clay or Shale). 100 Barr Harbor Drive, West Conshohocken, United States.

ASTM C 67-02c, (2002). Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile, American Society for Testing and Materials, West Conshohocken, Pennsylvania. doi:10.1520/C0067-12.2.

ASTM D 4318, (2000). Standard Test Methods for Liquid Limit, Plastic Limit, and Plasticity Index of Soils. 100 Barr Harbor Drive, West Conshohocken, United States. doi:10.1520/D4318

Avudainayagam, S., Megharaj, M., Owens, G., Kookana, R.S., Chittleborough, D., and Naidu, R., (2003). Chemistry of chromium in soils with emphasis on tannery waste sites. Rev. Environ. Contam. Toxicol. 178, 53–91.

Awashthi, S.K., (2000). Prevention of Food Adulteration Act no 37 of 1954. Central and State Rules as Amended for 1999. 3rd Edition, Ashoka Law House, New Delhi.

Bartlett, R., and James, B., (1979). Behavior of chromium in soils: III. Oxidation. J Env. Qual 8, 31–34.

Bartlett, R., (1991). Chromium cycling in soils and water: Links, gaps, and methods. Environ. Health Perspect. 92, 17–24. doi:10.1289/ehp.919217

Basegio, T., Beck Leão, A.P., Bernardes, A.M., Bergmann, and C.P., (2009). Vitrification: An alternative to minimize environmental impact caused by leather industry wastes. J. Hazard. Mater. 165, 604–611. doi:10.1016/j.jhazmat.2008.10.045

Basegio, T., Berutti, F., Bernardes, A., and Bergmann, C.P., (2002). Environmental and technical aspects of the utilisation of tannery sludge as a raw material for clay products. J. Eur. Ceram. Soc. 22, 2251–2259. doi:10.1016/S0955-2219(02)00024-9

Baskar, R., Begum, K.M.M.S., and Sundaram, S., (2006). Characterization and Reuse of Textile Effluent Treatment Plant Waste Sludge in Clay Bricks. J. Univ. Chem. Technol. Metall. 41, 473–478.

BDS 208, (2009). Specification for Common Building clay bricks (Third revision), Bangladesh Standards and Testing Institution, Tejgaon Industrial Area, Dhaka

Bhatnagar, J.M., and Goel, R.K., (2002). Thermal changes in clay products from alluvial deposits of the Indo–Gangetic plains. Constr. Build. Mater. 16, 113–122. doi:10.1016/S0950-0618(01)00031-9

BREDL, (2009). Waste gasification impacts on the environment and public health. The Blue Ridge Environmental Defence League.

BS 1377, (1990). Methods of test for soils for civil engineering purposes. Part 2: classification tests. London, England.

BUET, (2007). Small study on air quality of impacts of the North Dhaka brickfield cluster by modeling of emissions and suggestions for mitigation measures including financing models, Commissioned by the DoE (Department of Environment), Bangladesh and funded by the World Bank, Chemical Engineering Department, Dhaka.

Carson, B., Ellis, H., and McCann, J., (1986). Toxicology and Biological Monitoring of Metals in Humans: Including Feasibility and Need. Lewis, Chelsea, MI.

Cassano, A., Drioli, E., Molinari, R., and Bertolutti, C., (1997). Quality improvement of recycled chromium in the tanning operation by membrane processes.

Desalination 108, 193–203. doi:10.1016/S0011-9164(97)00027-1

Chang, G., Liu, J., and Lee, D., (2001). CO-conditioning and dewatering of chemical sludge and waste activated sludge. Water Res. 35, 786–794. doi:10.1016/S0043-1354(00)00326-2

Chiang, K.Y., Chou, P.H., Hua, C.R., Chien, K.L., and Cheeseman, C., (2009). Lightweight bricks manufactured from water treatment sludge and rice husks. J. Hazard. Mater. 171, 76–82. doi:10.1016/j.jhazmat.2009.05.144

Cultrone, G., Sebastián, E., Elert, K., Torre, M.J., Cazalla, O., and Rodriguez–Navarro, C., (2004). Influence of mineralogy and firing temperature on the porosity of bricks. J. Eur. Ceram. Soc. 24, 547–564. doi:10.1016/S0955-2219(03)00249-8

Cusidó, J.A., and Cremades, L.V., (2012). Environmental effects of using clay bricks produced with sewage sludge: Leachability and toxicity studies. Waste Manag. 32, 1202–1208. doi:10.1016/j.wasman.2011.12.024

ESMAP, (2011). Introducing Energy-efficient Clean Technologies in the Brick Sector of Bangladesh, Energy Sector Management Assistance Program, Washington D.C.

Gautam, S.P., Bundela, P.S., Pandey, A.K., Sarsaiya, S., (2010). Composting of Municipal Solid Waste of Jabalpur City Central Pollution Control Board , New Delhi , India. Glob. J. Environ. Res. 4, 43–46.

Hashem, A., Islam, A., Mohsin, S., and Tomal, S.N., (2015). Green environment suffers by discharging of high-chromium- containing wastewater from the tanneries at Hazaribagh, Sustain. Water Resour. Manag. 1, 343–347. doi:10.1007/s40899-015-0033-4

Hassan, K.M., Fukushi, K., Turikuzzaman, K., and Moniruzzaman, S.M., (2014). Effects of using arsenic-iron sludge wastes in brick making. Waste Manag. 34, 1072–1078. doi:10.1016/j.wasman.2013.09.022

Houshyar, Z., Khoshfetrat, A.B., and Fatehifar, E., (2012). Influence of ozonation process on characteristics of pre-alkalized tannery effluents. Chem. Eng. J. 191, 59–65. doi:10.1016/j.cej.2012.02.053

Kadir, A.A., and Sarani, N.A., (2012). An Overview of Wastes Recycling in Fired

Clay Bricks. Int. J. Integr. Eng. 4, 53–69.

Karaman, S., Ersahin, S., and Gunal, H., (2006). Firing temperature and firing time influence on mechanical and physical properties of clay bricks. J. Sci. Ind. Res. 65, 153–159.

Kiliç, E., Puig, R., Baquero, G., Font, J., Colak, S., and Gürler, D., (2011). Environmental optimization of chromium recovery from tannery sludge using a life cycle assessment approach. J. Hazard. Mater. 192, 393–401.

Kirk, D.W., Chan, C.C.Y., and Marsh, H., (2002). Chromium behavior during thermal treatment of MSW fly ash. J. Hazard. Mater. 90, 39–49. doi:10.1016/S0304-3894(01)00328-4

Kolomaznik, K., Adamek, M., Andel, I., and Uhlirova, M., (2008). Leather waste-Potential threat to human health, and a new technology of its treatment. J. Hazard. Mater. 160, 514–520.

Koroneos, C., and Dompros, A., (2007). Environmental assessment of brick production in Greece. Build. Environ. 42, 2114–2123. doi:10.1016/j.buildenv.2006.03.006

Lambe, T.W., (1993). Soil Testing for Engineers, 5th edition, Wiley Eastern Limited, New Delhi.

Liew, A.G., (2004). Incorporation of Sewage Sludge in Clay Brick and its Characterization. Waste Manag. Res. 22, 226–233.

Liew, A.G., Idris, A., Samad, A.A., Wong, C.H.K., Jaafar, M.S., and Baki, A.M., (2004). Reusability of sewage sludge in clay bricks. J. Mater. Cycles Waste Manag. 6, 41–47. doi:10.1007/s10163-003-0105-7

Magalhaes, J.M., Silva, J.E., Castro, F.P., and Labrincha, J.A., (2005). Physical and chemical characterisation of metal finishing industrial wastes. J. Environ. Manage. 75, 157–166. doi:10.1016/j.jenvman.2004.09.011

Manahan, S.E., (2005). Environmental Chemistry, 8th edition, Lewis Publisher.

Mason, K., (2007). Fuel for Free?, in: Waste Materials in Brick Making. Practical Action, Warwickshire, UK.

Megharaj, M., Avudainayagam, S., and Naidu, R., (1999). Hexavalent chromium reduction by bacteria isolated from a tannery contaminated soil, in: 5th International Conference on Biogeochemistry of Trace Elements, Vienna. pp. 760–761.

Milacic, R., and Stupar, J., (1995). Fractionation and oxidation of chromium in tannery waste and sewage sludge amended soils. Env. Sci Technol 29, 506–514.

Mishra, S., Shanker, K., Srivastava, M.., Srivastava, S., Shrivastav, R., Dass, S., and Prakash, S., (1997). A study on the uptake of trivalent and hexavalent chromium by paddy (Oryza sativa): possible chemical modifications in rhizosphere. Agric. Ecosyst. Environ. 62, 53–58.

Mohajerani, A., Kadir, A.A., and Larobina, L., (2016). A practical proposal for solving the world's cigarette butt problem: Recycling in fired clay bricks. Waste Manag. doi:10.1016/j.wasman.2016.03.012

Montañés, M.T., Sánchez-Tovar, R., and Roux, M.S., (2014). The effectiveness of the stabilization/solidification process on the leachability and toxicity of the tannery sludge chromium. J. Environ. Manage. 143, 71–79.

Muchuweti, M., Birkett, J.W., Chinyanga, E., Zvauya, R., Scrimshaw, M.D., and Lester, J.N., (2006). Heavy metal content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe: Implications for human health. Agric. Ecosyst. Environ. 112, 41–48. doi:10.1016/j.agee.2005.04.028

NEN 7345, (1993). Determination of the release of inorganic characteristics of inorganic constituents from construction materials and stabilized waste products. NNI Delft (Netherlands).

Nieboer, E., and Jusys, A., (1988). Biologic chemistry of chromium, in: Chromium in Natural and Human Environments. Wiley, New York, pp. 81–105.

Ottosen, L.M., Pedersen, A.J., Rörig-Dalgaard, I., (2007). Salt-related problems in brick masonry and electrokinetic removal of salts. J. Build. Apprais. 3, 181–194. doi:10.1057/palgrave.jba.2950074

Panjaitan, S.R.N., (2014). The Effect of Lime Content on the Bearing Capacity and Swelling Potential of Expansive Soil. J. Civ. Eng. Res. 4, 89–95.

Patel, H., and Pandey, S., (2012). Evaluation of physical stability and leachability of Portland Pozzolona Cement (PPC) solidified chemical sludge generated from textile wastewater treatment plants. J. Hazard. Mater. 207-208, 56–64.

Paul, H.L., Antunes, A.P.M., Covington, A.D., Evans, P., and Phillips, P.S., (2013). Bangladeshi Leather Industry : An Overview of Recent Sustainable Developments. SLTC J. 97, 25–32.

Prasetsan, S., (1995). Preliminary Study on Brick Making Industry in ASEAN Countries. Final Report (unpublished), Submitted to NRCT, Bangkok, Thailand.

Praveen, S., Bhagavathi, P.T., and Jegan, J., (2015). Utilization of Textile Effluent Waste Sludge in Brick Production. Int. J. Technol. Res. Eng. 2, 1–10.

Rahmat, M.N., (2001). Development of Environmentally Friendly Building Material: An Analysis of the use of Solidified Industrial Waste. Available from http://www.unu.edu/env/arsenic/Dhaka2003/15-Rouf.pdf

Renkow, M., Rubin, A.R., (1998). Does Municipal Solid Waste Composting Make Economic Sense? J. Environ. Manage. 53, 339–347.

Rhodes, D., and Hopper, R., (2000). Clay and Glazes for the Potter. Krause Publications.

Rouf, M.A., and Hossain, M.D., (2003). Effects of using arsenic-iron sludge wastes in brick making., in: Fate of Arsenic in the Environment. pp. 193–208.

SEPA, (1995). Environmental quality standard for soils. State Environmental Protection Administration, China.

Singh, K.P., Mohan, D., Sinha, S., and Dalwani, R., (2004). Impact assessment of treated/untreated wastewater toxicants discharged by sewage treatment plants on health, 55, 227–255.

Skeffington, R., Shewry, P., and Peterson, P., (1976). Chromium uptake and transport in barley seedlings (Hordeum vulgare L.). Planta 132, 209–214.

Swarnalatha, S., Ramani, K., Karthi, A.G., and Sekaran, G., (2006). Starved air combustion-solidification/stabilization of primary chemical sludge from a tannery. J. Hazard. Mater. 137, 304–13. doi:10.1016/j.jhazmat.2006.02.006

The Brick Industry Association, (2006). Technical Notes on Manufacturing of Brick, Technical Notes on Brick Construction. 1850 Centennial Park Drive, Reston, Virginia 20191.

Thomson, J.C., Azariah, J., and Viji, A.G.R., (1999). Impact of textile industries on river Noyyal and riverine groundwater quality in Tirupur, India. Environ. Monit. Assess. 18, 359–368.

Tunay, O., Kabdasli, I., Orhon, D., and Ates, E., (1995). Characterization and pollution profile of leather tanning industry in Turkey. Water Sci. Technol. 32, 1–9.

Ukwatta, A., Mohajerani, A., Eshtiaghi, N., and Setunge, S., (2016). Variation in physical and mechanical properties of fired-clay bricks incorporating ETP biosolids. J. Clean. Prod. doi:10.1016/j.jclepro.2016.01.094

UNIDO, (2011). Introduction to treatment of tannery effluents, United Nations Industrial Development Organization, Vienna, Austria.

UNIDO, (2001). Safe landfill for disposal of sludge from tannery effluent treatment plants. United Nations Industrial Development Organization, South-East Asia.

UNIDO, (1998a). Solidification and Stabilisation of Tannery Sludge, United Nations Industrial Development Organization, South - East Asia.

UNIDO, (1998b). Ultrafiltration Application in Tannery Waste Water. United Nations Industrial Development Organization, South - East Asia.

USEPA, (1996). Hazardous Waste Characteristics Scoping Study. US Environmental

Protection Agency, Office of Solid Waste.

USEPA, (1998). Identification and Listing of Hazardous Waste, Title 40 Code Federal Regulations (CFR). Part 261, App VIII (Chapter 1). US Environmental Protection Agency, Washington D.C.

USEPA, (1992). Toxicity Characteristic Leaching Procedure (TCLP). Standard SW-864, Method 1311, US Environmental Protection Agency, Washington D.C.

Weng, C.H., Lin, D.F., and Chiang, P.C., (2003). Utilization of sludge as brick materials. Adv. Environ. Res. 7, 679–685. doi:10.1016/S1093-0191(02)00037-0

Whittemore, O., (1994). Energy usage in firing ceramics and melting glass. Ceram. Eng. Sci. Proc. 15, 180–185.

Wilson, B., and Pyatt, F.B., (2007). Heavy metal dispersion, persistence, and bioaccumulation around an ancient copper mine situated in Anglesey. UK.

Ecotoxicol. Environ.Saf. 66, 224–231.

World Bank, (1999). Municipal solid waste incineration. Munic. waste Combust. Washington D.C..

Zupančič, G.D., Jemec, A., (2010). Anaerobic digestion of tannery waste: Semi-continuous and anaerobic sequencing batch reactor processes. Bioresour. Technol. 101, 26–33. doi:10.1016/j.biortech.2009.07.028

Appendix A

Appendix A contains the average results of different mechanical and physical properties of bricks and also contain the calculation of tank leaching test of TS bricks.

Table A- 1. Compressive strength of TS bricks fired at 900°C

% of sludge	Sample ID	Area cm^2	Strength kg/cm^2	Avg. strength kg/cm^2	SD	Strength loss wrt clay sample (%)
0% sludge (control)	0a	64	290	290		0
10% sludge mix	1a	64.72	230	216	12.17	25.52
	1b	63.72	208			
	1c	64.2	210			
20% sludge mix	2a	64.98	175	178	10.41	38.51
	2b	63	170			
	2c	64	190			
30% sludge mix	3a	65.54	130	138	7.55	52.41
	3b	62.7	139			
	3c	64.2	145			
40% sludge mix	4a	64.2	105	112	7.64	61.49
	4b	66.12	120			
	4c	65.54	110			

Table A- 2. Compressive strength of TS bricks fired at 950°C

% of sludge	Sample ID	Area cm^2	Strength kg/cm^2	Avg. strength kg/cm2	SD	Strength loss wrt clay sample (%)
0% sludge (control)	0B	63	350	341.5	12	0
	0N	62	333			

10% sludge mix	1A	69.2	280	282	18	18
	1B	68	265			
	1N	63	300			
20% sludge mix	2A	70	248	226	20	34
	2B	63.28	210			
	2N	64.98	220			
30% sludge mix	3A	62	150	164	14	52
	3B	63	177			
	3N	66.7	165			
40% sludge mix	4A	63.84	140	130	10	62
	4B	63.6	120			
	4N	65	130			

Table A- 3. Compressive strength of TS bricks fired at 1000°C

% of sludge	**Sample ID**	**Strength kg/cm2**	**Avg. strength kg/cm2**	**SD**	**Strength loss wrt clay sample (%)**
0% sludge (control)	0M	350	376	36	0
	0P	402			
10% sludge mix	1M	290	302	14	19.7
	1p	298			
	1q	318			
20% sludge mix	2M	251	257	11	31.6
	2p	270			
	2q	250			
30% sludge mix	3M	190	195	13	48.1
	3p	210			
	3q	185			
40% sludge mix	4M	170	165	13	56.1
	4p	175			
	4q	150			

Table A- 4. Average weight loss on ignition at 900°C

% of sludge	**Sample ID**	**Weight (gm)**	**Weight (gm)**	**Wt. loss on ignition (%)**	**Avg, wt. loss on ignition (%)**
0 % sludge	0a	479.17	443.52	5.52	5.52
10% sludfe	1a	480	471.6	8.4	8.59
	1b	498.23	489.48	8.75	
	1c	478	469.37	8.63	
20% sludge	2a	489.03	478.24	10.79	11.04
	2b	463.74	452.46	11.28	
	2c	473.11	414.55	11.1	
30% sludge	3a	479.23	465.73	13.5	13.66
	3b	493.23	419.26	13.82	
	3c	472.53	458.85	13.68	
40% sludge	4a	475.21	460.65	14.56	14.82
	4b	485.95	470.87	15.08	
	4c	475.21	460.39	14.82	

Table A- 5. Average weight loss on ignition at 950°C

% of sludge	**Sample ID**	**Weight (gm)**	**Weight (gm)**	**Wt. loss on ignition (%)**	**Avg, wt. loss on ignition (%)**
0 % sludge	0N	475	442	6.9	6.9
10% sludfe	1A	473	429.52	9.2	9.3
	1B	498.63	453.28	9.1	
	1N	467.45	423.32	9.4	
20% sludge	2A	485.65	428.23	11.8	11.8
	2B	474.98	417.85	12.0	
	2N	470.59	415.68	11.7	
30% sludge	3A	490.23	419.98	14.3	14.08
	3B	488.73	421.85	13.7	
	3N	465.73	398.78	14.4	
40%	4A	478.37	401.63	16.0	15.89

sludge	4B	485.72	410.28	15.5	
	4N	491.23	411.42	16.2	

Table A- 6. Average weight loss on ignition at 1000°C

% of sludge	Sample ID	Weight after 105°C (gm)	Weight after 1000°C (gm)	Wt. loss on ignition (%)	Avg, wt. loss on ignition (%)
0 % sludge	0M	479.17	443.52	7.5	7.5
10% sludge	1p	480.25	430.26	10.4	10.1
	1q	505.72	453.28	10.4	
	1M	467.45	423.32	9.4	
20% sludge	2p	489.03	428.23	12.6	12.4
	2q	463.74	407.23	12.4	
	2M	473.11	414.55	12.2	
30% sludge	3p	492.08	417	15.3	15.1
	3q	493.23	419.26	15.0	
	3M	456.18	386.92	15.2	
40% sludge	4p	498.94	414.53	16.9	16.5
	4q	505.44	420.28	16.8	
	4M	497.39	419.42	15.7	

Table A- 7. Average bulk density of TS bricks fired at 1000°C temperature

% of sludge	Sample ID	Volume after firing at 1000°C	Weight after firing at 1000°C	Bulk density gm/cm^3	Average B. density gm/cm^3	SD
0 % sludge	0M	238.844	447.29	1.87	1.872	
10% sludge	1p	265.716	430.26	1.61	1.68	0.10
	1q	277.574	453.28	1.63		
	1M	233.856	423.32	1.81		
20% sludge	2p	283.464	430.99	1.52	1.54	0.08
	2q	276.48	409.27	1.48		

	2M	254.88	416.65	1.63		
30% sludge	3p	280.3392	419.22	1.49	1.50	0.02
	3q	273.06	419.26	1.53		
	3M	266.2335	394.64	1.48		
40% sludge	4p	278.61	414.53	1.48	1.50	0.01
	4q	278.9652	420.28	1.51		
	4M	275.502	419.42	1.52		

Table A- 8. Tank Leaching test of 10% TS bricks according to NEN 7345

Netherlands tank leaching test (NEN 7345)

0% sludge (Control Brick)

Time (day)	**Cr (mg/l)**	**Cr (mg/m^2)**	**Zn (mg/l)**	**Zn (mg/m^2)**	**Cu (mg/l)**	**Cu (mg/m^2)**	**Pb (mg/l)**	**Pb (mg/m^2)**	**Ni (mg/l)**	**Ni (mg/m^2)**	**As (mg/l)**	**As (mg/m^2)**
0.25	0.007	0.0012	0	0.0000	0.023	0.0038	0.028	0.0047	0	0.0000	0.01	0.0022
1	0	0.0000	0	0.0000	0.015	0.0025	0.051	0.0085	0	0.0000	0.01	0.0014
2.25	0.001	0.0002	0	0.0000	0.018	0.0030	0.096	0.0160	0	0.0000	0.01	0.0013
4	0.001	0.0002	0.002	0.0003	0.018	0.0030	0.125	0.0208	0	0.0000	0.02	0.0026
9	0.01	0.0017	0.004	0.0007	0.015	0.0025	0.036	0.0060	0.009	0.0015	0	0.0000
16	0.008	0.0013	0.003	0.0005	0.019	0.0032	0.051	0.0085	0.011	0.0018	0	0.0000
36	0.02	0.0033	0.005	0.0008	0.021	0.0035	0.08	0.0133	0.016	0.0027	0	0.0000
64	0.001	0.0002	0.024	0.0040	0.001	0.0002	0.051	0.0085	0.011	0.0018	0	0.0000
Total	0.048	0.0078	0.038	0.0063	0.13	0.0215	0.518	0.0862	0.047	0.0078	0.04	0.0075

Table A- 9. Tank Leaching test of 10% TS bricks according to NEN 7345

Netherlands tank leaching test (NEN 7345)

10% sludge amended bricks

Time (day)	**Cr (mg/l)**	**Cr (mg/m^2)**	**Zn (mg/l)**	**Zn (mg/m^2)**	**Cu (mg/l)**	**Cu (mg/m^2)**	**Pb (mg/l)**	**Pb (mg/m^2)**	**Ni (mg/l)**	**Ni (mg/m^2)**	**As (mg/l)**	**As (mg/m^2)**
0.25	0.043	0.0069	0	0	0.018	0.0029	0.051	0.0081	0	0	0.01	0.0016
1	0.044	0.0070	0	0	0.016	0.0026	0.088	0.0141	0.001	0.0002	0.01	0.0022
2.25	0.08	0.0128	0.01	0.0016	0.013	0.0021	0.125	0.0200	0.004	0.0006	0.02	0.0035
4	0.1	0.0160	0	0	0.018	0.0029	0.155	0.0248	0.002	0.0003	0.01	0.0019
9	0.111	0.0177	0.029	0.0046	0.018	0.0029	0.051	0.0081	0.008	0.0013	0.01	0.0016
16	0.138	0.0220	0	0	0.023	0.0037	0.08	0.0128	0.012	0.0019	0.02	0.0032
36	0.118	0.0189	0	0	0.02	0.0032	0.096	0.0153	0.019	0.003	0.01	0.0016
64	0.421	0.0673	0.024	0.0038	0.007	0.0011	0.039	0.0062	0.012	0.0019	0.01	0.0016
Total	1.055	0.1686	0.063	0.0101	0.133	0.0212	0.685	0.1094	0.058	0.0093	0.11	0.0172

Table A- 10. Tank Leaching test of 20% TS bricks according to NEN 7345

Netherlands tank leaching test (NEN 7345)

20% sludge amended Bricks

Time (day)	**Cr (mg/l)**	**Cr (mg/m^2)**	**Zn (mg/l)**	**Zn (mg/m^2)**	**Cu (mg/l)**	**Cu (mg/m^2)**	**Pb (mg/l)**	**Pb (mg/m^2)**	**Ni (mg/l)**	**Ni (mg/m^2)**	**As (mg/l)**	**As (mg/m^2)**
0.25	0.086	0.01425	0	0	0.015	-0.0014	0.051	0.00415	0	0	0.008	-0.0009
1	0.129	0.02326	0	0	0.018	0.0005	0.08	0.00523	0	0	0.0041	-0.0007
2.25	0.214	0.03841	0.009	0.0016	0.023	0.0009	0.11	0.00252	0.005	0.0009	0.0058	-0.0004
4	0.246	0.04418	0	-0.0004	0.016	-0.0004	0.155	0.00541	0	0	0.0077	-0.0014
9	0.212	0.03643	0	-0.0007	0.018	0.0005	0.036	0	0	-0.0016	0.01	-0.0014
16	0.227	0.03949	0.046	0.0078	0.03	0.002	0.096	0.00812	0.009	-0.0004	0.02	-0.0014
36	0.181	0.02903	0	-0.0009	0.023	0.0004	0.096	0.00289	0.016	0	0.013	-0.0014
64	0.665	0.11975	0.013	-0.002	0.003	0.0004	0.007	-0.0079	0.019	0.0014	0.02	-0.0014
Total	1.96	0.34481	0.068	0.0054	0.146	0.0029	0.631	0.02038	0.049	0.0004	0.0886	-0.0035

Table A- 11. Tank Leaching test of 30% TS bricks according to NEN 7345

Netherlands tank leaching test (NEN 7345)

30% sludge amended Bricks

Time (day)	Cr (mg/l)	Cr (mg/m^2)	Zn (mg/l)	Zn (mg/m^2)	Cu (mg/l)	Cu (mg/m^2)	Pb (mg/l)	Pb (mg/m^2)	Ni (mg/l)	Ni (mg/m^2)	As (mg/l)	As (mg/m^2)
0.25	0.083	0.0141	0	0.0000	0.015	-0.001	0.066	0.0070	0	0	0.0085	-0.0009
1	0.116	0.02146	0	0	0.018	0.0006	0.096	0.00832	0	0	0.0077	0.00
2.25	0.16	0.02941	0.003	0.0006	0.02	0.0004	0.14	0.00814	0	0	0.0144	0.0012022
4	0.192	0.03533	0	-0.0004	0.018	0	0.17	0.00832	0	0	0.016	0.00
9	0.158	0.02737	0.006	0.0004	0.022	0.0013	0.073	0.00684	0.014	0.0009	0.013	0.000185
16	0.198	0.03514	0	-0.0006	0.021	0.0004	0.096	0.00832	0.013	0.0004	0.012	0.000185
36	0.198	0.03292	0	-0.0009	0.025	0.0007	0.088	0.00148	0.012	-0.0007	0.012	0
64	0.511	0.09433	0.035	0.002	0.006	0.0009	0.087	0.00666	0.008	-0.0006	0.013	0
Total	1.616	0.29002	0.044	0.0011	0.145	0.0028	0.816	0.05512	0.047	0	0.0966	0.0007028

Table A- 12. Tank Leaching test of 30% TS bricks according to NEN 7345

Netherlands tank leaching test (NEN 7345)

40% sludge amended Bricks

Time (day)	Cr (mg/l)	Cr (mg/m^2)	Zn (mg/l)	Zn (mg/m^2)	Cu (mg/l)	Cu (mg/m^2)	Pb (mg/l)	Pb (mg/m^2)	Ni (mg/l)	Ni (mg/m^2)	As (mg/l)	As (mg/m^2)
0.25	0.331	0.0600	0.009	0.0017	0.021	-0.0004	0.066	0.007	0.001	0.00019	0.0068	-0.0012
1	0.204	0.0378	0	0.0000	0.016	0.0002	0.096	0.008	0	0	0.0079	-0.0001
2.25	0.248	0.0458	0	0.0000	0.017	-0.0002	0.14	0.008	0.006	0.00111	0.008	0.0000
4	0.333	0.0615	0.002	0.0000	0.023	0.0009	0.17	0.008	0	0	0.0071	-0.0016
9	0.028	0.0033	0	-0.0007	0.018	0.0006	0.066	0.006	0.006	-0.00056	0.0072	-0.0009
16	0.357	0.0647	0	-0.0006	0.02	0.0002	0.096	0.008	0.005	-0.00111	0.008	-0.0006
36	0.315	0.0547	0	-0.0009	0.024	0.0006	0.118	0.007	0.011	-0.00093	0.0078	-0.0008
64	0.927	0.1715	0.018	-0.0011	0.006	0.0009	0.098	0.009	0.008	-0.00056	0.0083	-0.0009
Total	2.743	0.4993	0.029	-0.0017	0.145	0.0028	0.85	0.062	0.037	-0.00185	0.0611	-0.0059

Appendix B

In this section, calculation of liquid limit, plastic limit and plasticity index of both clay and sludge – clay mixture as well as compaction test for determining OMC has been illustrated. Calculation for energy savings for TS bricks has also been stated.

Table B- 1. Atterberg Limit test of 10% sludge – clay mixture

Geotechnical Engineering Laboratory
Department of Civil Engineering, BUET

Atterberg Limit Test

Soil sample: 100% clay Date: 10.07.2015 Tested by: Md. Ariful Islam Juel

Liquid Limit					
No. of Blows	18	21	26	33	39
Container No.	726	744	750	770	825
Wt. container, gm	8.1	9.5	10.8	7.1	7.1
Wt. Container + Wet soil	20.5	23	23.3	21.6	17.9
Wt. Container + dry soil	17.22	19.438	20.016	17.863	15.149
Wt. water, W_w in gm	3.28	3.562	3.284	3.737	2.751
Wt. dry soil, W_s in gm	9.12	9.938	9.216	10.763	8.049
Water content, W, in %	35.96	35.84	35.63	34.72	34.17

Plastic Limit					
Container No.	770	825	835		
Wt. container, gm	10.2	6.9	7.2		
Wt. Container + Wet soil	24.1	21.8	20.6		
Wt. Container + dry soil	22.08	19.607	18.656		
Wt. water, W_w in gm	2.02	2.193	1.944		
Wt. dry soil, W_s in gm	11.88	12.707	11.456		
Water content, W, in %	17.0	17.25	16.96		

Result Summary:

Liquid Limit	Plastic Limit	Plasticity Index
35.2	17	18.2

Table B- 2. Atterberg Limit test of 10% sludge – clay mixture

Geotechnical Engineering Laboratory
Department of Civil Engineering, BUET

Atterberg Limit Test

Soil sample: 10% sludge + clay Date: 11.07.2015

Tested by: Md. Ariful Islam Juel

Liquid Limit					
No. of Blows	14	20	26	32	37
Container No.	726	744	750	770	825
Wt. container, gm	7.2	10.8	10.8	7.1	6.9
Wt. Container + Wet soil	21.3	22.7	23.3	21.7	18.1
Wt. Container + dry soil	17.22	19.438	20.016	17.863	15.149
Wt. water, W_w in gm	4.08	3.262	3.284	3.837	2.951
Wt. dry soil, W_s in gm	10.02	8.638	9.216	10.763	8.249
Water content, W, in %	40.72	37.76	35.63	35.64	35.77

Plastic Limit					
Container No.	869	885	841		
Wt. container, gm	11.2	7.2	7.3		
Wt. Container + Wet soil	24.2	22	20.9		
Wt. Container + dry soil	22.08	19.607	18.656		
Wt. water, W_w in gm	2.12	2.393	2.244		
Wt. dry soil, W_s in gm	10.88	12.407	11.356		
Water content, W, in %	19.48	19.28	19.76		

Result Summary:

Liquid Limit	Plastic Limit	Plasticity Index
37.1	19.5	17.6

Table B- 3. Atterberg Limit test of 20% sludge – clay mixture

Geotechnical Engineering Laboratory
Department of Civil Engineering, BUET

Atterberg Limit Test

Soil sample: 20% sludge + clay

Date: 11.07.2015

Tested by: Md. Ariful Islam Juel

Liquid Limit					
No. of Blows	19	26	30	33	39
Container No.	18	29	143	405	607
Wt. container, gm	7.2	7.2	7.3	6.8	6.9
Wt. Container + Wet soil	21.8	23.6	19	23.6	18.8
Wt. Container + dry soil	17.7	18.9	15.6	18.9	15.4
Wt. water, W_w in gm	4.1	4.7	3.4	4.7	3.4
Wt. dry soil, W_s in gm	10.5	11.7	8.3	12.1	8.5
Water content, W, in %	39.04	40.17	40.96	38.84	40

Plastic Limit					
Container No.	156	858	877		
Wt. container, gm	7	7.7	7.2		
Wt. Container + Wet soil	23.4	23.9	24.8		
Wt. Container + dry soil	20.2	20.7	21.4		
Wt. water, W_w in gm	3.2	3.2	3.4		
Wt. dry soil, W_s in gm	13.2	13	14.2		
Water content, W, in %	24.24	24.61	23.94		

Result Summary:

Liquid Limit	Plastic Limit	Plasticity Index
39.8	24.26	15.54

Table B- 4. Atterberg Limit test of 30% sludge – clay mixture

Geotechnical Engineering Laboratory
Department of Civil Engineering, BUET

Atterberg Limit Test

Soil sample: 30% sludge + clay

Date: 12.07.2015

Tested by: Md. Ariful Islam Juel

Liquid Limit					
No. of Blows	16	21	29	34	40
Container No.	26	106	210	211	742
Wt. container, gm	7.2	7.2	7.3	7.3	10.9
Wt. Container + Wet soil	19.3	20.3	22.2	26	25.2
Wt. Container + dry soil	15.7	16.4	17.8	20.4	20.9
Wt. water, W_w in gm	3.6	3.9	4.4	5.6	4.3
Wt. dry soil, W_s in gm	8.5	9.2	10.5	13.1	10
Water content, W, in %	42.35	42.39	41.90	42.74	43

Plastic Limit					
Container No.	786	801	907		
Wt. container, gm	10.9	7	7.5		
Wt. Container + Wet soil	23	21.7	20.3		
Wt. Container + dry soil	20.3	18.4	17.5		
Wt. water, W_w in gm	2.7	3.3	2.8		
Wt. dry soil, W_s in gm	9.4	11.4	10		
Water content, W, in %	28.72	28.94	28		

Result Summary:

Liquid Limit	Plastic Limit	Plasticity Index
42.47	28.55	13.92

Table B- 5. Atterberg Limit test of 30% sludge – clay mixture

Geotechnical Engineering Laboratory
Department of Civil Engineering, BUET

Atterberg Limit Test

Soil sample: 40% sludge + clay

Date: 13.07.2015
Tested by: Md. Ariful Islam Juel

Liquid Limit					
No. of Blows	17	22	28	33	39
Container No.	15	26	32	145	652
Wt. container, gm	7.2	7.2	8.1	7.9	8.9
Wt. Container + Wet soil	19.62	20.61	22.3	26.15	26.5
Wt. Container + dry soil	15.7	16.4	17.8	20.4	20.9
Wt. water, W_w in gm	3.92	4.21	4.5	5.75	5.6
Wt. dry soil, W_s in gm	8.5	9.2	9.7	12.5	12
Water content, W, in %	46.11	45.76	46.39	46	46.66

Plastic Limit					
Container No.	654	801	880		
Wt. container, gm	10.6	7.35	7.61		
Wt. Container + Wet soil	23.6	22.28	20.9		
Wt. Container + dry soil	20.3	18.4	17.5		
Wt. water, W_w in gm	3.3	3.88	3.4		
Wt. dry soil, W_s in gm	9.7	11.05	9.89		
Water content, W, in %	34.02	35.11	34.37		

Result Summary:

Liquid Limit	Plastic Limit	Plasticity Index
46.2	34.5	11.7

Table B- 6. Optimum Moisture content for 100% Clay

Geotechnical Engineering Laboratory
Department of Civil Engineering, BUET
Compaction test
Date: 14.07.15 Sample No: 100% Clay Tested by: Md. Ariful Islam Juel

Sl No.	Can No.	Wt. of can (gm)	Wt. of can+wet soil (gm)	Wt. of can + dry soil (gm)	Wt. of dry soil (gm)	Wt. of moisture (gm)	M.C in %	Avg. M.C in %	Wt. of mold in gm	Wt. of mold + compacted soil in gm	Wt. of compacted soil (gm)	Wt.density Kg/cm3	Dry density Kg/cm3
1	18	7.3	23	20.9	13.6	2.1	15.4	15.3	4200	5930	1880	2.0288	1.76
	29	7.2	21.7	19.8	12.6	1.9	15.1						
2	106	7.2	21.8	19.5	12.3	2.3	18.7	18.3	4200	6040	1970	2.1259	1.71
	143	7.2	21	18.9	11.7	2.1	17.9						
3	210	7.3	23.4	20.7	13.4	2.7	20.1	19.7	4200	6060	1960	2.1151	1.69
	405	6.8	21	18.7	11.9	2.3	19.3						
4	607	6.9	22	19.2	12.3	2.8	22.8	22.9	4200	6030	1950	2.1043	1.6
	756	7	23.5	20.4	13.4	3.1	23.1						
5	858	7.7	27.8	23.8	16.1	4	24.8	24.8	4200	5980	1880	2.0288	1.52
	877	7.1	23.2	20	12.9	3.2	24.8						

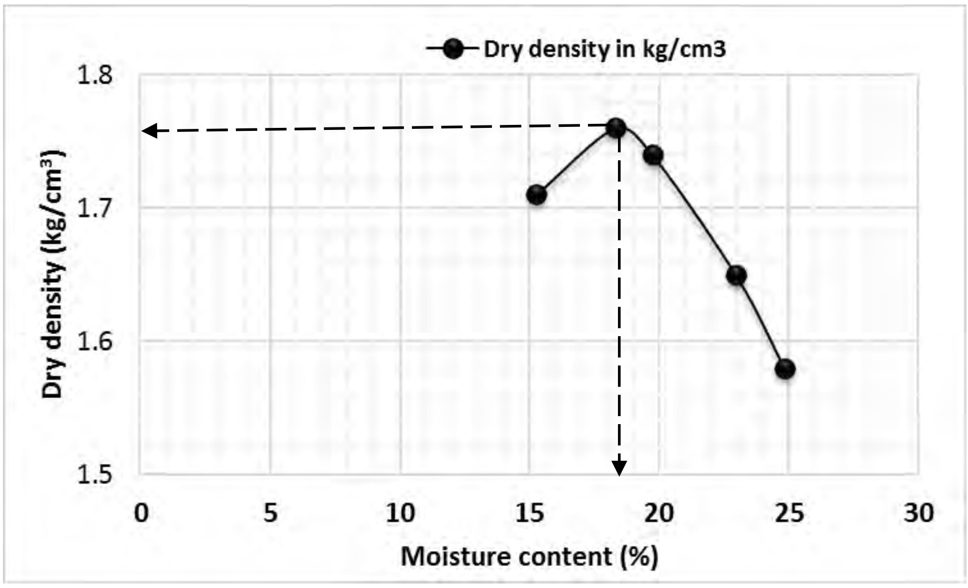


Table B- 7. Optimum moisture content of 10% sludge – clay mixture

Geotechnical Engineering Laboratory													
Department of Civil Engineering, BUET													
Compaction test													
Date: 14.07.15				Sample No: 10% sludge				Tested by: Md. Ariful Islam Juel					
Sl No.	Can No.	Wt. of can (gm)	Wt. of can+ wet soil (gm)	Wt. of can + dry soil (gm)	Wt. of dry soil (gm)	Wt. of moisture (gm)	M.C in %	Avg. M.C in %	Wt. of mold (gm)	Wt. of mold + compacted soil (gm)	Wt. of compacted soil (gm)	Wt.density Kg/cm3	Dry density Kg/cm3
1	122	7.5	19.5	17.8	10.3	1.7	16.5	17.5	4190	5970	1780	1.92	1.59
	726	7.2	20.7	18.6	11.4	2.1	18.4						
2	744	10.8	24.5	22.2	11.4	2.3	20.2	20.0	4190	6050	1860	2.01	1.61
	750	10.8	25.9	23.4	12.6	2.5	19.8						
3	770	7.2	21.6	18.9	11.7	2.7	23.1	22.2	4190	6020	1830	1.97	1.58
	793	10.7	23.8	21.5	10.8	2.3	21.3						
4	797	7.2	27	23.1	15.9	3.9	24.5	25.2	4190	6000	1810	1.95	1.46
	825	6.9	24.4	20.8	13.9	3.6	25.9						
5	869	11.2	30.1	26.2	15	3.9	26	26.9	4190	5970	1780	1.92	1.41
	885	7.2	28.4	23.8	16.6	4.6	27.7						

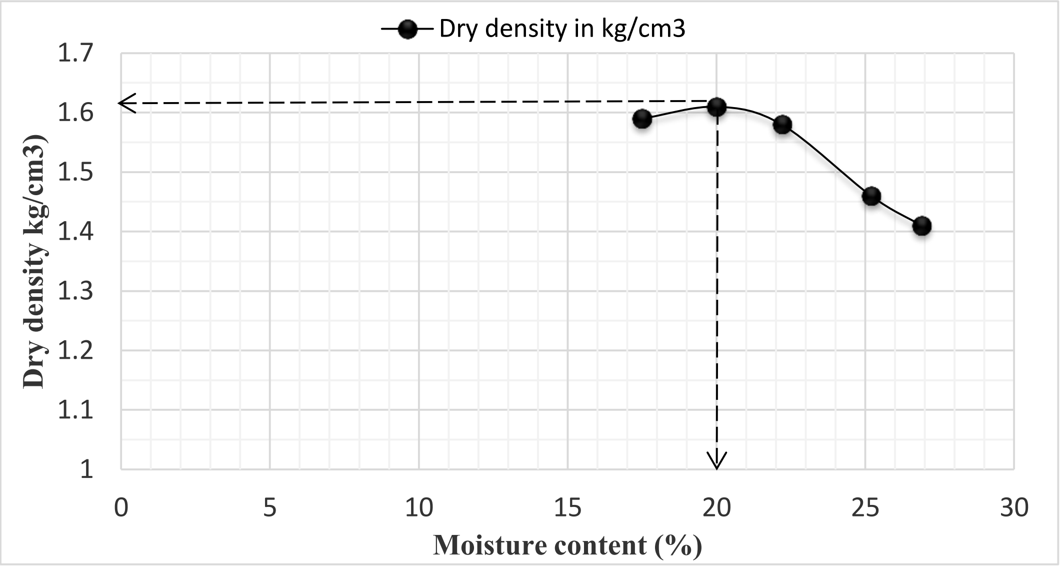


Table B- 8. Optimum moisture content of 20% sludge – clay mixture

Geotechnical Engineering Laboratory													
Department of Civil Engineering, BUET													
Compaction test													
Date: 14.07.15				Sample No: 20% sludge					Tested by: Md. Ariful Islam Juel				
Sl No.	Can No.	Wt. of can (gm)	Wt. of can+ wet soil (gm)	Wt. of can + dry soil (gm)	Wt. of dry soil (gm)	Wt. of moisture (gm)	M.C in %	Avg M.C in %	Wt. of mold (gm)	Wt. of mold + compacted soil	Wt. of compacted soil (gm)	Wt.density Kg/cm3	Dry density Kg/cm3
1	125	7.2	19.5	17.8	10.6	1.7	16	17.2	4190	5970	1770	1.91	1.54
	786	7.2	20.7	18.6	11.4	2.1	18.4						
2	704	10.6	24.5	22.2	11.6	2.3	19.8	20.2	4190	6050	1860	2.01	1.58
	742	11.2	25.9	23.4	12.2	2.5	20.5						
3	768	10.3	21.6	18.9	8.6	2.7	31.4	26.2	4190	6020	1870	2.02	1.62
	780	10.5	23.8	21.5	11	2.3	20.9						
4	792	10.6	27	23.1	12.5	3.9	31.2	28.8	4190	6000	1860	2.01	1.46
	802	7.2	24.4	20.8	13.6	3.6	26.5						
5	825	11.2	30.1	25.2	14	4.9	35	33.4	4190	5970	1780	1.92	1.45
	850	10.2	28.4	24	13.8	4.4	31.9						

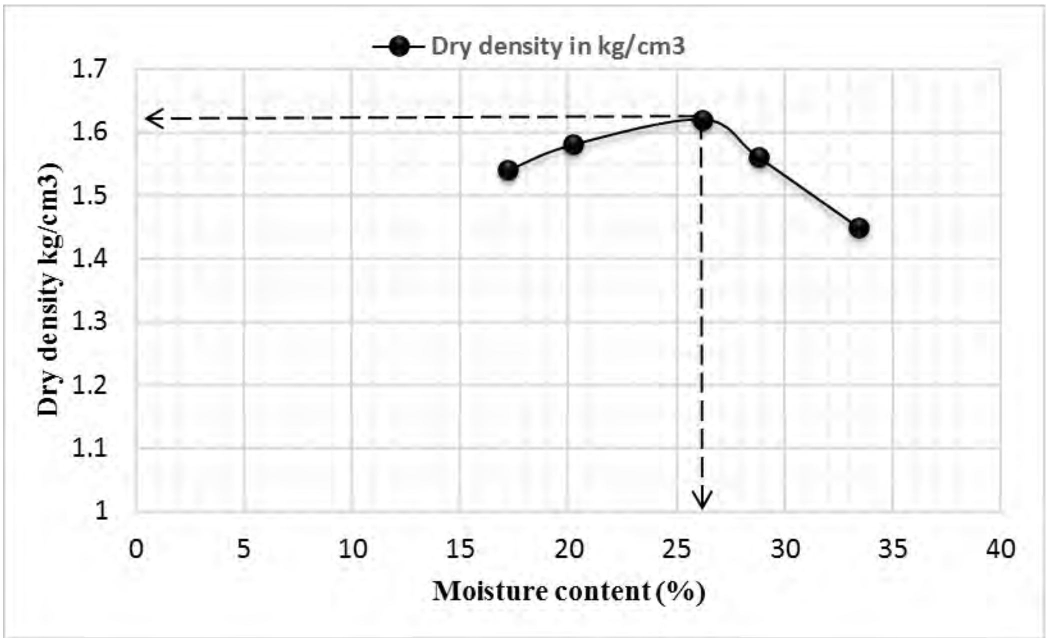


Table B- 9. Optimum moisture content of 30% sludge – clay mixture

Geotechnical Engineering Laboratory													
Department of Civil Engineering, BUET													
Compaction test													
Date: 16.07.15				Sample No: 30% sludge				Tested by: Md. Ariful Islam Ju					
Sl No.	Can No.	Wt. of can (gm)	Wt. of can+ wet soil	Wt. of can + dry soil	Wt. of dry soil (gm)	Wt. of moisture (gm)	M.C in %	Avg M.C in %	Wt. of mold (gm)	Wt. of mold + com	Wt. of compacted	Wt. density Kg/cm3	Dry density Kg/cm3
1	125	7.2	23.5	20.5	13.3	3	22.6	21.0	4190	5970	1770	1.91	1.51
	786	7.2	22.5	20	12.8	2.5	19.5						
2	704	10.6	24.8	22	11.4	2.8	24.6	25.2	4190	6050	1860	2.01	1.53
	742	11.2	26.3	23.2	12	3.1	25.8						
3	768	10.3	24.2	20.9	10.6	3.3	31.1	30.6	4190	6020	1870	2.02	1.59
	780	10.5	23.9	20.8	10.3	3.1	30.1						
4	792	10.6	26.8	22.5	11.9	4.3	36.1	36.3	4190	6000	1860	2.01	1.52
	802	7.2	26.3	21.2	14	5.1	36.4						
5	825	11.2	30.1	24.8	13.6	5.3	39	38.1	4190	5970	1780	1.92	1.48
	850	10.2	31.2	25.5	15.3	5.7	37.3						

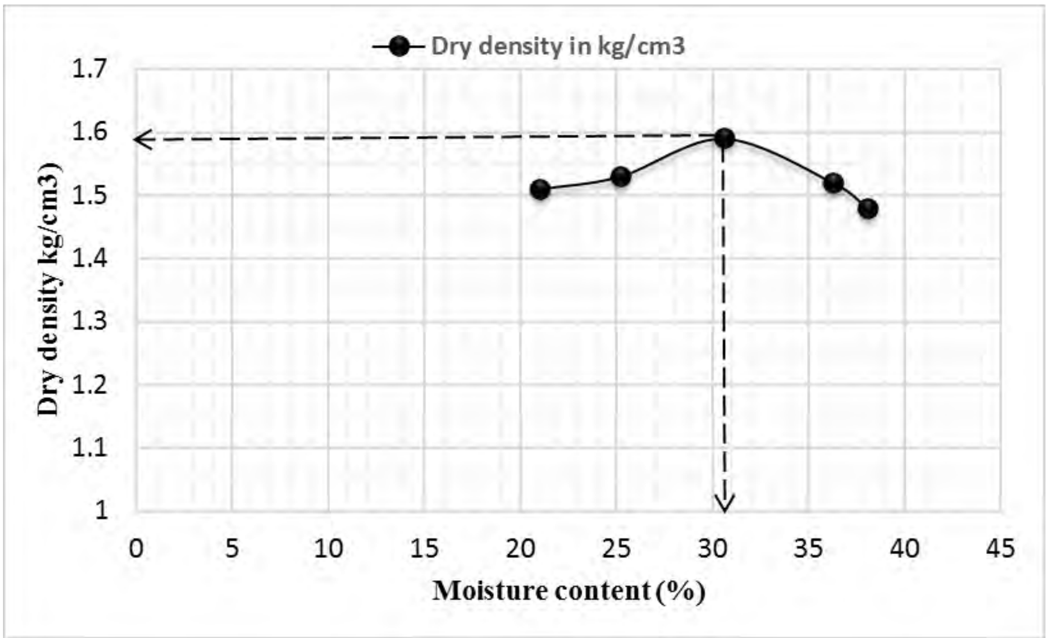


Table B- 10. Optimum moisture content of 40% sludge – clay mixture

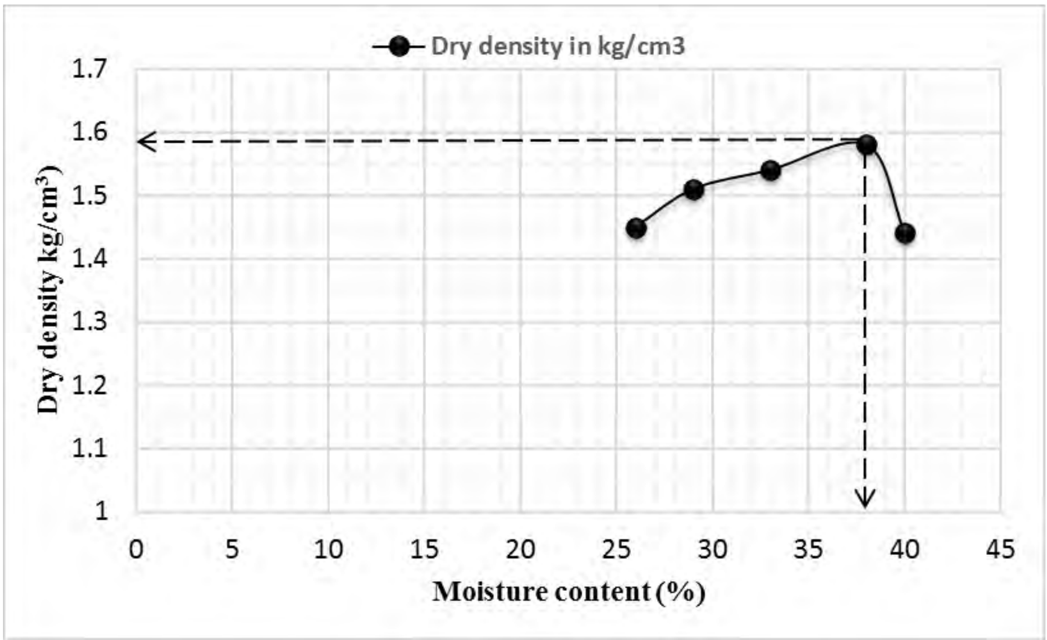
Geotechnical Engineering Laboratory

Department of Civil Engineering, BUET

Compaction test

Date: 21.07.15 Sample No: 40% sludge Tested by: Md. Ariful Islam Juel

Sl No.	Can No.	Wt. of can (gm)	Wt. of can+ wet soil	Wt. of can + dry soil	Wt. of dry soil (gm)	Wt. of moisture(gm)	M.C in %	Avg M.C in %	Wt. of mold (gm)	Wt. of mold + compacted	Wt. of compacted soil	Wt.density Kg/cm3	Dry density Kg/cm3
1	101	7.3	23.5	20	12.7	3.5	28	26	4190	5970	1750	1.89	1.45
	285	7.5	22.5	19.5	12	3	25						
2	456	10.5	26	22.5	12	3.5	29	29	4190	6050	1790	1.93	1.51
	502	11.5	26.3	23	11.5	3.3	29						
3	540	10.1	24.2	20.6	10.5	3.6	34	33	4190	6020	1820	1.96	1.54
	650	10.6	23.9	20.7	10.1	3.2	32						
4	658	10.2	26.8	22.3	12.1	4.5	37	38	4190	6000	1850	2.00	1.58
	780	7.2	26.3	21	13.8	5.3	38						
5	790	10.2	30.1	24.4	14.2	5.7	40	40	4190	5970	1810	1.95	1.48
	860	8.3	31.2	24.7	16.4	6.5	40						



Calculation of energy savings for 10% TS bricks during firing

Specific Energy used for brick firing, q = 2.5 MJ/kg

Mass of control brick, m_1 = 0.505 kg

Mass of TS incorporated brick, m_2 = 0.489 kg

Mass of Tannery sludge in TS brick, m_3 = 0.049 kg

Calorific Value of Tannery sludge found, CV = 5.85 MJ/kg

Energy used for control brick, $Q_1 = q.m_1$ = 2.5×0.505 = 1.2625 MJ

Energy used for TS brick, $Q_2 = q.m_1 - \left(q.m_2 - CV.m_3\right)$ = 0.9355 MJ

Energy Saved, $\Delta E(\%) = \frac{Q_1 - Q_2}{Q_1} \times 100$

$$= \frac{1.2625 - 0.9355}{1.2625} \times 100$$

$$= 25.90\%$$

Calculation of energy savings for 20% TS bricks during firing

Specific Energy used for brick firing, q = 2.5 MJ/kg

Mass of control brick, m_1 = 0.505 kg

Mass of TS incorporated brick, m_2 = 0.473 kg

Mass of Tannery sludge in TS brick, m_3 = 0.094 kg

Calorific Value of Tannery sludge found, CV = 5.85 MJ/kg

Energy used for control brick, $Q_1 = q.m_1$ = 2.5×0.505 = 1.2625 MJ

Energy used for TS brick, $Q_2 = q.m_1 - \left(q.m_2 - CV.m_3\right)$ = 0.6326 MJ

Energy Saved, $\Delta E(\%) = \frac{Q_1 - Q_2}{Q_1} \times 100$

$$= \frac{1.2625 - 0.6326}{1.2625} \times 100 = 50\%$$

Appendix C

Bangladesh Standard

SPECIFICATION FOR COMMON BUILDING CLAY BRICKS

(3rd Revision)

1. SCOPE

This standard lays down requirements for dimensions, strength and other quality requirements of common burnt clay building bricks.

2. TERMINOLOGY

For the purpose of this standard following definitions shall apply

2.1 Bricks

The burnt clay building bricks which are commonly used in building and civil engineering construction purposes.

3. DIMENSIONS

3.1 Size- The standard dimensions of common burnt clay bricks shall be of following:

TABLE 1: SIZE OF BRICKS

Dimension	**cm**
Length	24
Width	11.5
Height / Depth	7

NOTE- One bedding face of each brick shall have a recess, panel or frog. The size of the frog for the standard brick shall not exceed 13cmx 5cmx 1cm as shown in fig. 1. This would not apply to brick manufactured by extrusion process or any special bricks required by the purchaser.

3.2 Variation - Small variation for Grade A and B in the dimension shall be permissible to the following extent only:

TABLE 2: MAXIMUM PERMISSIBLE VARIATION OF BRICKS

Specified Dimension	Maximum Permissible Variation
Over 5 cm and up to 7.5cm	± 2.0 mm
Over 7.5 cm and up to 10 cm	± 3.0 mm
Over 10 cm and up to 15 cm	± 5.0 mm
Over 15 cm and up to 25 cm	± 6.0 mm

4. CLASSIFICATION

Three grades of bricks have been incorporated based on their strength properties. This will include reasonable variation in the quality of clays available locally.

TABLE 3: CLASSIFICATION OF BRICKS

Grade	Mean for twelve halved bricks	Minimum for individual halved bricks
S	280 kg^f/cm^2	245 kg^f/cm^2
A	175 kg^f/cm^2	154 kg^f/cm^2
B	140 kg^f/cm^2	105 kg^f/cm^2

Grade S: This type of bricks may be used for breaking into aggregate for plain and reinforced concrete and for making base course of pavement.

Grade A: This type of bricks may be used in construction of buildings of long duration.

Grade B: This type of bricks may be used for one storied building, temporary shed, where intended durability is not very long.

5. WATER ABSORPTION

Water absorption by weight shall not exceed 20% for bricks of Grade B and l5% for bricks of Grade A and l0% for bricks of Grade S.

6. MEASUREMENT OF DIMENSION AND SIZE

6.1 Number of Specimens- 24 bricks, for carrying out dimensional tests as per procedure set out in clauses 6.3 to 6.5 of this standard shall be taken.

6.2 Preparation of specimens - Any blister or other small project together with-any loose particles of clay which might have adhered to the face of brick shall be removed before the bricks are assembled for measurement.

6.3 Length- a) 24 Bricks laid end to end on a level surface in contact in a straight line shall measure between 568 cm to 588 cm when all frog face upwards as shown in Figure 2.

b) 24 Bricks laid in a similar manner as in clause 6.3 (a) above but having alternate frogs facing upwards and downwards shall also measure between 568 cm to 588 cm as shown in Figure 3. The difference between the length noted in clause 6.43 (a) above and this system will not be more than 17 mm

6.4 Width- a) 24 Bricks laid side by side on level surface in contact in a straight line shall measure between 281 cm to 291 cm when all frogs face upwards as shown in Figure 4.

b) 24 Bricks laid in a similar manner as in clause 6.4 (a) above but having alternate frogs facing upwards and downwards shall also measure between 281 cm to 291 cm as shown in Figure 5. The difference between the length noted in clause 6.4 (a) and this system will not be more than 8 mm.

6.5 Depth- 24 bricks laid on edge bedding surface to bedding surface on a level surface in contact in a straight line will measure 165 cm to 171 cm

NOTE: - When bricks without frogs are to be measured the system for clauses 6.3 and 6.4 shall be arranged by reversing sides of alternate bricks.

6.6 Measurement- The overall length of the assembled bricks shall be measured with a steel tape of other suitable inextensible measure long enough to measure the whole row at once. Measurement by repeated application of a short rule or measure shall not be considered satisfactory. If, for any reason, it is found impracticable to measure 24 bricks in one row the samples may be divided into two rows of 12 bricks which shall be measured separately to the nearest of l. 5 mm to their measurement added,

6.7 Compliance - If the measurements in clauses 6.3 to 6.5 are fulfilled, the whole consignment from which the sample is drawn shall be deemed to comply with the specification and these specimens shall thereafter be used for other specified tests. If the specimens do not comply, the whole consignments from which the specimens are drawn shall be rejected and no further tests in regard to crushing strength, water absorption and efflorescence are needed to be carried out.

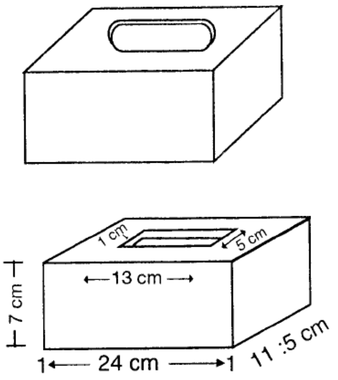


FIG NO. 1

FIG NO. 2

FIG NO. 3

FIG NO. 4

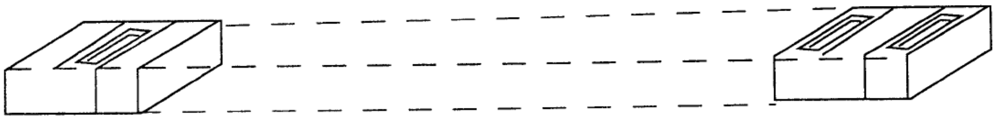


FIG NO. 5

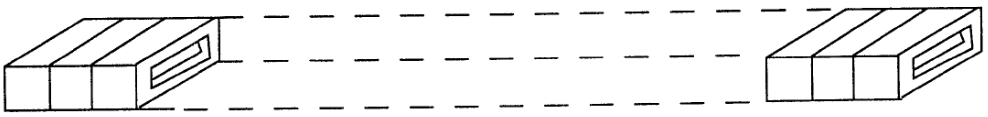


FIG NO. 6

7. DETERMINATION OF CRUSHING STRENGTH

7.1 Specimens – Twelve bricks taken at random from sample shall be halved and one half from each whole brick used for determining the crushing strength as detailed in7.2. The overall dimension of each bedding face shall be measured to the nearest of 1.3 mm and the area of the face having smaller area shall be taken as the area of the bricks for testing the crushing strength.

Sample sizes for crushing strength are as follows:

TABLE 4: SAMPLE SIZE FOR CRUSHING STRENGTH

Lot size	**Sample size**
2.001 to 10.000	5
10,001 to 35,000	10
35.001 to 50.000	15

7.2 Procedure

Bricks without frogs - These shall be immersed in water at l5ºC to 20ºC for 24 hours. They shall then be removed and allow to dry at room temperature for about 5 minutes. Their frogs shall be filled with cement sand mortar of 1: 1 ½, sand being clean and well graded passing 3.2 mm sieve. The mortar shall be trowelled off flush with surface of the bricks. The bricks shall then be stored under the damp sacks for 24 hours after filling the frogs and shall then be immersed in water for six days before bricks are considered ready for testing*. After seven days of filling the mortar, specimens will be taken out wiped dry with damp cloth and used plaster of Paris or sulfur capping to ensure a uniform surface of brick for crushing strength test and carefully centered between the plates of the compression testing machine. The compressing plates of the testing machine shall have a blasting in the form of a portion of sphere, the center of each coinciding with the center of the face of the plate. The load shall be applied axially at a uniform rate of 140 kg/cm^2 per minute, until failure.

7.3 Results- Maximum load in kilogram at failure divided by the minimum area of the bedding surface of the half bricks in square centimeter shall be taken as the crushing strength whole limiting values are given in 7.4. The main crushing strength of twelve half bricks along with that of each individual half bricks shall be noted.

7.4 Limiting value - The value of crushing strength in kilogram per square centimeter shall not be less than the figures given in table 3.

7.5 Compliance - If the mean crushing strength of twelve bricks falls below the limiting crushing strength given 7.4 above, the batch from which the sample is taken shall be deemed not to comply. If however, any individual brick gives the crushing strength less than the minimum value for an individual brick given in 7.4 above, the test will be repeated as detailed in Para 7.2 over twice the number of bricks that have failed provided the number of individual brick not complying of any does not exceed clause 4. If on retest them crushing strength of any individual bricks still falls below the minimum value given in para7.4 the sample as a whole shall be deemed not to comply with the crushing strength values.

8. DETERMINATION OF WATER ABSORPTION

8.1 Specimen- The specimens shall consist of whole bricks. Six specimens shall be tested for water absorption as detailed in 8.2.

8.2 Procedure - The test specimen shall be dried in a ventilated oven at 110ºC-115ºC for 48 hours or more until constant weight. The specimen shall be deemed to have reached the constant weight when after 2 hours drying in the same over the loss in weight does not exceed 0.1%. Each specimen shall immediately be weighed which shall be called the dry weight of the specimen. The dry specimen shall then be cooled in air at room temperature for about 2 hours after which they shall be immersed completely in clean soft water at ** l5ºC for 24 hours. Each specimen shall then be removed from the water, the surface wiped off with a damp cloth and the specimen weighed. Weighing of any one specimen shall be completed within 3 minutes after removing the specimen from the water. This shall be called the wet weight.

* When the test on the mortar is cubes shows that the compressive strength of the mortar is not less than 280 kg^f/cm^2 and not exceeds 420 kg^f/cm^2. The failure shall be deemed to have occurred when no further increase in the load is registered with unchanged rate of moving head travel.

** Specimen noticeably warm to the touch shall not be immersed water.

8.3 Result- The percentage of water absorption by weight shall be calculated as,

$$\frac{W_2 - W_1}{W_1} \times 100$$

Where,

W_1 = Dry weight of the specimen

W_2 = Wet weight of the specimen

8.4 Limiting value - The average value of the six specimens shall be taken as the water absorption of the batch shall be given in art 5.

8.5 Compliance - In case the average absorption value of the specimen exceeds the limiting value given in clause 8.4 above the test will be repeated on the same number of bricks. If after the test the absorption value exceeds the prescribed limit the batch from which the samples taken shill be deemed not to comply with this clause.

9. INITIAL RATE OF ABSORPTION (SUCTION)

9.1 Apparatus:

9.1.1 Trays or Containers - Watertight trays of containers, having an inside depth of not less than 12.7 mm and of such length and width that an area of not less than 1935.5cm2 of water surface in provided. The bottom of the tray shall provide a plane, horizontal upper surface, when suitably supported, so that an area not less than 203.2 mm in length by 9.2.4 mm in width will be level when tested by a sprit level.

9.1.2 Supports for Brick/Block – Two non corrodible metal supports consisting of bars between 127 mm and 152.5 mm in length, having triangular, half round, or rectangular cross section such that the thickness (height) will be approximately 6.35 mm. The thickness of the two bars are rectangular in cross section, their width shall not exceed 1.94 mm.

9.1.3 Means for Maintaining Constant Water Level – Suitable means for controlling the water level above the upper surface if the supports for the brick/block within + 0.25 mm (see note 3) , including means for adding water to the tray at a rate corresponding to the rate of removal by the brick/block undergoing test (see note 4). For use in checking the adequacy of the method of controlling the rate of; flow of the added water, a reference brick/block or half brick/block shall be provided whose displacement in 3.18mm of water corresponds to the brick/block or half brick/block to be tested within + 2.5 %. Completely submerge the reference brick/block in water for not less than 3 h preceding its use.

Note - A suitable means for obtaining accuracy in control of the water level may be provided by attaching to the end of one of the bars two stiff metal wires that project upward and return, terminating in points; one of which is 3.18 – 0.25 mm and other 3.18 – 0.25 mm above the upper surface or edge of the bar. Such precise adjustment is obtainable by the use of depth plates of a micrometer microscope. When the water level with respect to the upper surface of edge of the bar is adjusted so that the lower point dimples the water surface when viewed by reflected light and the upper point is not in contact with the water, the water level is within the limits specified. Any other suitable means for fixing and maintaining a constant depth of immersion may be used if equivalent accuracy is obtained. As an example or such other suitable means, there may be mentioned the use of rigid supports movable with respect of the water level.

Note -A rubber tube leading from a siphon of gravity feed and closed by a spring clip will provide a suitable manual control. The so-called “chicken-feed” devices as a rule lack sensitivity and do not operate with the very small changes in water level permissible in this test.

9.1.4 Balance, having a capacity of not less than 3000 g. and sensitive to 0.5 g.

9.1.5 Drying Oven that provides a free circulation of air through the oven and is capable of maintaining a temperature between 110 and 115° C.

9.1.6 Constant – Temperature Room, maintained at a temperature of 21± 1.4°C.

9.1.7 Timing device - A suitable timing device, preferably a stop watch of stop clock, which shall indicate a time of 1 min to the nearest 1 s.

9.2 Test specimen, consisting of whole brick/block. Five specimens shall be tested.

9.3 Procedure:

9.3.1 Drying- Dry the test specimens in a ventilated oven at 110 to 115° C for not less than 24 h and until two successive weighing at intervals of 2 hours show an increment of loss not greater than 0.2 % of the last previously determined weight of the specimen.

9.3.2 Cooling – After drying, cool the specimens in a drying room at a temperature of 24 ± 8°C, with a relative humidity between 30 and 70 %. Store the units free from drafts, unshackled, with separate placement for a period of at least 4 h. Do not use specimens noticeably warm to the touch for any test requiring dry units.

9.3.2.1 An alternative method of cooling the specimens to approximate room temperature may be used as follows: Store units, unstacked, with separate placement, in a ventilated room for a period of 4 h, with a current of air from an electric fan passing over them for a period of at least 2h.

9.3.2 Measure to the nearest 1.27mm the length and width of the flatwise surface of the test specimen of rectangular units or determine the area of other shapes to similar accuracy that will be in contact with the water. Weigh the specimen to the nearest 0.5 g.

9.3.3 Adjust the position of the tray for the absorption test so that the upper surface of its bottom will be level when tested by a sprit level, and set the saturated reference brick (9.1.3) in place on top of the supports. Add water until the water level is 3.18 + 0.25 mm above the top of the supports. When testing tile with scored bed surfaces, the depth of water level is 3.18 + 0.25 mm plus the depth of scores.

9.3.4 After removal of the reference brick/block, set the test brick/block in place flatwise, counting zero time as the moment of contract of the brick/block with the water. During the period of contact (1 min + 1 s) keep the water level within the prescribed limits by adding water as required. At the end of 1 min + 1 s , lift the brick/block from contract with the water, wipe off the surface water with a damp cloth, and reweigh the brick/block to the nearest 0.5 g. Wiping shall be completed within 10 s of removal from contract with the water, and weighing shall be completed within 2 min.

Note – Place the brick/block in contact with the water quickly, but without splashing. Set the brick/block in position with a rocking motion to avoid the entrapping of air on it's under surface. Test brick/block with frog of depression uppermost.

9.4 Calculations and Report:

9.4.1 The difference in weight in grams between the initial and final weighings is the weight in grams of water absorbed by the brick/block during 1-min contact with the water. If the area of its flatwise surface (length times width) does not differ more than + 4.84 cm^2 (+ 2.5%) from 193.55 cm^2, report the gain in weight in grams as the initial rate of absorption in 1 min.

9.4.2 If the area of its flatwise surface differs more than + 4.84 cm^2 (+ 2.5%) from 193.55 cm^2 as follows:

$$X = \frac{193.55\,W}{LB}$$

Where:

X = Gain in weight corrected to basis of 193.55 cm^2 flatwise area,

W = actual gain in weight of specimen, g

L = length of specimen, cm and

B = width of specimen, cm.

9.4.3 Report the corrected gain in weight, X, as the initial rate of absorption 1min.

9.4.4 If the test specimen is a cored brick calculate the net area and substitute for LB in the equation given in 9.4.2. Report the corrected gain in weight as the initial rate of absorption in 1 min.

9.4.5 If specimen is non-prismatic, calculate the net area by suitable geometric means and substitute for LB in the equation given in 9.4.2.